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Single ensemble catalysis: acetylene semi-hydrogenation on indium oxide

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Despite increasing resource scarcity and environmental awareness, industrial hydrogenation catalysts still heavily rely on expensive noble metals such as palladium or platinum modified with toxic selectivity enhancers.[1] Among intensive efforts to address this, one approach involves the untapped potential of metal oxides. In this regard, cerium oxide emerged as an efficient catalyst for the semi-hydrogenation of acetylene,[2] an important reaction for the purification of olefin streams for downstream polymerization processes. To date, no other metal oxide has been identified that selectively catalyzes this reaction, leaving ample room for a more extensive investigation on the abilities of oxides in hydrogenation catalysis. Here, we have explored the potential of indium oxide to hydrogenate acetylene, uncovering a remarkable 85% selectivity to ethylene at full conversion in continuous-flow tests at ambient pressure (Figure 1a). Detailed analyses by temperature-programmed reduction with H_2, *in situ* diffuse reflectance infrared Fourier transform and Raman spectroscopy, transmission electron microscopy, and density functional theory link the excellent hydrogenation performance with a surface reconstruction during the reaction leading to the creation of well-defined In_3O_5 sites, consisting of an oxygen vacancy, an In trimer and adjacent oxygen atoms, where C_2H_2 and H_2 can co-adsorb and react (Figure 1b). This unusual configuration, which we have named 'single ensemble', comprises a new type of active site in hydrogenation catalysis.

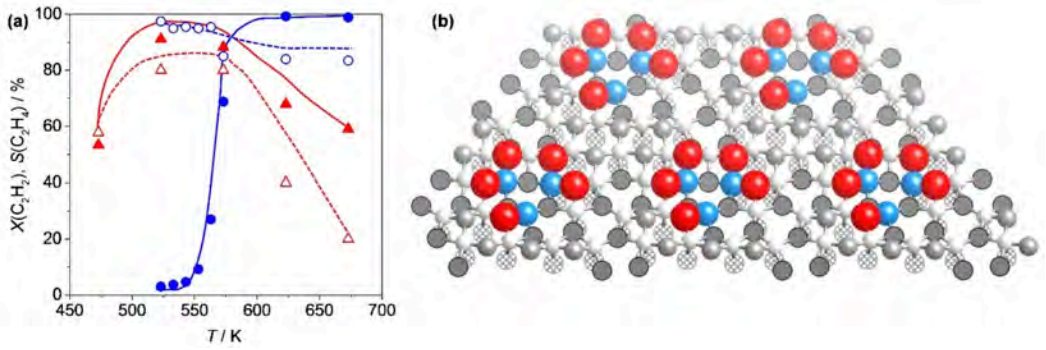

Figure 1 (a) Acetylene conversion (solid symbols) and selectivity to ethylene (open symbols) versus temperature over In_2O_3 (blue) and CeO_2 (red). Conditions: H_2:C_2H_2 = 30, t = 1 s, P = 1 bar. (b) Oxygen vacancy formation on In_2O_3(111) under reaction conditions leads to the development of In_3O_5 single ensembles. In and O atoms of the ensemble are colored in blue and red, respectively.

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Water Oxidation Catalysis by Molybdenum-doped Manganese Oxide

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Designing a high efficient, cheap and green water oxidation catalyst (WOC) is one of the most important challenges in the sustainable energy field. The $CaMn_4O_5$ cluster in nature's photosystem II catalyzes photosynthetic splitting of water into oxygen and protons.[1] Therefore, many researchers focus on modelling this metalloenzyme center by metal complexes with different ligands, as well as through various metal oxides.[2] According to undeniable role of manganese in the natural water oxidation reaction, manganese oxides are promising as environmentally friendly catalysts.[2] Their optimization is a sustainable way to robust materials for applications. In this work, molybdenum doped manganese oxide was synthesized and characterized by PXRD, XPS, TGA, FT-IR, Raman, BET, SEM, and HRTEM. In addition, the catalytic activity of doped molybdenum manganese oxide in chemical, photochemical and electrochemical water oxidation reactions are investigated. Results show that molybdenum has a significant effect on the chemical activity of manganese oxide in ceria solution. The water oxidation experiment under the photochemical conditions with Mo doped $Mn_2O_3/[Ru(bpy)_3]^{2+}/S_2O_8^{2-}$ also led to promising results (TOF ~0.83 μmol $O_2.m^{-2}.s^{-1}$).

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Cobalt-Functionalised Metalorganic Frameworks as Hydroformylation Catalysts: A new Approach for an Old Problem.

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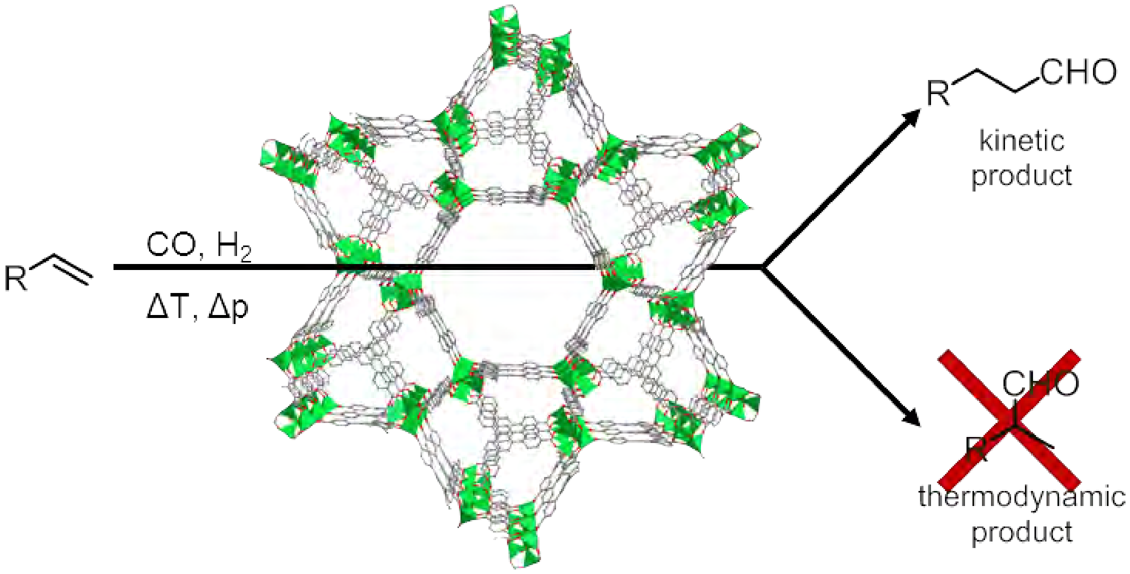
An interesting research field emerged in the last decade: the investigation of metal-organic frameworks (MOFs) as catalysts.[1],[2] Their structural versatility, tuneable pore size and modularity give a plethora of structures and possibilities to optimise the catalytic performance. The porous framework structures are not just used to “heterogenise” homogenous catalysts; their specific pore size and cavity shape can be thought of as to provide host-guest properties similar to enzymes.[3] Therefore MOFs are ideal candidates to force the hydroformylation reaction from a preferentially thermodynamic regime into the desired kinetic regime to selectively afford *n* -aliphatic aldehydes.[4] With the MOF providing the structural rigidity the focus can be drawn on fine-tuning of the electronic properties of the metal complex to achieve both, high reactivity *and* high selectivity.



The synthesis of different functionalised MOF structures is described using phosphines as anchoring groups. The MOFs are post-synthetically modified with cobalt, the active site for the hydroformylation. The catalytic performance is then tested *in vitro* on a range of different *n* -aliphatic olephines. In parallel *in silico* studies describe the steric and electronic properties of the active centre, in order to map and predict reactivity and selectivity of MOFs. Subsequently this information is fed into the design of new MOF materials to improve and fine tune the catalytic performance.

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Single crystal studies to evaluate the structure sensitivity of the Oxygen Evolution Reaction (OER) under acidic conditions

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From fundamental point of view, the Oxygen Evolution Reaction (OER) is the decisive process in electrolysers. The efficiency of the device is mainly limited by this reaction, which exhibits a large overpotential on all known catalysts. Over the last years many efforts have been addressed to develop more stable and active catalysts. However, most of these studies involved nanostructured catalysts deposited on different types of supports, while just a few works tried to understand the fundamentals of this reaction. Such investigation can be used to improve actual catalysts, but they are also an important link between theory and experiment. One of the main issues that still wait to be experimentally explored is the structure sensitivity of the OER. Usually such studies are done with single crystal electrodes of different surface orientations. However, there are many drawbacks in the use of this approach for studying the OER. The main challenge is that the surface loses its order once overpotential is driven to higher values and metal oxides start to form. This process is inevitable since the oxide is an intermediate in the reaction mechanism, while surface reorganisation cannot be easily avoided. Despite these intrinsic limitations, we have been able to retain structural information developing an investigation approach based on electrochemical and spectroscopic techniques. This approach allowed us to investigate the structure sensitivity of the OER on Pt single crystals and hopefully soon can be applied to more relevant systems.

Characterizing the 3-Dimentional Structure of Hydrodesulfurization Catalyst Particles

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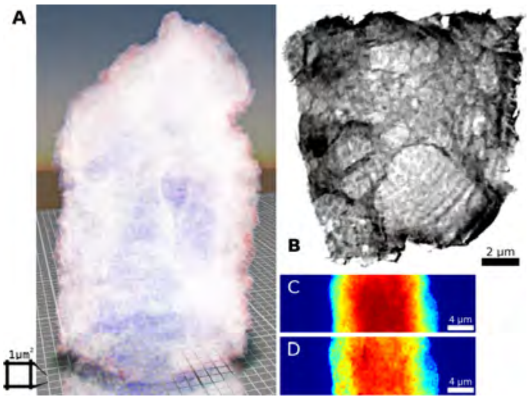
Hydrodesulfurization (HDS) is a catalytic process widely used to remove sulfur from refined petroleum products [1 , 2]. One purpose for removing the sulfur is to reduce the toxic sulfur dioxide emissions resulting from burning oil-based fuels. Another important reason is that sulfur, even in extremely low concentrations, poisons the noble metal catalysts - platinum and rhenium, in the catalytic reforming units downstream. Given the more stringent legislation, and the changing composition of crude oil which may contain compounds that are more difficult to desulfurize as global petroleum supplies dwindle and processing of "dirtier" feeds increases [1], there are large industrial and academic efforts to improve HDS catalysis.

HDS catalysts are composites consisting of nickel- or cobalt-doped molybdenum or tungsten sulfides supported by porous alumina particles. The porosity in these particles (the typical scale of which varies from a few nm up to several µm) is essential for the large molecules to diffuse to and from the active sites, therefore understanding its structure is key for optimizing the catalyst's performance. The relationship between the pores' geometry and the active particles' locations is of importance as well.



Due to the enormously diverse scales, structure sensitivity to the environment and to manipulations, and very fine structural details, it is extremely difficult to characterize these structures using well established techniques. We make use of state-of-the-art synchrotron 3D imaging (holotomography, ptychographic nano-tomography, fluorescence tomography) to characterize the porous structure and the elemental distribution in these particles on multiple scales, and other advanced techniques (such as scanning nano-beam diffraction) to determine the orientational relation between the active particles and the support structure. Also, computational techniques are being developed to process these kinds of data for the more general use cases.

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Bulk and surface properties of Sr_2TaO_3N by density functional theory

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Ruddlesden-Popper structured oxides are promising candidate materials for water-splitting catalysts [1], superconductors [2] and photovoltaic materials [3]. Furthermore, the substitution of oxygen with nitrogen in perovskite oxides lead to novel physical and chemical properties due to their difference in electronegativity [4-5]. However, the electronic features of oxynitrides with layered perovskite structure has not been studied rigorously.
In the present work, we perform first-principles density functional theory (DFT) calculations to investigate the electronic properties of the bulk Ruddlesden-Popper oxynitride Sr_2TaO_3N as well as its (001) surface. We show that the energetically favoured Sr_2TaO_3N bulk structure contains octahedral rotations combined with a *cis*-type ordering of the nitrogen anions on the equatorial sites of the octahedra. Besides the anion-*p* valence band and the Ta-*d* conduction band, the electronic density of states (DOS) of the bulk shows an unoccupied Ta-*d* state below the conduction band. This state also exists at the TaON terminated (001) surface but is slightly higher in energy than in the bulk, which means that excess electrons are preferentially accommodated in the bulk and subsurface layers. At the same time, the N-derived valence-band edge is shifted to higher energies at the surface, which implies that holes are preferentially located in the surface layer. These results show that photo-excited charge carriers remain spatially separated in the surface region, which should drastically reduce their recombination and lead to improved photocatalytic properties.

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Hydrodeoxygenation of bio-derived phenols over Pt Nanoparticle/Ionic Liquid Catalytic System under mild conditions

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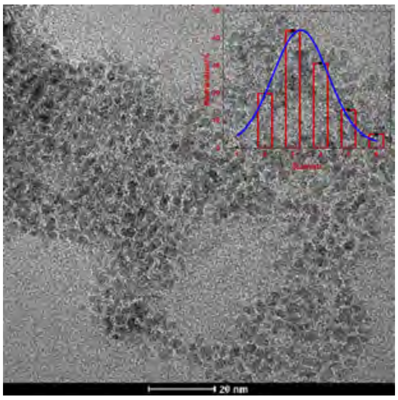
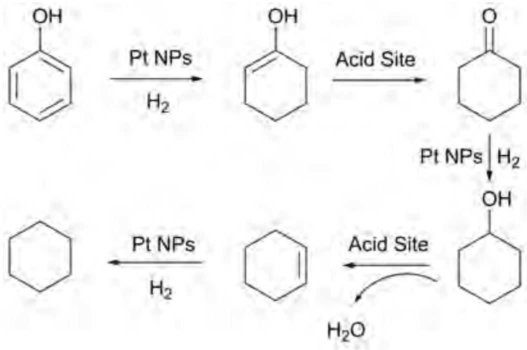
Due to the lower heating value and thermal instability, bio-oil cannot be used directly to replace diesel.[1] To upgrade bio-oil through hydrodeoxygenation (HDO), appropriate catalysts and solvent systems would be indispensable.[2] In our study, uniformly stabilized platinum metal nanoparticles (NPs) in ionic liquids (ILs) formed an efficiency catalyst system that performs the HDO of phenol, one of the most abundant components in bio-oil, under mild conditions (60 °C, 1.0 MPa H_2). Pt NPs with a mean diameter of 3.4 nm (Fig. 1) in ILs with full conversion and maximum 94% selectivity to cyclohexane and cyclohexene, is the best combination. A possible reaction pathway of the HDO of phenol is proposed (Scheme 1). Further optimization of the reaction conditions including temperature, pressure, time and the preparation of the NPs were also carried out.



To figure out the C-O cleavage behavior between aromatic units, dimeric model compound diphenyl ether with C-O bonds (4-O-5) were investigated, meanwhile, other substituted phenols with hydroxy groups rather than methoxy groups, such as catechol, guaiacol and resorcinol were studied as well. In most cases afforded derivatives of cyclohexanes in good yields. Our findings indicate that the presented NPs/ILs catalytic systems are more active towards the removal of hydroxy groups rather than methoxy groups.



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Mo-based catalysts for CO_2 (electro)reduction

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[1]ETH Zürich

Though CO_2 is a potential carbon source, it has found only a few direct applications so far, and is best known as an environmentally harmful waste ("greenhouse gas"). Its industrial use often implies a preliminary reduction into products of higher added value like CO, formic acid or, preferentially, methanol.[1] Unfortunately, with carbon in its highest oxidation state, CO_2 is a highly stable molecule (C=O bond: 803 $kJ.mol^{-1}$) and its successive reductions require a catalyst for both activation and selectivity. So far, Cu-based catalysts have remained the most popular ones due to their ability to allow CO_2 reduction up to methane, but their good activity is usually at the expense of a low selectivity.

Contrariwise, molybdenum is a relatively abundant and non-toxic element of which the CO_2 reduction properties have received little attention. However, two recent results have been hinting to its potential as a catalyst: commercial MoO_2 microparticles have been shown to present electrocatalytic CO_2 reduction abilities, especially in the presence of an ionic liquid as co-catalyst,[2] and some mixed Mo-Bi systems exhibit good selectivity towards methanol, one of the most interesting CO_2 reduction products.[3]

This poster will present some of our recent results on the synthesis, characterization and study of the (electro)catalytic properties of different materials prepared by grafting molybdenum-based precursors ($Mo(CO)_6$, $MoCl_5$, polyoxomolybdates) on either TiO_2 particles or TiO_2-coated fluorine tin oxide (FTO) electrodes. The CO_2 reduction ability of these systems has been followed by spectroscopy (IR, UV-Vis) and electrochemistry, and the reduction products analyzed by on-line GC and HPLC techniques.

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Development of continuous heterogeneously-catalyzed acylation processes for vitamin synthesis

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[1]ETH Zurich, [2]DSM

Vitamins are organic compounds that are vital for human and animal nutrition.[1] The production of these organic compounds typically involves multiple steps that still mainly rely on stoichiometric reactions conducted in batch operation. In addition to generating large quantities of waste, obtaining high selectivity and conversion can be difficult, thereby increasing the cost and environmental footprint. For example, acylation reactions are typically catalyzed by mineral acids or bases. This work targets the development of a continuous heterogeneously-catalyzed acylation process (**Figure 1**). The first step involves the identification of promising catalytic materials and suitable reaction conditions to obtain high selectivity, which is particularly important if there are multiple possible reacting centers. Zeolites are crystalline microporous solids that can be prepared in large scale with tailored acid (Brønsted/Lewis), base, or redox functionalities.[2] The confinement of well-defined active sites within pores of molecular dimensions provides unique opportunities for the design of highly selective catalysts.[3] After establishing the thermal and chemical stability of the substrates, a broad set of zeolite catalysts are first screened in batch operation to compare the activity and selectivity as well as the possible substrate-catalyst interactions. Once potential leads are discovered, they will be further studied under continuous operation.

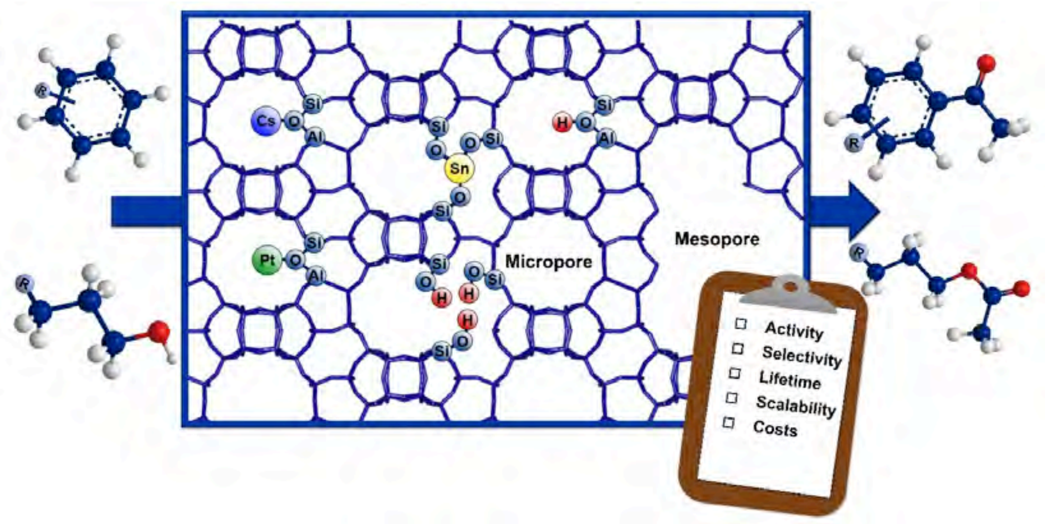

Figure 1 Scheme illustrating the tunable functionality of zeolites and design criteria for the development of a continuous acylation process.

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Catalyst Overcoating by Non-hydrolytic Sol–gel Technique

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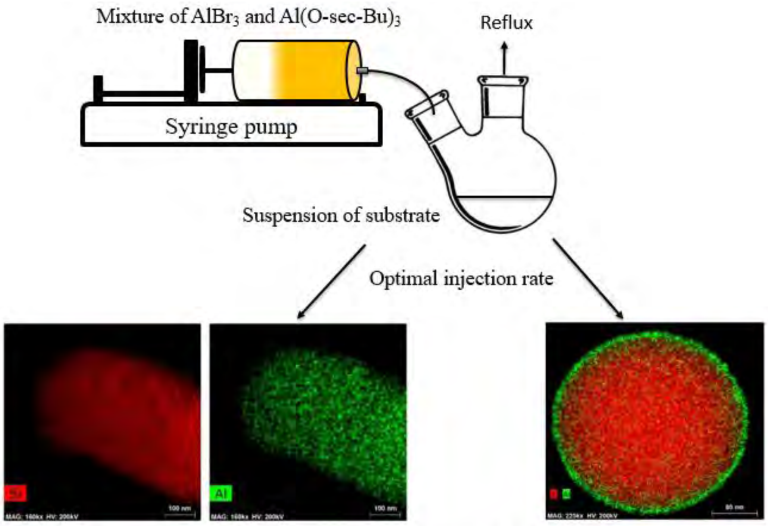
Catalyst overcoating has recently gained more attention in the area of catalyst synthesis. The overcoat can encapsulate active sites and serve as a physical barrier to isolate the nanoparticles, which prevents the sintering of particles during catalytic reactions. The overcoat can be tailored by varying synthesis parameters during methods including atomic layer deposition (ALD) or sol-gel techniques.

ALD has been widely applied to improve the stability of heterogeneous catalysts.[1,2] However, conducting ALD on powder samples is relative costly and difficult to scale up. On the other hand, sol-gel chemistry provides a more affordable and scalable alternative as well as allowing increased control over overcoat’s porosity. Among various metal oxides, alumina (Al_2O_3) coating is particularly challenging since the kinetics of alumina precursors are too fast to be controlled using traditional sol-gel techniques. Herein, we demonstrate a novel strategy for coating Al_2O_3 based on non-hydrolytic sol-gel (NHSG) chemistry.[3] The precursor was prepared by mixing aluminum bromide and aluminum sec-butoxide. The gelation of this precursor cannot occur unless it is at high temperature. We controlled the kinetics of this alumina precursor by syringe pump injection, which allows us to uniformly overcoat alumina onto different supports with surface areas ranging from 15 m^2/g to 400 m^2/g. Further characterizations suggested that the coated samples had unusual strong Lewis acidity compared to commercial alumina supports. Current efforts are focused on applying this NHSG coating approach to design bi-functional heterogeneous catalyst for upgrading monomers derived from lignin—a major plant fraction that is one of the few natural sources of aromatic molecules.



Conformal overcoat formation on (left) SBA-15 and (right) silica sphere

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CO_2 Electro-reduction on three dimensional Cu skeleton catalysts

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The electrochemical reduction of CO_2 into products of higher value (in the following referred to as CO_2RR) offers the unique chance to make a significant contribution to the closing of the anthropogenic CO_2 cycle and is therefore currently in the focus of research activities worldwide. Energy needed for such electro-conversion processes might originate from excesses of renewables like hydro, wind and solar energy (power to value concept). Among the vast number of materials screened so far, it is Cu which deserves particular attention since it is the only catalyst which is capable to convert CO_2 into hydrocarbons and alcohols in considerable amounts. The activity and product selectivity of 3D Cu skeleton type of catalysts were studied with regard to CO_2RR applications thereby focusing on C_2 hydrocarbon formation. The 3D skeleton (sponge) itself reveals only a poor catalytic activity towards CO_2RR which can mainly be assigned to contaminations/residuals from the production process which can hardly be removed even by electropolishing. It will be demonstrated that an activation of the largely inactive Cu skeleton can be achieved either by (i) thermal annealing or (ii) by Cu form electrodeposition. The concept of HER (hydrogen evolution reaction) assisted Cu foam electrodeposition was successfully transferred from planar supports to 3D skeletal supports. Both treatments lead to active Cu catalysts which favor the C_2 pathway (C_2H_4 and C_2H_6) whereas the C1 pathway (CH_4) towards hydrocarbons remains fully suppressed. Both modified catalysts can be considered as oxide-derived and both show a preferential (100) texturing in their XRD analysis thus favoring the C_2 pathway. Differences in their C_2 reaction pathway concern the particular ratio of C_2H_6/C_2H_4 product formation which is higher in case of the electrodeposited Cu foam. This observation could be rationalized by the presence of µm-sized pores within the Cu foam thus leading to a more efficient trapping of reaction intermediates (e.g. C_2H_4) as compared to the annealed skeleton sample and by this to a longer mean residence time of the intermediates inside the catalyst modified by the foam electrodeposition. This effect clearly favors the fully reduced C_2 product.

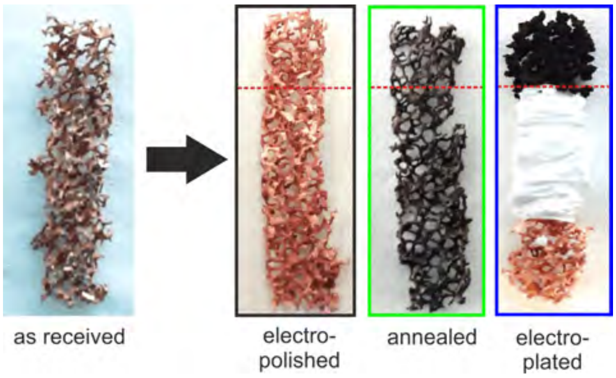

Fig.1 Optical images of the Cu skeleton type of catalysts used in this study: (i) electropolished Cu skeleton; (ii) annealed Cu skeleton (at 300°C for 12h); (iii) functional Cu foam electrodeposited on the Cu skeleton.

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A novel synthesis approach towards Fe-based non-noble metal oxygen reduction catalysts with finely tunable composition

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Due to their high power-to-weight ratio, their emission-free operation and their fast start up time, polymer electrolyte fuel cells are excellently suited energy conversion devices for the electric-automotive sector [1]. However, the sluggish kinetics of the oxygen reduction reaction at the cells' cathode limit their overall efficiency. Currently, platinum is used to catalyze said reaction, but its high price motivates the search for inexpensive alternatives. Non-noble metal catalysts (NNMCs) represent a route towards greatly reducing the catalyst cost and therefore the price of the overall stack and have recently been shown to be a viable replacement in terms of initial activity [2,3].

Despite these advancements, NNMC widespread application is hindered by the catalysts' instability. This is believed to be partially caused by the materials' inhomogeneous composition, which not only consists of active sites (typically pictures as an N-coordinated Fe^{II}-ion), but also of inactive side phases (e.g. iron carbides or oxides). The latter could catalyze side reactions and possibly contribute to the depletion of ORR-active sites and membrane poisoning [4].

Looking for approaches to minimize the content of these instability-inducing side phases, in this work we present a new pyrolysis-based synthesis pathway for the preparation of Fe-based NNMCs in which polyacrylonitrile is used as a C- and N-precursor, a Fe-phenanthroline complex as a metal source and a thermally decomposable compound as a pore inducing agent. The latter is chosen as to offer porosity control while going hand in hand with the need for inexpensive catalyst production (as compared to approaches based on the use of costly metalorganic frameworks [3]). The influence of different synthesis parameters is studied by the means of electrochemical activity measurements as well as surface- and bulk-property characterization techniques. We show how the catalytic activity as well as the catalysts' composition are not only determined by the chosen content of pore inducing agent and the final iron content, but also by the choice of pyrolysis temperature and atmosphere enabling improvement and fine-tuning of these crucial Features.

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Catalytic conversion of CO_2 to formate mediated by an aliphatic Pd-PCP pincer complex

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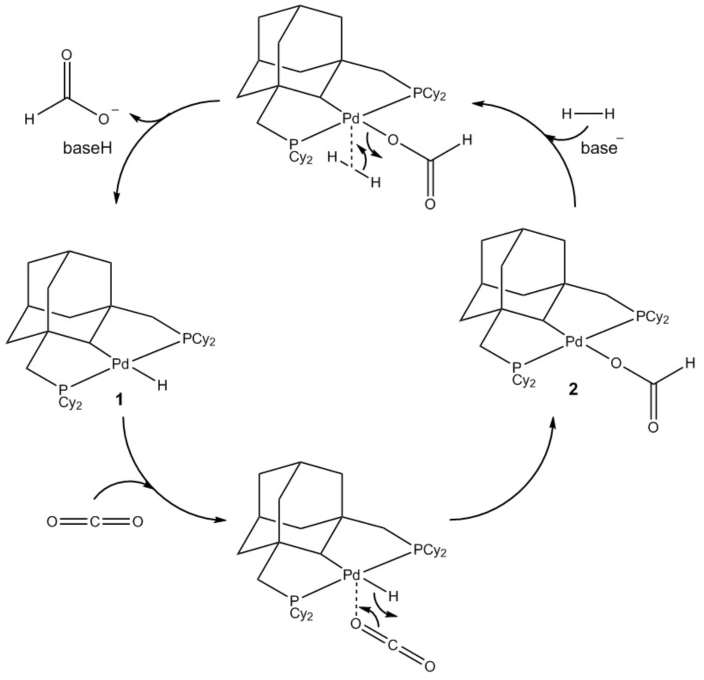
[1]ZHAW

We report the palladium-catalyzed transformation of CO_2 and H_2 to formate at low pressure (2 bar) and ambient temperature in presence of a base. Palladium-hydride complex **1** was synthesized from its chloride precursor with NaH in THF. The ^{1}H-NMR spectrum shows a triplet at δ -3.40 ppm with a $^2J_{P\text{-}H}$ coupling constant of 20.7 Hz. The formate complex **2** was obtained by exposing **1** to CO_2 as indicated by a triplet signal in the ^{1}H-NMR spectrum at δ 9.18 ppm with a $^4J_{P\text{-}H}$ coupling constant of 1.7 Hz and a singlet signal at δ 166.6 ppm in the broadband decoupled ^{13}C-NMR spectrum. After degassing of complex **2**, addition of a base and application of a H_2-atmosphere regenerated the hydride complex **1**, thus completing the proposed catalytic cycle. The formation of formic acid was confirmed by NMR and headspace GC-MS measurements after treatment with HCl.



CH_4 oxidation on a Pd-only three-way catalyst under fluctuating rich/lean conditions

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The current technology for the control of the exhaust gas of natural gas fueled passenger vehicles (NGV) is based on three-way catalysts (TWC) that are set to operate around stoichiometry ($\lambda = 1$) [1]. TWC contain predominantly palladium as the active phase because this metal is the most efficient for C-H activation of methane (CH_4), the major component of natural gas. Targeted catalyst development, which appears to lag behind that of TWC for gasoline applications, would be helpful to improve the performance of present catalysts and control strategies of stoichiometric engines, but the understanding of the chemistry of TWC for NGV is still limited. Here, we show the effect of rich/lean operation on CH_4 conversion.

A honeycomb Pd-only TWC subjected to linear temperature ramps in the presence of CO, NO, CH_4 and water displayed very poor CH_4 oxidation activity in a continuous feed corresponding to $\lambda = 1$. Both CH_4 and NO conversions reached high levels (>90%) when the catalyst was subjected to an oscillating rich/lean feed that is more representative of TWC operation. CO was fully removed in the whole temperature range showing that CO oxidation occurs constantly and irrespective of the presence of CH_4. In a second series of experiments, the catalyst was tested at 425°C while decreasing the mean O_2 concentration in the feed stepwise from 7000 ppm to 0 ppm. Contrary to the typical behavior of a TWC, CH_4 oxidation and NO reduction did not occur at $\lambda = 1$ but CH_4 removal was more efficient under rich of stoichiometry [2]. CH_4 oxidation initiated only when CO was removed completely confirming the inhibition of CH_4 oxidation by CO [3]. When these experiments were conducted under oscillating rich/lean feeds the O_2 concentration for maximum CH_4 conversion moved towards the $\lambda = 1$ value and the window of CH_4 oxidation broadened. The need to periodically switch the feed to reducing conditions to enhance CH_4 removal confirms that steam reforming is a preferred route for CH_4 oxidation and NO reduction occurs predominantly by H_2.

Hence, significant improvement of CH_4 abatement can be achieved on TWC under realistic periodic conditions compared to steady state conditions. This observation points to the need to study such catalysts under relevant operation conditions. The results suggest that the CH_4 abatement potential and the operation window of the TWC can be improved upon adequate control strategies, thus potentially contributing to further develop targeted after-treatment technologies for NGV.

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Modulated excitation Raman spectroscopy of V_2O_5-TiO_2 and V_2O_5-WO_3-TiO_2

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Raman spectroscopy is the technique of choice to obtain the structure of atomically and nanodispersed metal oxides of transition elements [1] supported, e.g. on Al_2O_3, SiO_2 and TiO_2 that are active for a number of catalytic industrial processes. Nevertheless, when used under reaction conditions, it becomes difficult to isolate the contribution of that fraction of M=O and M-OH species that are effectively involved in adsorption and reaction from that of the overall phase constituted by the transition metal oxide. We have applied the modulated excitation (ME) approach [2] to increase our sensitivity to such species in the case of typical catalysts used for the selective catalytic reduction of NO_x by NH_3, e.g. V_2O_5-TiO_2 and V_2O_5-WO_3-TiO_2. ME consists in subjecting the sample to repeated pulses, e.g. alternate reducing and oxidizing conditions, while acquiring spectroscopy data with sufficient time resolution. Finally, the spectroscopic data are processed by phase sensitive detection (PSD) to eliminate the contribution of species not responding to the perturbation of the gas phase applied to the sample.

Here, we show that in simple ME experiments where water is repeatedly added to an O_2 feed on V_2O_5-TiO_2 V=O and V-O-V signals are greatly enhanced. These signals represent only a small fraction of the overall time-resolved signals suggesting that only a fraction of the available V is perturbed and can be detected with high sensitivity upon PSD: the fwhm of the V=O signal at 1024 cm^{-1} was of only 14 cm^{-1} after PSD. Additionally, we show by the same approach that NH_3 adsorption can be monitored on V_2O_5-TiO_2 and V_2O_5-WO_3-TiO_2 when pulsing NH_3 in various feeds also by the perturbation of the TiO_2 signal at 700-300 cm^{-1}. This region is otherwise omitted when experiments are performed under steady state conditions because of the strong intensity and the subtle changes. Comparison between V_2O_5-TiO_2 and V_2O_5-WO_3-TiO_2 clearly demonstrated that PSD enables a careful differentiation of the contribution of the responsive V=O (1028 cm^{-1}) and W=O (1012 cm^{-1}) species within the broad signal of unresponsive species.

The sensitivity obtained by the ME approach potentially defines new frontiers for the application of Raman spectroscopy to the characterization of dispersed transition metal oxide catalysts. Moreover, it calls for combination with detailed theoretical simulation in order to understand precisely the origin of signal shifts.

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Carbon Dioxide as Versatile Hydrogen Storage Vector

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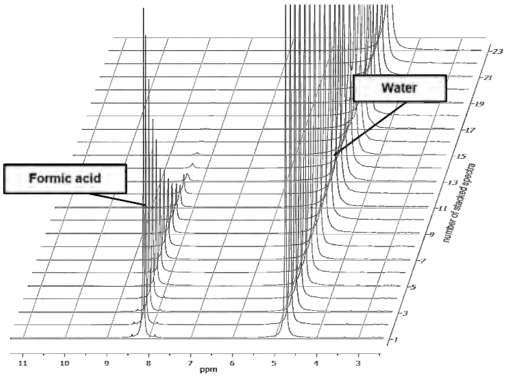
The combustion of fossil energy reserves releases the stored carbon as CO_2, which was identified to be most responsible for global warming and the greenhouse effect.[1] Molecular hydrogen, produced with renewable energy sources, offers a viable alternative as energy vector. Hydrogen, when chemically bound to certain molecules, avoids many hazards linked to free hydrogen gas and the products exhibit a series of other advantages such as a higher volumetric density, easy to handle, etc. The catalytic reduction of CO_2 under mild conditions with homogeneous catalysts to formic acid is a promising solution for save hydrogen storage.[2, 3] Numerous catalysts are known to either bind (hydrogenation) or release (dehydrogenation) H_2 with high turnover numbers (TON) on demand.[4, 5] Several PEM fuel cells allow the direct utilization of the H_2/CO_2 mixture and the afterwards released CO_2 can be recycled to obtain a carbon neutral hydrogen battery.[6,7]

An excellent group of catalysts are iridium complexes with the general formula [Cp*Ir(N,N')Cl]X, where Cp* is a cyclopentadienyl moiety, X a counter ion and N,N' are part of a bidentate nitrogen donor ligand. Our researched aimed to identify a more powerful catalyst from this group by systematically introducing N,N' ligands with different steric and electronic properties. We determined characteristic numbers such as turn over frequency, kinetic and mechanistic information and activation energy to describe our catalytic systems accurately.[8]

Acknowledgement: EPFL and SCCER are thanked for financial support.



^1H NMR (400 MHz, 10 mm) stacked spectra; 4,5 M FA in D_2O at 60°C; c(Ir) = 1,2-diaminocyclohexane = 0,009 M; intervals 450 s;

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Furfural hydrogenation on P-promoted Ru/Al_2O_3

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Hydrogenation of furfural has gained increasing attention as it represents one of the platform chemicals with a large pool of useful chemical products such as furfuryl alcohol [1]. Investigation of phosphorus as a promoter for Ru nanoparticles (NP) supported on Al_2O_3 for the selective hydrogenation of furfural to furfuryl alcohol in isopropanol has been the focus of this work. For this purpose, two Ru/Al_2O_3 catalysts were prepared by impregnation of ɣ-Al_2O_3 with $Ru(NO)(NO_3)_3$. The resulting Ru_{salt}/Al_2O_3 was split in two batches. The first batch was processed by reduction at 500°C, while the second batch was further impregnated with $NH_4H_2PO_2$ followed by reduction at 500°C. The catalysts were characterized by XRD, STEM, NMR, CO and pyridine adsorption and XAS at the Ru k-edge. The sample treated with P exhibited a homogeneous dispersion of small Ru NP. Beside the difference in Ru particle size between the two samples, the catalysts exhibited different acidic properties. RuP/Al_2O_3 displayed predominantly Brønsted acidity, which may also contribute to the better conversion rate and selectivity towards furfuryl alcohol compared to the Ru/Al_2O_3 homologue. Finally, catalytic activity was also compared to that of commercial Ru/C in batch reactor at 180°C and 5 bar of H_2. Phosphorus also improved the stability of the catalyst; leaching tests indicated a loss of 4% Ru in RuP/Al_2O_3 that did not change further after the first cycle, whereas Ru/C showed an initial loss of 7%. Despite the difficulty to discriminate the contribution of Brønsted acidity and smaller and well dispersed Ru NP, phosphorus appears to be a promising catalyst promoter for the selective hydrogenation of furfural to furfuryl alcohol.

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Impact of degree of interaction and particle size on the efficiency of In_2O_3-based catalysts for CO_2 hydrogenation to methanol

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

In order to reduce anthropogenic CO_2 emissions, the identification of routes in which carbon dioxide can be utilized as a chemical feedstock is a highly sought goal in the scientific community. One attractive approach comprises its hydrogenation to methanol, which serves as a fuel and a starting material for the manufacture of a multitude of chemicals. So far, only one commercial process for CO_2-based methanol production has been developed (Carbon Recycling International, 5 million liters in 2015),[1] since most of the heterogeneous catalysts investigated suffer from limited selectivity, mainly due to the competitive reverse water gas shift reaction, and/or short lifetime. Recently, we have introduced indium oxide (9 wt.%) supported on zirconia as a highly selective and extraordinarily stable material for this transformation.[2] In that study, we gathered evidence that the electronic interaction between the carrier and the active phase as well as the reaction conditions play a crucial role in the formation of selective active sites, *i.e.*, surface oxygen vacancies. Here, we aim at achieving a deeper understanding of this catalyst to improve its methanol space time yield. In order to vary the distribution and degree of contact between In_2O_3 and ZrO_2, we applied various preparation methods, *i.e.*, wet impregnation, spray deposition, ball milling, hydrothermal synthesis, and co-precipitation. Preliminary tests under industrially-relevant temperature and pressure conditions showed that the first two protocols produce superior catalysts (**Figure 1**). Since XRD indicated that the particle size of In_2O_3 is smaller in these solids, we are currently producing additional materials with variable In content to tune the dimensions of the In_2O_3 crystallites. Characterization through a battery of state-of-the-art techniques will be coupled to the catalytic assessment to establish structure-performance relations and attain even more efficient materials.

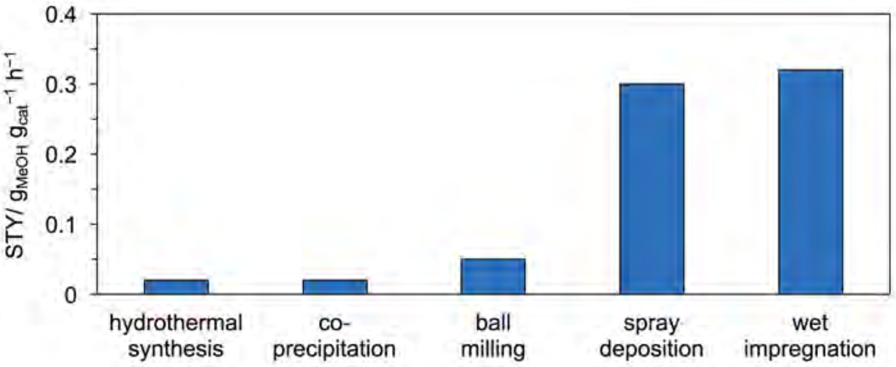

Figure 1 Space time yield (STY) of methanol in the direct hydrogenation of CO_2 over In_2O_3-ZrO_2 catalysts prepared by different synthesis methods.

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Understanding the ammonia synthesis catalyst poisoning: laboratory experiments to enhance the reactors performances

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The catalytic ammonia synthesis from H_2 and N_2 is one of the most important industrial reactions. The catalyst is made from iron oxide with a little percentage by weight of other oxides added as promoters. Despite the improvement made in recent years the catalyst is still sensitive to the poisoning due to oxygenates compounds (CO, O_2 and H_2O). 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[1-2]. In this work we have investigated the influence of few ppm of oxygenates compound (O_2 and H_2O) on the poisoning behavior of ammonia synthesis catalyst. 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.

To investigate the poisoning effect, an ammonia industrial synthesis catalyst was used: firstly, crushed and then in its granular form to understand the intrinsic loss of activity and the one at real industrial conditions. Since it is well known that the poisoning by CO and CO_2 has the same effect of the H_2O and O_2[1], the research was performed using only H_2O and O_2 with a ratio of 2.5:2.5 ppm. The experiments were performed in a fixed bed tubular lab scale reactor between 350°C and 450°C at a pressure of 100 bar. Different gas hourly space velocities (GHSV h^{-1}) were used to investigate the catalyst performances close to and far from the equilibrium conditions. The experiments consisted, after reaching the steady state conditions, in switching on/off the feed containing the oxygenates compounds. In this way the dynamics of the poisoning/cleaning effect were investigated. From the results obtained it was understood that a low amount of oxygenates compounds reversibly poisons the catalyst, even in a long time period. When the high purity of the gas mixture is restored the catalyst goes back to its original performances with no loss of activity. The temperature played a critical role, for example at 380°C the poisoning rate was faster compared to the one at 430°C. The cleaning rate was the opposite: the higher the temperature, the higher the oxygen desorption rate and thus the catalyst recovery. This information revealed that the oxygen desorption rate was faster at 430°C, indicating that the poison effect can be reduced when the temperature is increased. The data obtained were then compared with data from industrial reactors. A correlation between lab scale tests and data from industrial reactors was found. Start-up conditions of industrial reactors were found to be critical. The reduction of the poisoning effect in the reactors start-up conditions can enhance the life and performances of the catalyst. The ratios between poisoning and cleaning at different temperatures were compared and correlated with measurements of oxygen adsorption and desorption on the catalyst surface. The correlations found were then used to define the criteria to extend catalyst stability and life. Finally, the catalytic tests made with granules demonstrated how it is important to study also the catalyst "as it is fed" in the industrial reactors to achieve better performances in poisoning conditions.

In conclusion, the importance of understanding the poisoning and cleaning rate of the ammonia synthesis catalyst has been demonstrated. A procedure to evaluate the poisoning rate and degree for the industrial catalyst was identified. A correlation between lab experiments and data from industrial reactors was found and used to increase the reactors' performances. Moreover, the information can be used in the industrial reactors and extend catalyst life under industrial conditions.

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Structural Design, Computational Modeling, and Catalytic Pathways of Zn-Polyoxotungstate Catalysts

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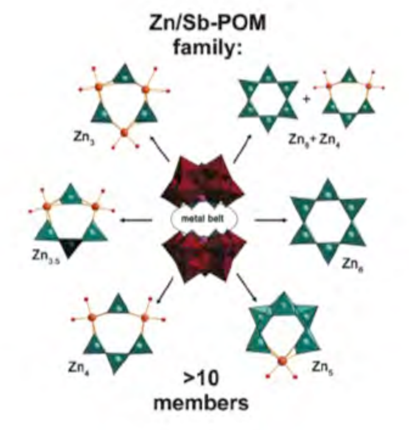
Polyoxometalates (POMs) are a fascinating class of metal-oxo clusters containing transition metal ions in their high oxidation states. Over the last 50 years, POMs have been widely explored for numerous applications in catalysis, as well as for their biomedical and magnetic features.[1] These metal-oxo clusters offer undeniable qualities for future applications, resulting from a remarkably wide structural and compositional diversity.

The number of POM architectures keeps growing steadily, and transition metal substituted POMs attract special attention as a rich reservoir for new catalyst developments. [2]

We introduce a new series of more than ten $\{Zn_nNa_{6-n}(B\text{-a-}SbW_9O_{33})_2\}$ (n = 3-6) POMs with tunable Zn-cores that are sandwiched between two $\{B\text{-}\alpha\text{-}SbW_9O_{33}\}$ shells. This series shows high activity and selectivity in H_2O_2-assisted alcohol oxidation. Spectroscopic and kinetic studies suggest that the reaction proceeds via peroxotungstate intermediates, and strong experimental evidence for a radical mechanism is provided. These results are compared to a full scale solution-based computational modeling of the intermediates and transition states for $[Zn_6Cl_6(SbW_9O_{33})_2]^{12-}$ as a representative alcohol oxidation catalyst among the series.



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A manganese oxide-based electrode as an efficient water-oxidizing anode

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Water splitting into O_2 and H_2 is a promising way to prepare eco-friendly fuels in the future. However, the anodic half-reaction in this process is a pivotal point, causing the vast majority of kinetic losses. Compared to the present-day price of the artificial photosynthetic systems, fossil fuels are still the utmost available and inexpensive energy sources [1]. Hence, developing fast and low-cost methods to fabricate efficient water-oxidizing anodes is the bottleneck for the commercialization of hydrogen production from water splitting reaction. In this work, a manganese oxide/FTO electrode was fabricated and used in water oxidation reaction. After optimization steps concerning thickness of the layer and calcination temperature, the electrode was used as an efficient water-oxidizing electrode at pH=7. A stable current density of 1.0 $mA.cm^{-2}$ was achieved at an over potential of ~480 mV for more than 100 hours. The fabricated electrodes were characterized with different methods such as FT-IR, Raman, SEM, HRTEM, XRD and XPS before and after long time electrolysis.

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Understanding the mechanisms of catalytic fast pyrolysis by unveiling reactive intermediates in heterogeneous catalysis

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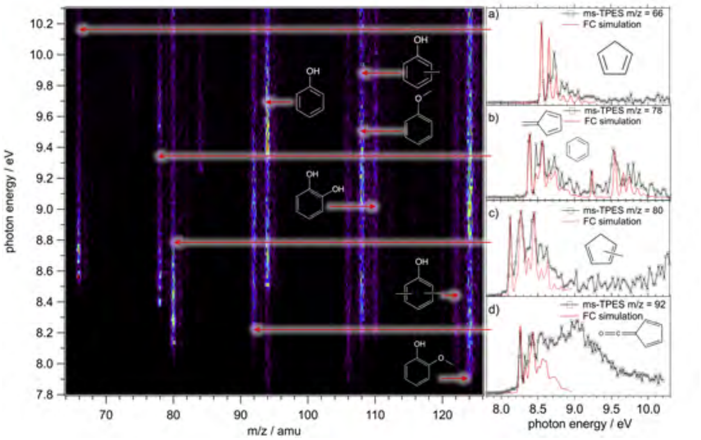
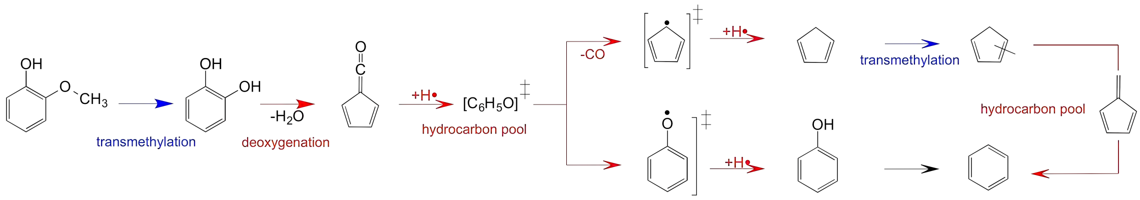
Catalytic fast pyrolysis (CFP) is very a promising way to convert lignin, a stable macromolecule abundant in biomass, into fine chemicals and transportation fuels, but current approaches lack selectivity and yield unsatisfactory conversion. We believe that understanding the CFP reaction mechanism at the molecular level will help to make this sustainable process more economic. Highly reactive intermediates are responsible for product branching and are notoriously difficult to detect isomer-selectively using standard chemical analysis tools such as GC/MS or NMR. However they hold the key to unveiling these mechanisms.

We have investigated the CFP of guaiacol, a lignin model compound, using photoelectron photoion coincidence (iPEPICO) spectroscopy with vacuum ultraviolet (VUV) synchrotron radiation, which allows for isomer-selective detection of reactive intermediates. To identify the isomeric contributions we have recorded photoion mass-selected threshold (near-zero kinetic energy) photoelectron spectra (TPES) at the exit of a catalytic reactor. The vibrational fine structure of these TPES is an isomer-specific fingerprint, which can be used to assign the species with the help of calculated Franck–Condon (FC) factors (see figure).



In combination with ambient pressure CFP, py-iPEPICO identified the fulvenone ketene (c-C_5H_4=C=O) as the central reactive intermediate, generated by catalytic dehydration of catechol (1,2-benzenediol), which is the demethylation product of guaiacol. This fulvenone ketene is responsible for the formation of e.g. phenol, cresols and cyclopentadiene (see following scheme).[1]

More broadly, we are convinced that py-iPEPICO opens new opportunities for isomer-resolved probing in catalysis, and holds great potential for achieving a mechanistic understanding of complex, real-life catalytic processes beyond CFP.



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Ionic Liquids – Catalysts for the Synthesis of Quinazoline-2,4-diones from 2-Aminobenzonitrile and CO_2

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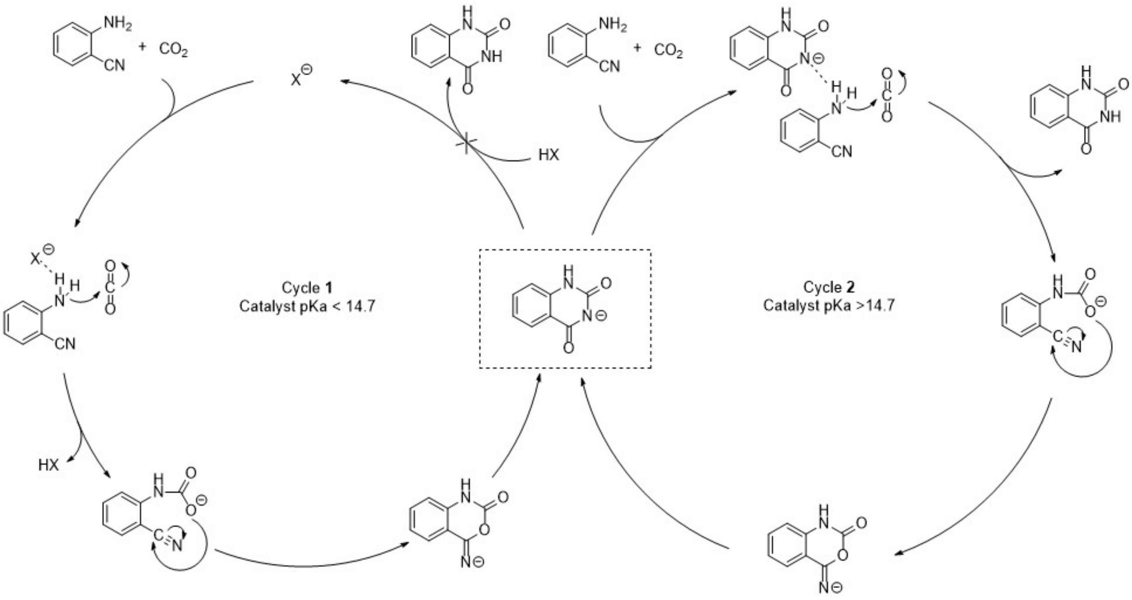
Ionic liquids (ILs) are versatile solvents and catalysts for the synthesis of quinazoline-2,4(1H,3H)-dione from 2-aminobenzonitrile and CO_2. However, the catalytic role of the IL in this reaction is poorly understood. Here, we present a systematic investigation of a series of ILs in this reaction and showed that the IL cation does not play a significant role in the catalytic activation of the substrates. The IL cation only plays a secondary role in contributing to the control of the desired physical properties of the IL. A linear relationship between the pKa of the IL anion and the reaction rate was identified with maximum catalyst efficiency observed at a pKa of 14.7 and above in DMSO. The base catalyzed reaction is limited by the acidity of the quinazoline-2,4(1H,3H)-dione product, which is deprotonated by more basic catalysts leading to the formation of the quinazolide anion (conjugate acid pKa 14.7). Neutralization of the original catalyst and formation of new quinazolide anion catalyst leads to the observed reaction limit. Finally, we demonstrate that ILs containing the quinazolide anion are the most active base catalysts for the synthesis of quinazoline-2,4(1H,3H)-dione from 2-aminobenzonitrile and CO_2.



Heterogenization of Pd/Cu catalysts for Wacker Oxidation

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

The Wacker process is one of the most efficient organic synthetic methods for manufacturing aldehydes and ketones. This liquid-phase homogeneous process, however, suffers from serious drawbacks such as the difficulty in the separation of the products from the catalyst solution; high corrosivity associated with the excess of HCl; and the formation of undesired chlorinated byproducts. Moreover, the production of these chlorinated compounds increases with the olefin's chain length, and thus it is difficult to apply this process to the oxidation of higher alkenes [1].

Heterogenization of a chloride-free Wacker catalyst system on a support holds a great potential to overcome these problems. Cu-and-Pd-exchanged zeolite Y catalyst proves to be one of the most active and stable catalysts for heterogeneous Wacker oxidation reported in the literature but ultimately suffers from rapid loss of its high initial activity [2]. Evidence of catalyst particle sintering and deposition of carbonaceous products is shown after the reaction by ex situ TEM. To optimize the catalyst, the effects of varying metal loading; pretreatment and reaction conditions; and kind of support on the performance of the catalyst were investigated. Lower Pd loading and a higher Cu/Pd ratio resulted in a more active and selective catalyst for Wacker oxidation (Figure 1). Regeneration of the catalyst at different conditions was also explored in order to recover the initial activity completely or partially. Moreover, in situ XAS studies revealed the presence of Pd(II) and Cu(II) species in the fresh catalyst; and the formation of Pd(0) through the course of the Wacker process.

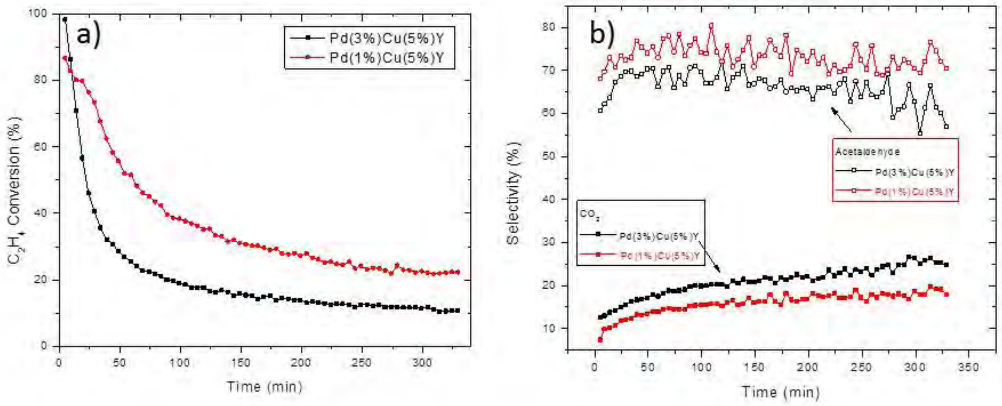

Figure 1. Ethylene conversion over Cu-Pd-exchanged zeolite Y catalyst with varying Pd loading and Cu/Pd ratio vs time on stream (a) and the corresponding selectivities for acetaldehyde and CO_2 (b).

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Exploration of activated copper sites for conversion of methane to methanol at low temperature

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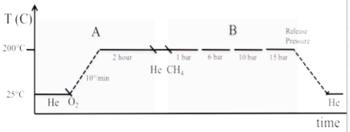
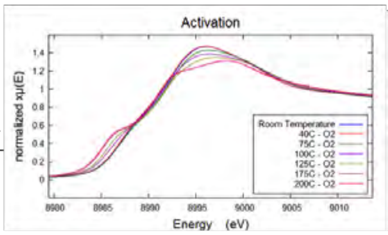
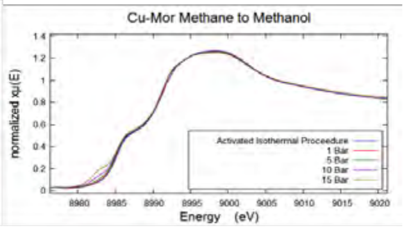
Conversion of methane into methanol provides a promising route for harnessing untapped methane resources that are otherwise discarded or flared into the atmosphere. Due to the tendency for methane to fully oxidize, the scientifically challenging part is to only partially oxidize the methane[1]. With the combination of the appropriate micropore environment and an exchanged cation, Cu-mordenite and Cu-ZSM-5 can achieve selective methane activation.

Copper in the form of di- or tri cores has been reported as an active species in the conversion of methane to methanol, but requires high temperature activation, typically at 450°C in an oxygen environment. This high temperature activation step has become a standard step in stepwise conversion of methane to methanol throughout literature[2,3,4]. Contrarily, when the reaction takes place at high methane pressures, Tomkins et al. have shown that high yield (56.2 μmol·g^{-1}) can be achieved without this high activation temperature[5]. Specifically, methane to methanol conversion can be performed isothermally at low temperatures (200°C). These temperatures are well below the activation temperature of the active sites previously proposed (di- or tri-Cu cores).







This work focuses on using in-situ XAS to elucidate the copper speciation and active site responsible for the conversion of methane to methanol under high pressure, low temperature isothermal conditions for copper exchanged mordenite, zeolite Y, and omega. Preliminary results show that, at pressures higher than 1 bar, copper interacts with methane without the need of activating the sample at 450 C. Even for a zeolite like Cu-Y which generally shows low conversion of methane to methanol, a significant increase in conversion is suggested by the XANES results at pressures at or above 15 bar.

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CO_2 Hydrogenation of Copper Nanoparticles Supported on Zirconium Modified Silica

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To date, there is no efficient way to employ and transform the ever-increasing amount of carbons dioxide (CO_2) into more valuable resources. One approach to use CO_2 could be its transformation into more valuable compounds such as methanol (MeOH). [1] Copper based catalysts have shown promising efficiency in terms of activity and selectivity for transforming CO_2 to MeOH when supported on specific metal oxides. Of them zirconia (ZrO_2) is known to promote MeOH synthesis. [2] Recently we proposed a reaction mechanism leading to MeOH occurring on the interface between copper and zirconia going via formate as an intermediate.[3]

Herein we use a surface organometallic chemistry (SOMC) combined with a thermolytic precursor (TMP) approach as well as incipient wetness impregnation (IWI) to maximize the ratio between Zr at the interface vs. the bulk on silica (SiO_2). Cu nanoparticles on such supports show greatly enhanced activity and selectivity towards MeOH under CO_2 hydrogenation conditions compared to Cu nanoparticles on SiO_2.

Solid state nuclear magnetic resonance spectroscopy and X-ray absorption spectroscopy was further used to investigate the catalyst and reaction intermediates.

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Hybrid palladium nanoparticles for direct H_2O_2 synthesis: the key role of the ligand

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Hydrogen peroxide, H_2O_2, attracts growing attention as a green alternative to traditional stoichiometric oxidants in a wide range of applications. Its direct synthesis from H_2 and O_2 is an appealing substitute to the current manufacture based on the anthraquinone route, having the potential to be exploited in decentralized plants at any scale due to the (i) absence of organic substrates, (ii) utilization of environmentally-friendly solvents such as water or methanol, and (iii) simplified purification. In this work,[1] we demonstrate that ligand-stabilized palladium nanoparticles deposited on a carbon support are, by virtue of their unique nanostructure, active, selective, and stable catalysts for the direct synthesis of H_2O_2. In fact, progressive addition of the ligand was shown to boost the selectivity from 10% for bare nanoparticles up to 80% (**Figure 1a**), thus rivalling that obtained with state-of-the-art bimetallic catalysts.[2] Furthermore, the catalyst remains stable over five consecutive reaction runs owing to the high resistance to leaching of the organic moiety, which arises from its strong interaction with the metal surface. Density Functional Theory studies rationalized this behavior based on the adsorption mode of reaction intermediates on the metal surface (**Figure 1b**). Whereas they lie flat in the absence of the organic shell, their electrostatic interaction with the ligand results in a unique vertical configuration which increases the activation energy associated with further dissociation and over-hydrogenation (**Figure 1b**). These results demonstrate the applicability of hybrid materials for the direct synthesis of H_2O_2 and highlight the importance of understanding the molecular role of the organic ligand for the design of novel nanocatalysts.

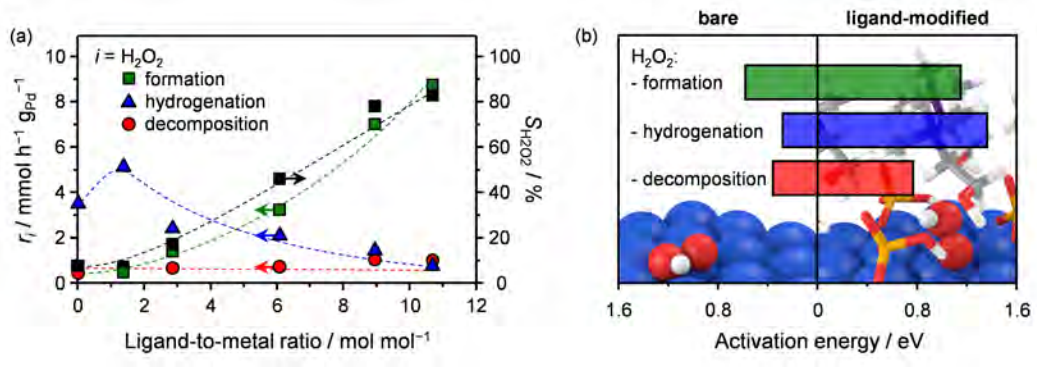

Figure 1 (a) Effect of the ligand-to-metal molar ratio on the H_2O_2 formation, decomposition, and hydrogenation reactions and (b) the activation energies of these reactions over the bare and hybrid palladium nanoparticles. The drawings in panel (b) represent the configuration of the adsorbed hydroperoxyl (OOH) intermediate.

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Design of a technical Mg-Al mixed oxide catalyst for the continuous manufacture of glycerol carbonate

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[1]ETH Zurich

Glycerol carbonate, obtained by the carbonylation of waste glycerol with urea, is an important bioderived chemical with applications as a solvent and an intermediate. Its preparation would ecologically and economically benefit from the availability of a heterogeneous catalyst, which contains cheap and abundant elements, has a scalable synthesis, is highly active and stable, retains its performance upon shaping into a technical form, and can be operated in continuous mode. In this work,[1] we show that a mixed oxide of Mg and Al is a promising active phase for this reaction. The solid comprises widely available and non-toxic metals, is easily obtained through the thermal decomposition of a hydrotalcite-like material, and can almost match the product yield of state-of-the-art Zn-based catalysts[2] (**Figure 1a**), while displaying an outstanding resistance against leaching, which causes the rapid dissolution of the latter. In-depth characterization uncovered that Lewis-basic centers are crucial to activate glycerol through dehydrogenation. Their concentration was maximized by optimizing the composition and calcination temperature of the precursor, thus reaching up to 60% glycerol carbonate yield (**Figure 1a**). Millimeter-sized extrudates showing comparable basic properties to the powder sample, a well-developed meso- and macroporosity, and high mechanical stability were obtained using a natural clay, bentonite, as a binder and thermally activating the hydrotalcite only after shaping. Upon testing in a continuous reactor under tuned conditions of temperature and pressure and in the presence of an aprotic solvent, the system showed the same glycerol yield as in the batch tests. During 100 h on stream, its activity decreased by 20% due to fouling (**Figure 1b**), but could be fully restored upon burning-off of the carbonaceous deposits. This work discloses the development of a green material that exhibits high efficacy in a sustainable transformation, highlighting key parameters for consideration in the design of an industrially-relevant chemocatalytic technology.

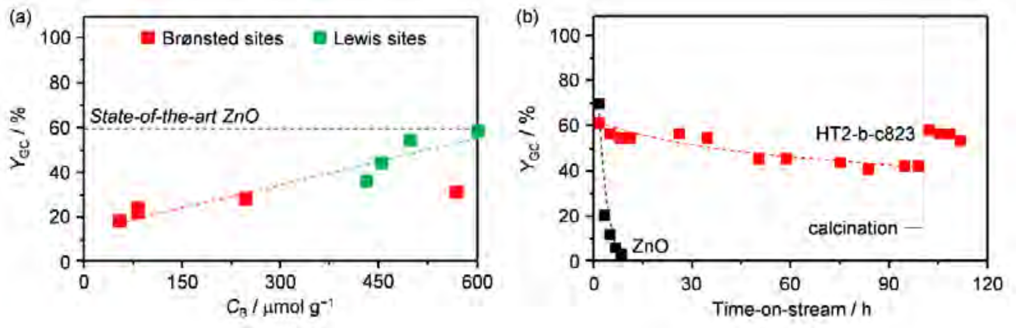

Figure 1 (a) Glycerol carbonate yield *versus* the concentration of basic sites for the hydrotalcite-derived catalysts and (b) evolution of the glycerol carbonate yield over 100 h and effect of regeneration by calcination on the performance.

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Enhanced electrochemical reduction of CO_2 over Cu-based catalysts modified with p-block elements

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The coupling of electrosynthesis technologies with renewable energy sources can potentially turn CO_2 emissions into a valuable feedstock for the production of fuels and chemicals while contributing to closing the anthropogenic carbon cycle.[1,2] Copper foil electrodes prepared from the reduction of thick oxide films (OD Cu) effectively target the reduction of CO_2 to CO at moderate overpotentials.[3] However, such electrodes display modest current densities, and their preparation on bulk metallic substrates makes them unsuitable for practical applications. In this context, we have recently shown that Cu_2O nanocatalysts prepared by a simple and potentially scalable solvothermal route are more active and selective for CO evolution than OD Cu electrodes under similar conditions.[4] Additionally, the performance of these catalysts can easily be enhanced by introducing Sn and In into the Cu_2O matrix through the addition of the corresponding precursors to the synthesis medium (**Figure 1**). Based on this insight, we extend this methodology to evaluate the catalytic effect of introducing most non-hazardous p-block elements as modifiers, revealing a powerful strategy to tune the selectivity toward other eCO_2RR products while maintaining a high selectivity at reduced overpotentials.

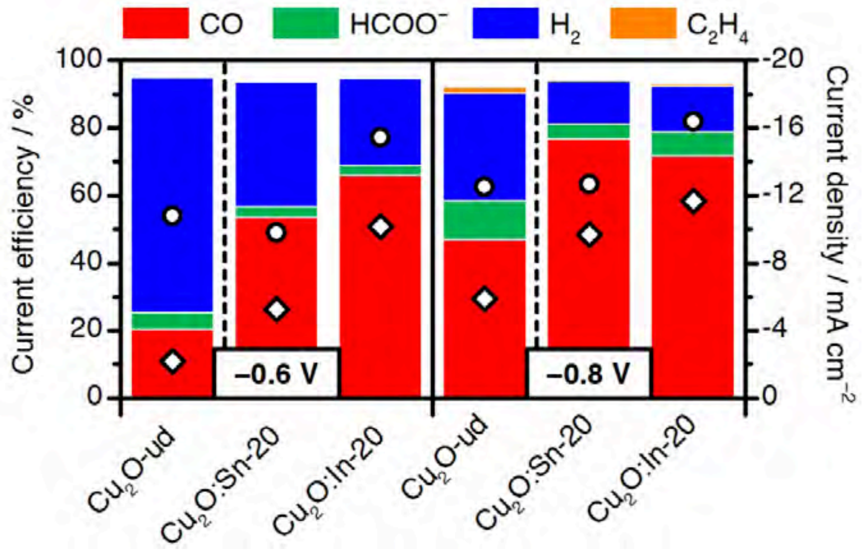

Figure 1 Current efficiency (bars), total current density (circles) and partial current density for CO (diamonds) in CO_2 electroreduction over unmodified (Cu_2O-ud) and Sn- and In-modified Cu_2O electrocatalysts prepared by a simple and potentially scalable solvothermal synthesis (potential indicated *versus* RHE in CO_2-saturated 0.1 M $KHCO_3$). The number in the codes indicates the Cu:Sn or Cu:In ratio of the catalyst.

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Local Connectivity and Confining Environments of Sn-Sites in Sn-Chabazites Are Distinguishable Using DNP-NMR

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Chabazite molecular sieves with isomorphously substituted framework Sn heteroatoms (Sn-CHA) constitute model stannosilicate zeolites comprising a single crystallographically unique tetrahedral-site (T-site). The predominant incorporation of isolated Sn sites within framework positions was assessed from UV-Visible absorption edge energies (>4.1 eV), four-coordinate Sn centers measured after dehydration by X-ray absorption spectroscopy (XAS) and ^{119}Sn dynamic nuclear polarization nuclear magnetic resonance (DNP NMR), and Lewis acid site fractions of nearly unity quantified by ammonia and acetonitrile titration. Aqueous-phase glucose-fructose isomerization turnover rates on Sn-CHA (per extracrystalline framework site) were similar to rates on an amorphous stannosilicate, while intermolecular Meerwein-Pondorff-Verley propionaldehyde reduction and Oppenauer ethanol oxidation (MPVO) reactions confirm that Sn sites confined within micropores behave as Lewis acids capable of catalyzing intermolecular hydride shift steps.

The increased sensitivity afforded by DNP NMR enabled performing 2D ^{119}Sn cross polarization magic angle turning (CPMAT) NMR experiments, which allows the detection of different sites having the same isotropic chemical shift but different chemical shift anisotropy (CSA) parameters, an unexpected result considering the presence of single T-site in CHA framework. By using pyridine as a probe molecule, which is too large to enter the pore of CHA framework, the Sn sites within mesoporous voids and at extracrystalline surfaces can be selectively detected by IR and ^{15}N/^{119}Sn DNP enhanced NMR. Experimentally measured ^{119}Sn NMR CSA parameters were compared to values estimated using density functional theory (DFT), supporting the presence of defect-open and closed Sn sites in dehydrated samples, which evolves into hydrated defect-open and hydrolyzed-open sites respectively upon hydration. These findings highlight the characterization of local structures of active sites in Sn zeolites enabled by DNP NMR with the aid of DFT calculations, and the crucial role of the confining environment in zeolitic porous framework in Lewis acid promoted reactions.

Formation of Formic Acid via CO_2 Hydrogenation with Silica-Supported Transition Metal Pincer Complexes

H. Lo[1], I. Thiel[1], C. Copéret[1]*

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Over the past decades, the hydrogenation of CO_2 to more valuable products such as formic acid or methanol has been highly emphasized in the academic field because of the continuous increase of CO_2 in the earth’s atmosphere. The challenge of converting CO_2 results mainly from its considerable Gibbs free energy ($\Delta G° = -394.4$ kJ/mol). Therefore active co-reactants and/or catalysts are usually needed. Formic acid, one of the CO_2 hydrogenation derivatives, is an efficient hydrogen carrier and has great potential to be applied in fuel cells. Nowadays various efficient homogeneous catalytic systems have been developed to convert CO_2 to formic acid, such as the iridium complexes with PNP pincer-type[1,2] and bipyridine-type ligands[3] or[4] ruthenium complexes with N-heterocyclic carbenes.[4] However, the above-mentioned homogeneous catalysts were only applied in batch reactors, which are less favored in industrial continuous processes, and efficient well-defined immobilized catalysts are still sparse in CO_2 hydrogenation. Here, we aim at synthesizing new immobilized catalysts, which are supported on well-defined silica-based hybrid materials or synthetic polymers, and applying them in a continuous CO_2 hydrogenation process.

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Synthesis-structure-function relationships K-CoMo catalysts supported on carbon nanofibers for higher alcohols synthesis

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

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

Higher alcohols (HA) find wide application in the chemical and energy industries and are currently produced by sugar fermentation and alkene hydration. The direct conversion of syngas could comprises a potentially more environmentally-friendly and economical route for their production since it involves a single step and enables a wider exploitation of unconventional and renewable resources. Although the reaction conceptually is a combination of methanol and Fischer-Tropsch synthesis, two well-developed technologies, no catalytic system reported to date has performed sufficiently well to justify an industrial implementation, mostly due to the poor HA selectivity. We believe that the establishment of clear structure-function relationships is crucial to attain improved catalysts.[1] In this contribution, we aim at identifying performance descriptors of K-CoMo-based catalysts. For this purpose, we prepare materials supported on carbon nanofibers with a low total metals loading (5 wt.%) to better control the nanostructure of the components and apply variable Co/Mo ratios (0.5−2), synthesis methods (dry impregnation (DI), sol-gel (SG), ball milling (BM)), and temperature and pressure conditions (523−773 K, 1−50 bar) upon activation by H_2. The Co/Mo ratio offers a means to balance C−C coupling and CO insertion activities, different preparation methods are instrumental to attain solids with a distinct distribution of the metal precursors, and the conditions of activation are vital to ensure high dispersion and interaction of metal phases. Preliminary catalytic results indicate that the sol-gel protocol leads to superior catalysts and that higher reduction temperatures lower the activity while promoting the HA selectivity (**Figure 1**). Accurate testing and in-depth characterization will be combined to attain a comprehensive description of these systems.

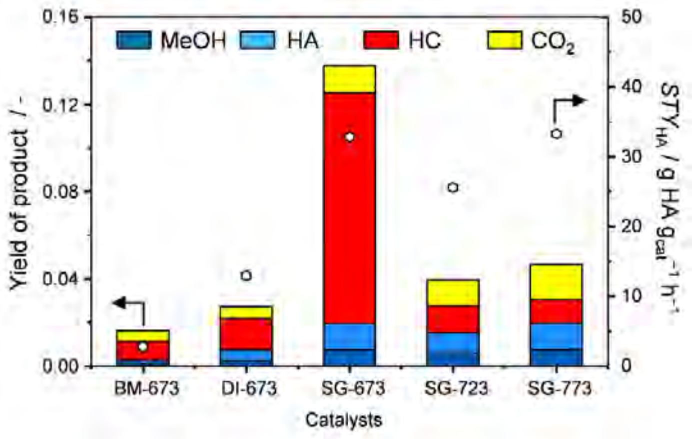

Figure 1 Effect of synthesis method and reduction temperature (673, 723, and 773 K) on the catalytic performance of K-CoMo/CNF systems.

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Effect of pretreatment on the production of phenol from lignin by catalytic fast pyrolysis over zeolites

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Lignin is a complex three-dimensional amorphous material, which contains methoxylated aromatic units with different linkages in the matrix.[1] By far, lignin is the most abundant renewable source and a potential sustainable candidate feedstock for aromatic chemicals.[2] Due to its complex structure and high thermal stability (high amount of C-C bond), the conversion of lignin is difficult.[3] Pretreatment of lignin is a potential way to reduce the amount of C-C bond and thus to increase the activity and selectivity to monomers, such as phenols.[4]

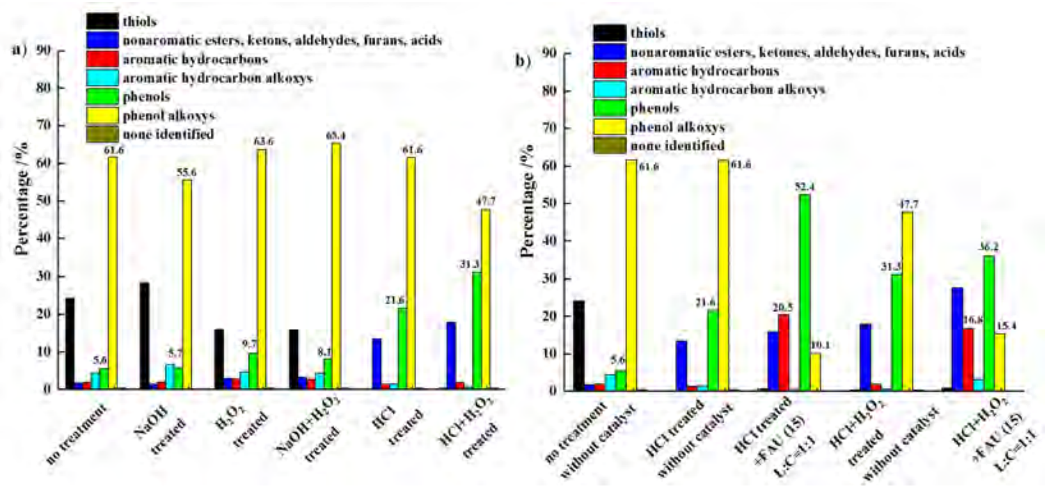

Figure 1: Effect of pretreatment on liquid product distribution (a) without zeolites (b) with FAU (15) zeolite. Pyrolysis conditions: 650 °C, 20 s, 20 °C/ms. In case of catalytic fast pyrolysis, pretreated lignin to catalyst weight ratio (L:C) = 1:1.[4]

The results present in this work show that simple pretreatment of lignin play an important role in catalytic fast pyrolysis, which significantly change the liquid product distribution. Especially after lignin pretreated with acid, such as hydrogen chloride, the production of phenols increased to a large extend. By choosing the proper pretreatment, catalyst and reaction conditions, a maximum selectivity to phenols (over 50 %) was obtained. Large pore zeolite (FAU) with medium Si/Al ratio (~15), medium catalyst-to-feed ratio (L:C=1:1), high pyrolysis temperature (650 °C) and heating rate (20 °C/ms), and long pyrolysis time (20 s) are essential to maximize the production of phenols from hydrogen chloride-treated Kraft lignin.

By chemically treating lignin, a more efficient conversion in catalytic fast pyrolysis can be achieved and higher yields of phenols can be obtained.

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$FeVO_4$, $CeVO_4$ and $ErVO_4$-based catalysts for the selective catalytic reduction of NO with NH_3

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Efficient removal of NO_x from exhaust gases of stationary sources is realized by reacting it with NH_3 on a solid catalyst according to the standard selective catalytic reduction (SCR). Metal vanadate-based SCR catalysts exhibit promising advantages over traditional vanadia-based catalysts. Some $MeVO_4$ were shown to be resistant to deactivation when supported on SiO_2-WO_3-TiO_2 (TWS) and remained active after aging up to 750°C [1]. Nevertheless, it was recently shown that supported $FeVO_4$ is not stable on TWS and decomposes into Fe_2O_3 and VO_x species above 600°C [2, 3]. The intrinsic activity of the $FeVO_4$-based SCR catalysts is rather low and is only enhanced by the thermal decomposition. In order to clarify the benefits of vanadates as SCR catalysts, we compared the activity and stability of $FeVO_4$, $CeVO_4$ and $ErVO_4$ on a TWS support.

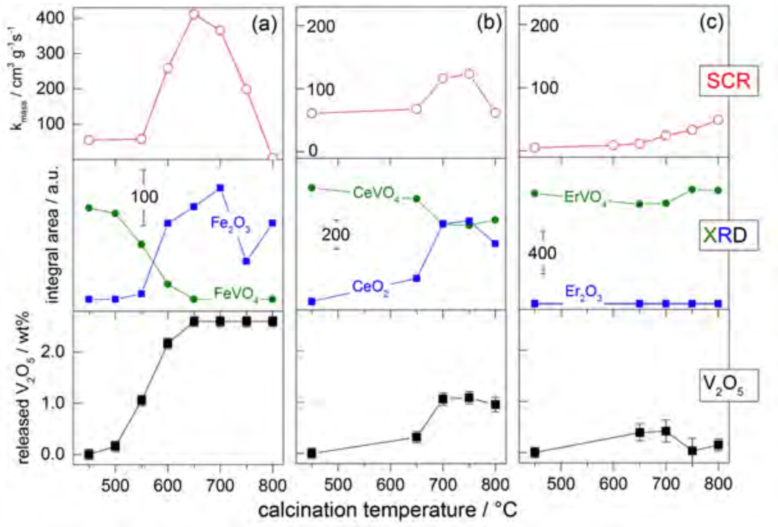

Figure 1. Top panels - rate constants, middle panels - important changes of XRD features; lower panels - derived fraction of released V_2O_5 of (a) $FeVO_4$-TWS, (b) $CeVO_4$-TWS and (c) $ErVO_4$-TWS.

It was shown that an increase of calcination temperature activates all catalysts (increase in rate constant k_{mass}, Figure 1) concurrent with the decrease of the metal vanadate peak integral from XRD. The decomposition of the metal vanadate gave rise to the corresponding metal oxides, but no traces of a new vanadium containing phase were observed. However, an estimation of released V_2O_5 could be derived from the loss of the metal vanadate phase (lower panels in Figure 1). The change of released V_2O_5 and k_{mass} are strongly correlated. While $FeVO_4$ decomposed completely, the maximum fraction of released V_2O_5 was 1.1 wt% for $CeVO_4$-TWS and 0.4 wt% for $ErVO_4$-TWS, hence $CeVO_4$ and $ErVO_4$ decomposed only partially. References with 0.5 and 1.0 wt% V_2O_5 on TWS showed very similar activity, indicating that the amount of released V_2O_5 is in fact responsible for the increase in activity. The existence of released V species from metal vanadates was proven using DRIFTS and DRUV, which revealed the predominant formation of extended VO_x units on the surface of TWS. Summarizing, metal vanadate catalysts supported on TWS become active only after their decomposition into metal oxides and free VO_x species.

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Continuous sol-gel synthesis of phosphated TiO_2 catalysts in a microreactor

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Continuous microreactors, featuring µm-sized tubes and thus a fast mass and heat transfer, enable a precise control of chemical processes, which leads to improved efficiency and safety with respect to conventional large-scale reactors.[1] In addition, their modular design adds unrivaled flexibility. While numerous catalyzed reactions in microreactors have been reported,[1] the preparation of heterogeneous catalysts in these systems has been greatly overlooked even though a controlled design of catalysts will be key for the development of more sustainable chemical processes.[2]

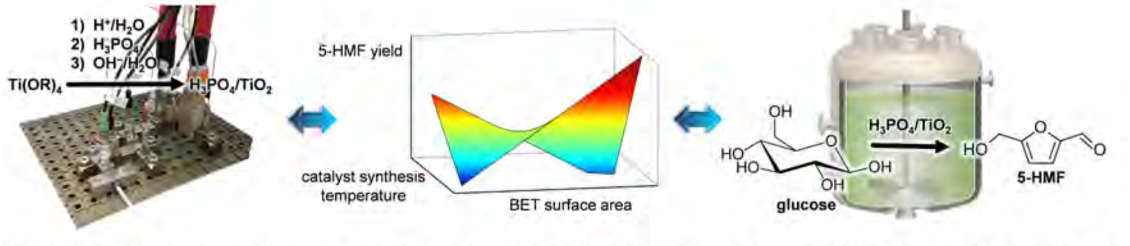

Figure 1. The DoE strategy applied herein correlates (center) the parameters of the preparation of phosphated TiO_2 *via* a novel continuous sol-gel route in a microreactor (left) with the resulting catalyst properties as well as the catalytic performance upon the 5-HMF synthesis from glucose (carried out in a batch reactor).

Therefore, we established a novel continuous sol-gel microreactor process for the production of phosphated TiO_2, which can be applied as cheap and eco-friendly catalyst for the selective synthesis of the platform chemical 5-hydroxymethylfurfural (5-HMF) from bio-derived glucose.[3] This approach allows a highly efficient catalyst preparation since all steps, *i.e.*, (*i*) sol formation, (*ii*) functionalization by H_3PO_4, and (*iii*) gel formation, are carried out in one continuous process (**Figure 1**, left). The catalytic performance was correlated with the catalyst properties (*e.g.*, surface area) and its synthesis parameters (*e.g.*, temperature) through design of experiments (DoE, **Figure 1**) to obtain the optimal catalyst preparation process and the material with the best catalytic results. Due to these correlations, we could additionally gather a deeper mechanistic understanding of both catalyst synthesis and catalyzed reaction. This was essential to rationalize phenomena occurring such as fouling, *i.e.*, blockage of the microchannels by large agglomerates, which can pose a critical challenge upon the catalyst production.

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Well-Defined Silica-Supported Nickel Surface Sites for the Direct Conversion of Ethylene to Propylene

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

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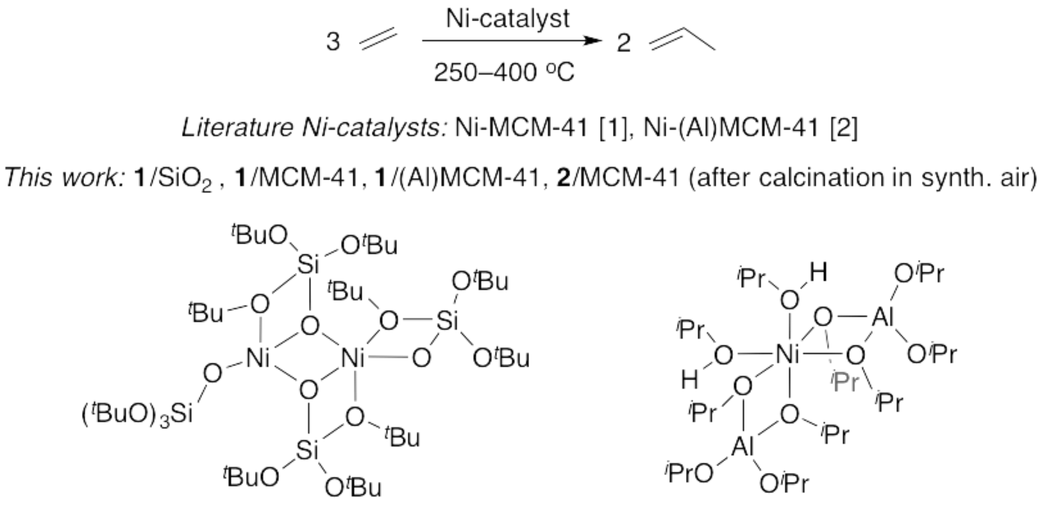
Ni-modified mesoporous MCM-41 catalyzes the direct transformation of ethylene to propylene, the so-called ETP reaction, with conversion up to 68 % and propene selectivity up to 48 % [1]. Incorporation of aluminum into Ni-MCM-41 increases the catalytic activity [2], however, the role of aluminum, the reaction mechanism and nature of the active sites remains unknown [3].

Scheme 1. Ni-based catalysts for ETP reaction



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

This work: **1**/SiO_2 , **1**/MCM-41, **1**/(Al)MCM-41, **2**/MCM-41 (after calcination in synth. air)

(1) **(2)**

Here, using a combination of surface organometallic chemistry and thermolytic precursor approach [4], we synthesized well-defined Ni(II) surface sites on silica-based supports (MCM-41 and Al-MCM-41) exploiting nickel siloxide (**1**) and aluminate (**2**, Scheme 1) molecular precursors. Their structure and reactivity towards ethylene will be discussed.

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The role of the support in gold-based catalysts for ethanol oxidation

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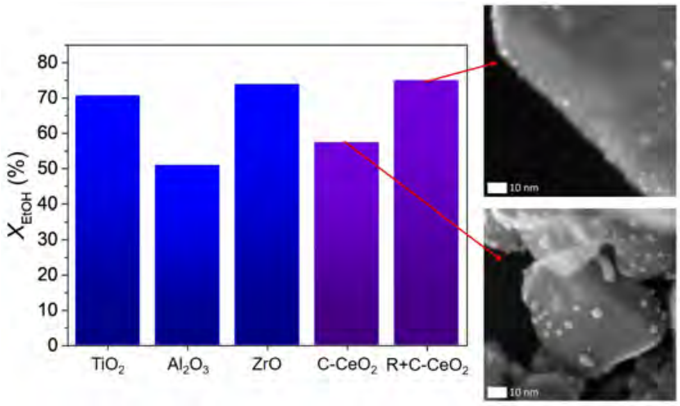
Supported gold nanoparticles are very efficient and selective oxidation catalysts.[1] The gold particle size is a major parameter that affects both conversion and selectivity.[2] The support choice is also very crucial; the best-performing catalysts are supported on reducible oxides, such as titania and ceria, which donate their lattice oxygen around the perimeter of the gold particle for the carbon monoxide oxidation, forming observable oxygen vacancies,[3-4] while on stable oxides, like alumina, the oxygen is directly activated on the gold particle.[5] Hence, the support actively participates in the reaction and its nature and structure can alter the catalytic properties.

In this work we investigate the effect of the support on the gold particle size and the catalytic activity of aqueous ethanol oxidation.[6] The ethanol conversion showed a dependence on the support (Figure; 1%Au/Support). For constant gold particle size (2 nm), over transition metal oxides, titania and zirconia, more than 70% of ethanol was converted at 423 K, while over alumina only 50%. Furthermore, the pre-treatment of the catalyst was decisive. 1%Au/CeO_2 powder underwent two different pre-treatment conditions, calcination at 473 K (C-CeO_2) and reduction at 423 K followed by calcination at 473 K (R+C-CeO_2). Both catalyst resulted in similar particle size (3.5 nm) but exhibited different ethanol conversion, 58 and 75%, respectively. Further characterization and testing of differently treated materials is pending that will allow us to define the catalytic performance descriptors with respect to the support effect.



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In-situ Raman spectroscopy of metal carbodiimide (MNCN) catalysts for electrochemical water oxidation

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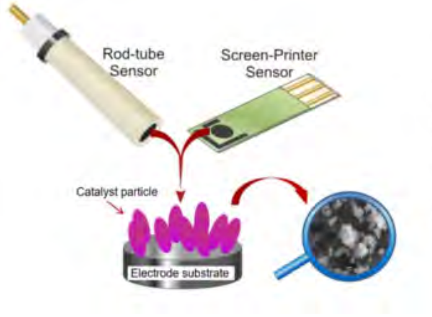
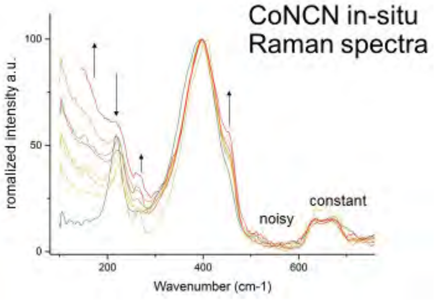
Cobalt carbodiimide (CoNCN) has recently been introduced as catalyst prototype for both visible light-driven and electrocatalytic water oxidation.[1] The well-defined all-nitrogen coordination environment of metal carbodiimide catalysts is an attractive model system that permits mechanistic insights into water oxidation catalyst design at the interface between molecular and solid state chemistry. This simple but versatile new system for fundamental electrocatalytic studies of structure–activity relationships, catalytic mechanisms and surface effects furthermore offers tuning options through modification of the carbodiimide matrix through substitution of cobalt by other transition metals.

Another application potential as Li^+ and Na^+ battery material has been proposed in 2016 and shows bulk transformation due to electrochemical intercalation reactions.[2]

During water oxidation major in-situ transformations of CoNCN into active secondary oxide species were excluded through XAS and Raman investigations of pre- and post-catalytic materials. Nevertheless, in-depth analyses were performed to address the possibility of catalytic contribution by in-situ formation of subtle but active surface oxide layers.

Raman spectroscopy was chosen in the first place as a surface sensitive technique to probe for different catalytic sites and temporary changes upon electrode polarization. The oxygen free MNCN type catalysts were deposited on versatile screen printed electrodes which offered a unique platform to study the heterogeneous electrocatalytic mechanism of water oxidation. Surface confined catalyst-oxygen interactions can be studied without the background signal of bulk material oxygen atoms. Results so far indicate no formation of such layers, and the applied setup is subject to further optimization for lowering the detection limits.





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Density functional theory study of anion ordering and chemical composition of different $LaTiO_2N$ surface orientations

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Perovskite oxynitrides are a promising class of materials for photocatalytic water splitting under solar light.[1-3] They have the advantage of a reduced band gap with respect to the pure oxides, however at the cost of diminished stability. Perovskite oxynitrides are characterised by a partial order of oxygen and nitrogen atoms on the anion sublattice. In the bulk several theoretical studies find cis-positioning of the N-atoms to be energetically most favourable.[4-5] The anion ordering at the surface and its resulting chemical composition, however, are still elusive, despite its direct implication on the water-splitting mechanism on oxynitride surfaces.

We perform density-functional theory calculations on one member of the perovskite oxynitride class, $LaTiO_2N$, to deduce the O/N distribution for a variety of surface orientations and establish the chemical composition of the various surfaces and terminations. Based on these results it is possible to deduce trends for the reactivity of different surface orientations, which we correlate with experimental results on thin films with different orientations.

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DFT calculations of photocatalytic water splitting on $NaTaO_3$ (113) and $SrTaO_2N$ (001) surfaces

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Photocatalytic water splitting is considered as a promising route to produce clean hydrogen fuel. Since the famous work of Fujishima and Honda on TiO_2 [1], a large variety of metal oxides have been considered for visible-light photocatalysis, perovskite structured materials that hold particular promise due to their structural and chemical flexibility [2]. Oxynitride perovskites benefit from a smaller band gap compared to pure oxides, making them even more promising for photocatalytic water splitting.

In this work, we want to compare oxides and oxynitrides in terms of their surface chemistry. To this goal, we studied the photo-oxidation of water on the lowest–energy $NaTaO_3$ (113) and $SrTaO_2N$ (001) surfaces, using density functional theory (DFT). We found NaTaO termination to be the most stable for $NaTaO_3$ whereas. For $SrTaO_2N$ the SrO and TaON terminations have approximately the same surface energy. The two materials differ in their water adsorption behavior, $SrTaO_2N$ dissociating water without a barrier on both terminations, whereas for $NaTaO_3$ dissociative adsorption occurs only at the Ta site but it is not barrierless.

To describe the electrochemical process of water splitting as a function of the applied bias and pH on our surfaces, Nørskov's approach has been used [3].

Based on our results it is possible to rationalize the photocatalytic performance of oxynitrides compared to pure oxides going beyond the usual band-gap arguments, considering also the thermochemistry of the water-oxidation reaction on their surfaces.

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Unravelling the chemical nature of anaerobic methane oxidation: the reaction profile maze

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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. An efficient stepwise process catalysed by copper-exchanged zeolites has been suggested; however, a detailed understanding of the mechanism of such a zeolite-catalysed conversion is still missing. One of the ongoing debates in studying copper-exchanged zeolites is the exact configuration of the available catalytic sites. Another open question is the role of the nature of the oxidant, and the mechanism of methane oxidation and regeneration of the copper oxide active site.

We have recently shown [1] that a direct stepwise method for converting methane into methanol with high selectivity over a copper-containing zeolite can be achieved by partial oxidation with water, and proposed a mechanism involving methane oxidation at Cu(II) oxide active centers, followed by Cu(I) reoxidation by water with concurrent formation of hydrogen. However, the possibility of formation of various copper oxide species as active centers [2-4] opens a Pandora box of potentially feasible reaction pathways, including, but not limited to, the reactions over the mono- [5], di- [6], or tricopper [7] active species.

We use ab initio calculations to carefully study and analyze the possibility of alternative reaction pathways, and show that the unique behavior of copper mordenite zeolite relates to the reactivity of zeolite-supported copper oxide species, facilitating the two-electron redox process. We suggest a novel reaction pathway, and critically discuss the possibility of using various copper oxide species.

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Design of efficient co-electrolyser systems for CO_2 reduction in gas phase

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The electrochemical CO_2 reduction reaction (CO_2RR) is a complex reaction which must be carried out in a highly selective and efficient manner. Many efforts are being taken to develop catalysts with improved reaction selectivity and efficiency and significant progress has been made in this area of research [1]. However, CO_2RR kinetics, product identification and quantification are mostly carried out in half-cell configurations using liquid electrolytes. This fundamental approach of studying CO_2RR is limited by the low solubility of CO_2 in water, the maximum CO_2 reduction current reported in the literature is in the range of 0.01- 0.02 A/cm^2 [2]. In order to overcome the solubility problem and to reach higher operating current densities, CO_2 reduction can be carried out in a co-electrolysis system where pure or diluted gaseous CO_2 is used. Our research efforts were focused on the design of an electrochemical cell for co-elecrolysis operating at high-current densities with good product selectivity.

The experiments were conducted in a membrane electrolyzer-like configuration setup. Various gold type cathode electrode materials were tested and the reaction pH was controlled by using different type of commercial ionic exchange membranes. The reaction products were analysed by on-line mass spectroscopy. The co-electrolyser performance and the selectivities of the various membrane electrode assemblies are examined in detail.

Acknowledgements
Financial support of this work by the Commission of Technology and Innovation Switzerland (CTI) and the Swiss Competence Center for Energy Research Heat and Electricity Storage are greatly acknowledged.

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Europium oxybromide catalysts for efficient bromine looping in natural gas valorization

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The bromine-mediated upgrading of natural gas, comprising mainly methane and other light alkanes, is an attractive technology for decentralized production of value-added commodities.[1,2] Its implementation primarily depends on the efficient recycle of stoichiometrically produced amounts of hydrogen bromide (HBr),[1,2] which can be approached by the promising routes of catalytic HBr oxidation and intensified methane oxybromination (MOB).[2,3] Nevertheless, the highly desirable low-temperature oxidation of HBr under a stoichiometric feed remains challenging since the extensive bromination of active catalysts (*e.g.* CeO_2) typically leads to severe deactivation.[2] In addition to stability and activity constraints, a high selectivity to methyl bromide (CH_3Br) in MOB is also critical in the catalyst design.[2,3] In this study, we demonstrate a novel europium oxybromide (EuOBr) catalyst exhibiting unprecedented performance in both HBr oxidation and MOB. In the former, EuOBr uniquely displays high bromine evolution activity at low-temperature and impeccable structural stability under practically-relevant conditions which are inaccessible by the state-of-the-art catalysts (**Figure 1a,b**). In the latter, a low propensity to combustion provides unparalleled selectivity to CH_3Br (**Figure 1c**). By devising strategies to support EuOBr on an appropriate carrier in extrudate form, the utilization of europium can be enhanced by over an order of magnitude while preserving the exceptional catalytic properties (**Figure 1d,e**). This discovery paves the way for the implementation of sustainable bromine-mediated processes to harvest stranded natural gas for the production of readily transported chemicals and fuels.

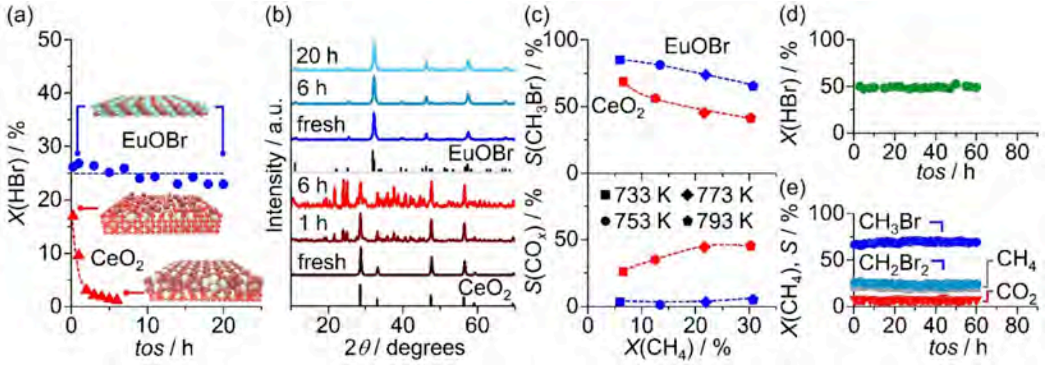

Figure 1 (a) HBr conversion, *X*(HBr), over EuOBr and CeO_2 *versus* time-on-stream, tos. (b) XRD patterns of the catalysts recovered after various tos. (c) Selectivity to CH_3Br, *S*(CH_3Br), and carbon oxides, *S*(CO_x), *versus* CH_4 conversion, *X*(CH_4), in MOB over EuOBr and CeO_2. (d) HBr oxidation over EuOBr/Al_2O_3 and (e) MOB over EuOBr/ZrO_2 *versus* tos.

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Location of active species in zeolites, the case of Cu-omega

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Copper-exchanged zeolites are active materials for the partial oxidation of methane to methanol (MtM), which is a potential alternative to petroleum-derived building blocks for the petrochemical industry. Many copper-exchanged zeolites of varying structure type are active for this reaction ([1],[2],[3]). During the course of a study to test the performance of copper-exchanged zeolites with 8- and 10-rings, we found that the methanol yield obtained using Cu-omega (**MAZ** framework type) (4) was significantly higher than that obtained with Cu-MOR, which is the most-often used material for this reaction ([4]). The framework structure of zeolite omega ([5]) is composed of gmelinite (*gme*) cavities stacked in columns parallel to *c*. They are connected laterally via ellipsoidal 8-rings to form a hexagonal array of columns that define a round 12-ring channel parallel to *c*. The 8-ring channels between the *gme* columns are not unlike those found in mordenite, but they are not accessible from the 12-ring channel. However, they do connect the *gme* cavities via a convoluted 3-dimensional 8-ring channel system. To investigate the reason for the remarkable catalytic performance of this material, we are using different characterization techniques, such as FTIR, XAS and X-ray diffraction, combined with molecular simulation. In this work, we present the results from a structure analysis using synchrotron powder diffraction data collected *in situ* during the activation of Cu-omega under oxygen and during the reaction itself. In the activated material, copper species are found in the 6-rings in the *gme* columns. They are single copper species, as opposed to the dimers generally accepted as the active species in the partial oxidation of methane to methanol ([6]). This material contains a low Cu/Al ratio (0.07) and is not very active in MtM, indicative of low activity of copper ions.

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The staff at the MS beamline (Swiss Light Source, Switzerland) is acknowledged for their help in data collection.

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Understanding zeolite-binder interactions in shaped catalyst bodies

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When applied in industry, zeolite catalysts are often shaped with the aid of binders and other additives into practical millimetre-sized forms.[1] The interaction of the component phases during the shaping and subsequent application can alter the type, amount, distribution, and accessibility of active sites, which can beneficially or detrimentally impact the catalyst performance compared to the pure zeolite powders typically studied in early development stages.[2] Although several mechanisms, such as the neutralization of acid sites *via* the migration of exchangeable cations, the insertion, substitution, or removal of framework metals, and the physical obstruction of micropores have been cited, the exact nature and extent of these effects are not well understood. By developing strategies to isolate the interface between common binders and zeolite crystals, we aim to correlate the morphological, compositional, and structural changes that occur under the conditions experienced by the catalyst in practice. For this purpose, approaches to representatively sample zeolite extrudates or to construct model interfaces, controlled (hydro)thermal treatments, catalytic evaluation in the conversion of methanol to olefins, and state-of-the-art characterization are coupled with the visualization through advanced microscopic and spectroscopic techniques (**Figure 1**). In particular, energy dispersive X-ray spectroscopy, electron energy-loss spectroscopy, and atom probe tomography are applied to map chemical interactions between the zeolite and binder phases, while the crystalline structure at the interface is tracked by electron diffraction. The attained insights have clear implications for advancing the understanding and development of novel porous solids in diverse industrial applications.

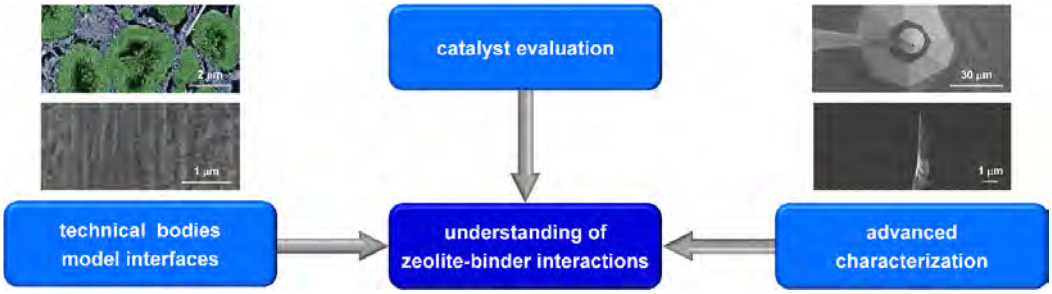

Figure 1 Approach to rationalize the effects of binder in shaped zeolite catalysts.

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Stabilization of Carbohydrates with Formaldehyde during Integrated Biomass 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.(*1*) Current methods lead to incomplete biomass depolymerization (producing only polysaccharides) and high process costs due to mineral acid recovery and enzyme production.(*2*) Lowering acid use to improve process economics requires the use of higher temperatures and generally leads to significant sugar degradation and low yields, which is why these strategies have generally been difficult to implement.

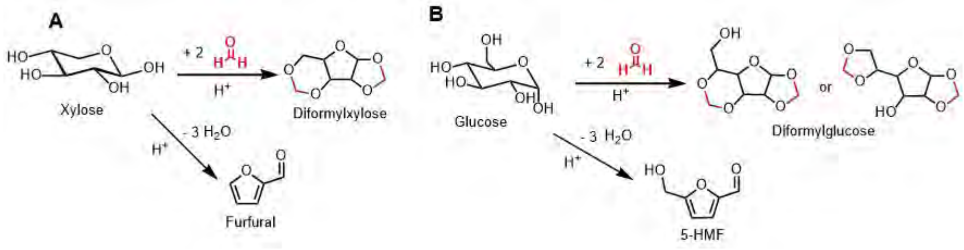

Figure 1. (A) Xylose conversion to diformylxylose and furfural (B) Glucose conversion to diformylglucose isomers and 5-hydroxymethylfurfural (5-HMF).

Recently, we have discovered that formaldehyde (FA) could be used to stabilize lignin and facilitate the conversion of extracted lignin to monomers at high yields (up to 97% of theoretical yield).(*3*) This method could also prevent xylan degradation by producing a stable xylose-derived molecule that we refer to as diformylxylose. In the current work, we study the stabilization of carbohydrates by the addition of FA during integrated biomass depolymerization. The low water content and the acidic environment in the biomass pretreatment allow FA to react with xylose, forming diformylxylose (Figure 1-A) at yields above 90% and minimizing xylose degradation into furfural. In comparison, reactions without FA lead to almost full xylose degradation into furfural with only 16% xylose recovery. Diformylxylose could be used as is or converted back to xylose at high yields in aqueous environments. A similar process is observed with glucose during cellulose acid depolymerization, forming diformylglucose (DG). The presence of FA led to the formation of two DG isomers from glucose by forming 1,3-dioxolane and 1,3-dioxane structures (Figure 1-B). As with DX, these structures stabilize glucose after depolymerization at conditions that were previously unfavorable due to carbohydrate degradation. Future efforts include the characterization of protected sugars and the removal of their protective groups.

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Electrochemical reduction of CO_2 into C2/C3 alcohols on tailored designed copper catalysts

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The electrochemical reduction of CO_2 (in the following referred to as CO_2RR) into products of higher value offers the unique chance to make a significant contribution to the closing of the anthropogenic CO_2 cycle and is therefore currently in the focus of research activities worldwide. Energy is needed for such electro-conversion processes might originate from excesses of renewables like hydro, wind and solar energy (power to value concept). A key challenge of the process development remains the product selectivity of the CO_2RR which can be directed by the choice of the catalyst required for such an electrochemical CO_2 conversion. Among the vast number of materials screened so far, it is Cu which deserves particular attention since it is the only catalyst which is capable to convert CO_2 into hydrocarbons and alcohols in considerable amounts.

In this study we focus on improved Cu catalysts which were obtained by an electrodeposition approach using 2D Cu meshes as technical supports. The catalysts were physically characterized by scanning electron microscopy (SEM), energy dispersive X-Ray spectroscopy (EDAX), X-Ray diffraction (XRD) and transmission electron microscopy (TEM). Potentiostatic electrolysis was carried out in CO_2 saturated aqueous 0.5 M $KHCO_3$ electrolyte. CO_2RR products were analyzed by gas chromatography (GC) and ion chromatography (IC) techniques.

We will demonstrate a superior activity of our Cu catalysts with highly valuable C2 (ethanol) and C3 (propanol) alcohols as CO_2RR products reaching a total faradaic efficiency of $FE_{alcohol} \sim 25\%$ at a moderate overpotential. High-resolution identical location SEM inspection was carried out prior and after the CO_2RR demonstrating that the actually active catalyst is formed only under *operando* condition of an ongoing CO_2RR.

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Additive assisted electrodeposition of highly faceted Ag Microcrystals: An application towards electrochemical CO_2 reduction

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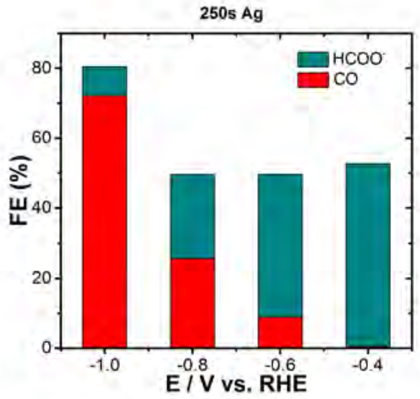
Ag micocrystals were prepared via an additive-assisted electrodeposition approach. They have been applied as efficient catalysts in CO_2 reduction reaction. Differently sized Ag microcrystals were prepared through four different deposition times (50s, 100s, 250s, and 500s) on polished graphite substrate. 3,6-dithia-1,8-octanediol ($OHCH_2CH_2SCH_2CH_2SCH_2CH_2OH$) was used as a complexing additive during the electrodeposition process. The catalysts were physically characterized by scanning electron microscopy (SEM), energy dispersive X-Ray spectroscopy (EDAX) and X-Ray diffraction (XRD). Electrolysis was carried out in aqueous 0.5 M $KHCO_3$ medium and formed products were analyzed by gas chromatography (GC) and ion chromatography (IC) techniques. There is a clear switching in the product distribution from formate to carbon monoxide by going from lower to higher overpotentials. The complexing additive, adsorbed on the Ag surface, plays a crucial role for the formate formation. Different treatments (annealing, negative potential application, H_2 evolution in th acidic media etc.) were developed to chemically remove the adsorbed additive from the surface. No formate was obtained on the Ag microcrystals after application any of these treatments. Untreated Ag microcrystal with 250s deposition time gives the highest faradaic efficiency of formate at low overpotentials whereas Ag with 500s deposition time gives the highest CO efficiency at higher overpotentials.

The following faradaic efficiency plot clearly shows the switching of the CO_2 reduction product distribution from formate at lower overpotentials to CO at higher overpotentials.



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Metal-Organic Frameworks, the Switch to the Improbable: Lewis Acidic Phosphonium Ions Catalyse Aldol-Tishchenko Reaction

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The development of efficient catalytic methods is crucial for nowadays endeavors to achieve a good economic and ecologic efficiency in organic syntheses. In this respect, phosphines play a pivotal role to ensure high reactivity and selectivity. Their main application lies in the field of transition metal catalyzed reactions,[1] but phosphorous compounds gain increased interest in organocatalytic reactions; especially C-C bond forming ones from activated alkenes, allenes, and alkynes.[2]

The strong nucleophilic nature of phosphines facilitates the reaction with unsaturated carbon atoms forming zwitterionic phosphonium species that makes such carbon atoms more reactive towards nucleophilic attacks, enabling a variety of different C-C bond forming reactions, such as Michael addition and Morita-Baylis-Hillman (MBH) reaction.[2] Even though phosphonium cations have shown to catalyze different coupling reactions, such as Mukaiyama-aldol[3] and other C-C, C-N and C-O bond formations,[4] they are rarely reactive moieties – if ever – when in a zwitterion.

In this contribution, we describe a triphenylphosphonium zwitterionic species that unprecedentedly catalyzes the Aldol- Tishchenko (AT) reaction *only* when metal-organic frameworks (MOFs) are introduced in the reaction mixture. The reactivity of a zwitterionic phosphonium intermediate produced by the reaction of triphenylphosphine (PPh3) with methyl vinyl ketone (MVK) was changed with a MOFs additive with MOF-5 and UMCM-1 topologies. Such intermediate is the key to generating MBH products in the presence of aliphatic aldehydes and normally acts as a precursor to form C-C bonds, but it reacts as Lewis acid through the phosphonium moieties when MOFs are added leading to the AT reaction of the aldehyde. These findings show that the presence of MOFs can completely alter the reactivity of a zwitterionic phosphonium organocatalyst from a nucleophile in solution to an electrophile in the framework. This switch in reactivity enables improbable, yet undescribed reaction pathways, which would not happen under standard reaction conditions.

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Direct catalytic oxidation of methane to methanol: Methanol protection using phosphoric acid

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The selective partial oxidation of methane to methanol is a difficult yet rewarding task as it has the potential to eliminate the prevalent natural gas flaring by providing novel routes to its valorisation. Despite the emerging number of disparate approaches for this reaction, none has been commercialized yet due to the low product yields as well as a host of engineering issues. A diligent analysis of the large body of work in this field reveals the failure of 'direct methane to methanol' (DMTM) systems to reach high yield (Fig. 1a)[1]. Furthermore, the better-performing ones incorporate specific measures to stabilize or derivatise methanol[2]. Such a protection of methanol enables these systems to overcome the rapid fall in product selectivity with increasing methane conversion: a thermodynamic issue that plagues the unprotected DMTM routes.

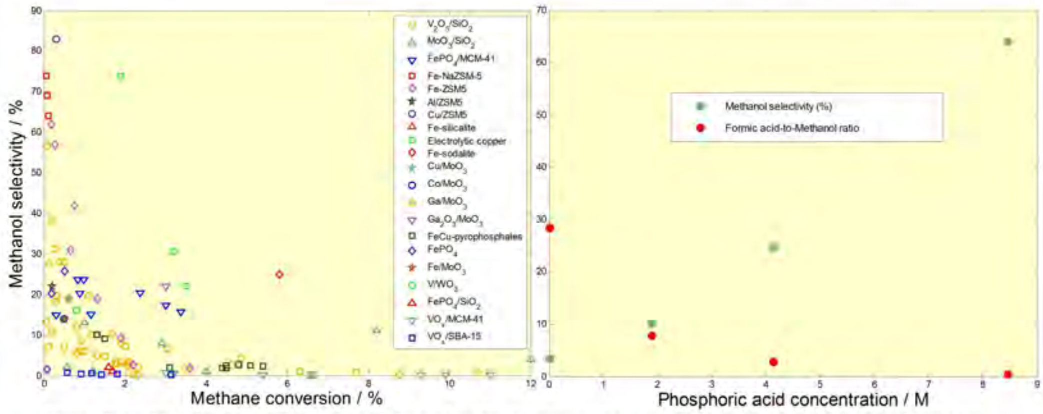

Figure 1: (a) Methanol selectivity as a function of methane conversion over heterogeneous catalysts (b) Methanol selectivity and formic acid-to-methanol ratio as a function of phosphoric acid concentration in methane oxidation reactions.

Iron-containing zeolites catalyze the conversion of methane to methanol and a number of other products with aqueous hydrogen peroxide as the oxidant[3]. Formic acid is the major product, formed by the over-oxidation of methanol. The current work shows the possibility of making this process methanol-selective using phosphoric acid. The addition of phosphoric acid to the reaction mixture protects methanol by suppressing its undesired over-oxidation to formic acid. This approach using phosphoric acid is characterized by a much higher methanol selectivity and a higher methanol concentration in solution (Fig. 1b). Furthermore, the efficacy of phosphoric acid is unique, as the use of other acids did not yield propitious results.

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Economic synthetic strategies for the optimization of cobalt oxides as water oxidation catalysts

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Artificial photosynthesis is a very promising method to harvest renewable energy. 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 (WOCs) is required. In this context, spinel-type Co_3O_4 attracts strong research interest as a low-cost and robust WOC[1]. However, keeping full control over its various performance parameters, like crystallinity, oxidation states, morphology and surface area[2], remains a preparative and analytical challenge. Therefore, the focus of this study is the cost efficient fast formation of spinel-type Co_3O_4 via short-time hydrothermal synthesis with quick regeneration options after prolonged periods of use. Furthermore, an efficient and low-cost cobalt oxide reference WOC formed under photochemical conditions is investigated and compared with state of the art WOCs in first economic analysis.

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A Diffusion and Surface Reaction Model for Highlighting Key Factors in the Enzymatic Hydrolysis of Lignocellulosic Biomass

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Efficient enzymatic hydrolysis of lignocellulosic biomass is essential to the cost effective production of fuels and chemicals from plants. However, due to the intricate nature of the substrates and the broad diversity of biomass and enzymes systems, an in-depth understanding of the key aspects governing this process, coming from both theoretical and experimental ends, is still lacking. While several factors, such as cellulose accessibility and unspecific adsorption of enzymes on the protective lignin barrier, have been suggested as major bottlenecks in the digestion process, a quantitative study assessing the relative importance of these mechanisms has yet to be done.

In the present study, we developed a flexible, comprehensive model of the enzymatic hydrolysis of lignocellulosic materials based on pore-diffusion and surface reactions. Relying on the initial composition and pore size distribution of the lignocellulosic substrate, predictions properly captured initial hydrolysis rates when compared to available data in literature. However, in contrast to the usual slowdown observed in the reaction rate for common enzyme loadings, computed yields showed no development of hindrance as the reaction proceeds. By correlating the enzyme loading in terms of accessible surface to the rate of glucose release, the model can not only shed light on the origin of this apparent decrease – heterogeneity in cellulose digestibility, enzyme deactivation pathways –, but also on the enzyme synergism regarding the surface accessibility. In this perspective, current work focuses on evaluating the implications of enzyme loadings on the hydrolysis rate of acid pretreated beech wood by comparing *in silico* results with experimental observations. The ultimate goal of our work is to facilitate the rational design of biomass processing and engineered cellulase cocktails.

Mechanism of ethylene oxychlorination on RuO_2 and CeO_2

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[1]ETH Zurich, [2]Institute of Chemical Research of Catalonia

The manufacture of polyvinyl chloride (PVC) relies on the production of vinyl chloride (VCM) *via* a two-step process comprising ethylene oxychlorination to ethylene dichloride (EDC) on intrinsically unstable cupric chloride catalysts and a subsequent energy-intensive thermal cracking. Recently, we demonstrated that certain oxides or oxychlorides (*e.g.*, CeO_2) could serve as stable bifunctional catalysts, performing the two reactions in a single step and attaining VCM in up to 25% yield.[1,2] To gain deeper understanding of the oxychlorination mechanism, we investigate the complex reaction network by density functional theory (DFT), kinetic testing, and advanced characterization. In a first step, decoupling the complexity of the reaction network and CeO_2, DFT calculations were conducted on the simpler RuO_2, revealing the thermodynamic and kinetic control of oxidation and chlorination processes, respectively. Furthermore, the degree of chlorine coverage emerged as a key factor governing the selectivity, as it confines or destabilizes intermediates and determines the ability of the surface to abstract H atoms. This enabled simplification of the reaction network (**Figure 1**) for its investigation on a CeO_2 {111} surface in a second step. Preliminary results suggest that an ideal CeO_2 surface is unable to catalyze oxychlorination as the barriers for all important chlorination and dehydrogenation steps are 1.7 eV and higher. The introduction of defects, *i.e.,* by replacing a surface O by a Cl atom which can react and form a vacancy, leads to at least 0.5 eV decreased barriers for most chlorination reactions. Inspired by these results, we are developing a microkinetic model and experimentally assessing the impact of vacancies formed by controlled reduction of CeO_2 on its oxychlorination performance. Previously, acidity was shown to be strongly related to VCM selectivity,[1,2] but the exact nature of the sites remained unknown. DFT indicates that ceria acts as a Brønsted and Lewis acid/base pair, encouraging the investigation of the acid sites by solid-state NMR spectroscopy after adsorption of the probe molecule trimethylphospine. The combination of these results will reveal the detailed mechanism of ethylene oxychlorination on oxide-based catalysts and guide the development of more selective VCM catalysts.

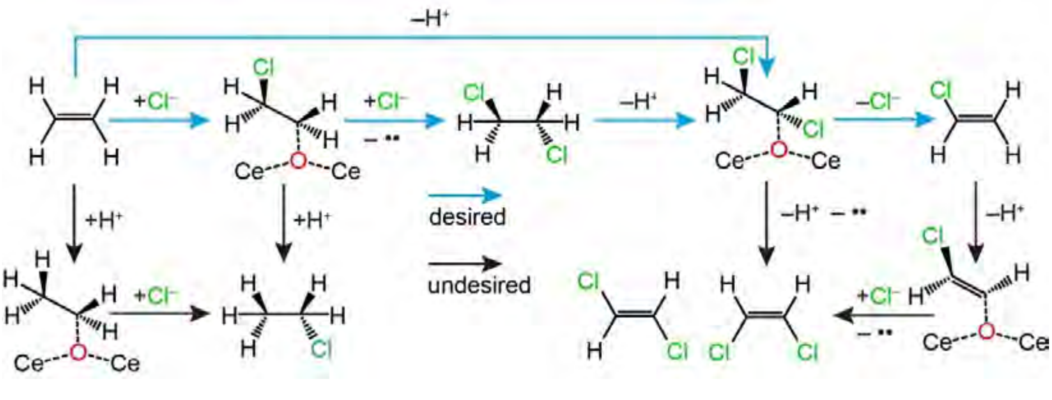

Figure 1 Simplified reaction network of ethylene oxychlorination, excluding oxidation steps which can start at any node.

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Using carbon-coated metal nanoparticles as support for magnetic reagents

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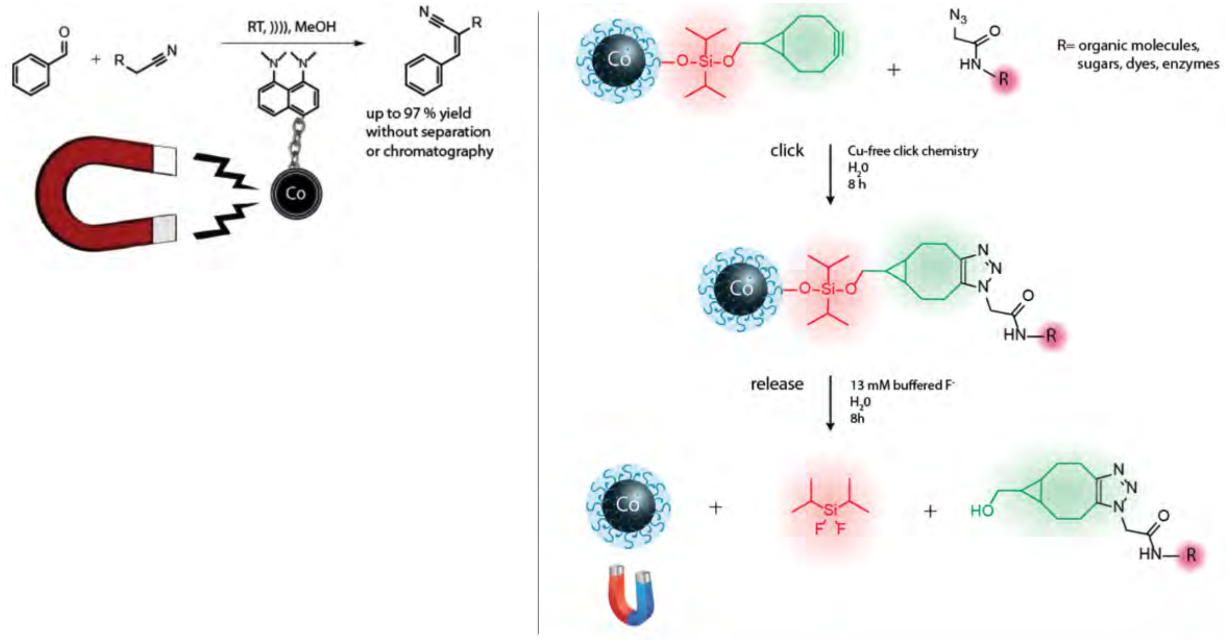
Carbon-coated cobalt nanoparticles are an ideal support for magnetic reagents for a wide range for applications.[1] In this talk, severall applications of these kind of reagents are presented, starting with immobilized organosuperbases, such as the classic proton sponge (1,8)-bis(dimethylamino)naphthalene (DMAN).[2] Using this heterogeneous system, catalysis of the Knoevenagel condensation can proceed smoothly and tedious work up procedures, such as column chromatography, can be avoided.



Furthermore, a magnetic "click and release" reagent has been synthesized, consisting of a cupper-free click reagent (strained alkyne) and a fluoride cleaveable linker.[3] This reagent can be used in biological media and is suitable to remove tagged enzymes from a environment and release them unharmed in another. Applications of this system are for example analysis of native protein complexes.

Additionally, futher mangetic reagents developed in our group are presented, such as magnetic EDTA and magnetic reducing agents (TCEP).

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Microfluidic Assay for Artificial Metalloenzyme Evolution

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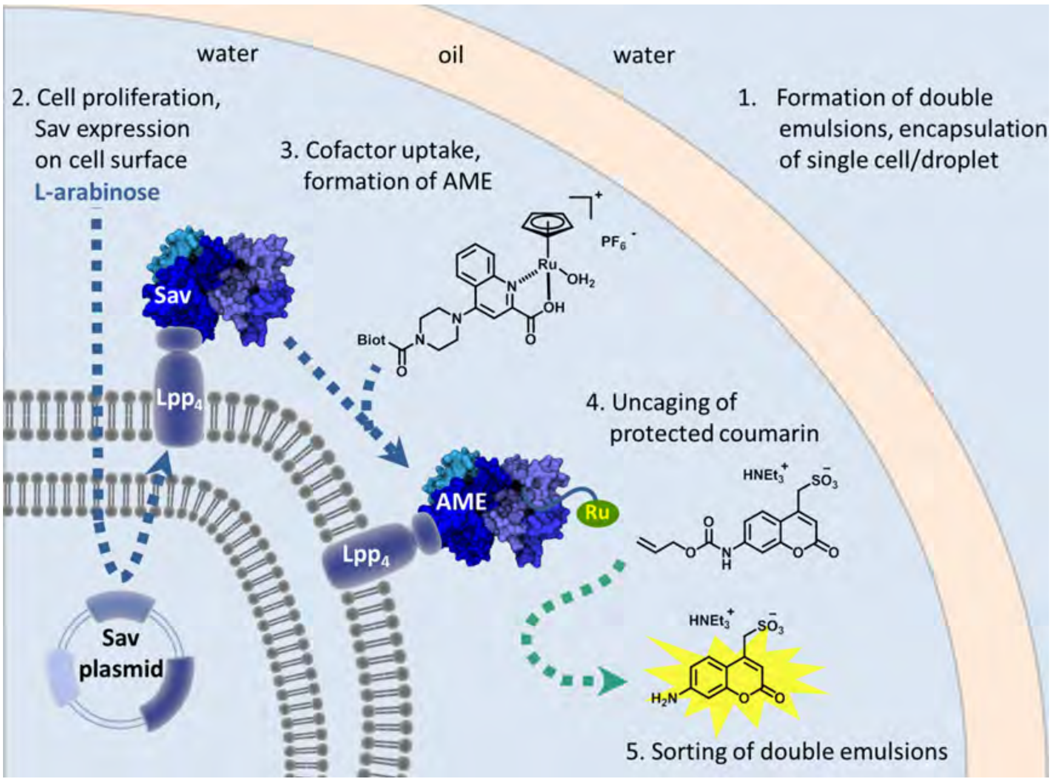
Artificial metalloenzymes (AME)[1] allow to extend the reaction scope of natural enzymes, enabling unprecedented chemical transformations in biological systems. The performance and substrate scope of such AME can be tuned by chemical optimization of the metal cofactor or by genetic engineering of the host protein.[2] Incorporation of these AME in cellular environments bears the potential to construct powerful catalytic cascades and the development of high-throughput assays for AME evolution.

Herein, we present a high-throughput microfluidic assay for an artificial allylic alkylase based on the biotin streptavidin technology. Streptavidin (Sav) is displayed on the surface of *E. coli* as a fusion with an anchoring protein (Lpp-OmpA). Upon binding of the biotinylated ruthenium cofactor [CpRu(Biot-Quinoline)][3] an AME is generated, which can uncage a fluorogenic allyl carbamate protected coumarin. Encapsulation in microdroplets ensures genotype-phenotype linkage and allows high-throughput screening of AME activity.



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Well-defined iron sites on the silica surface: characterization and reactivity

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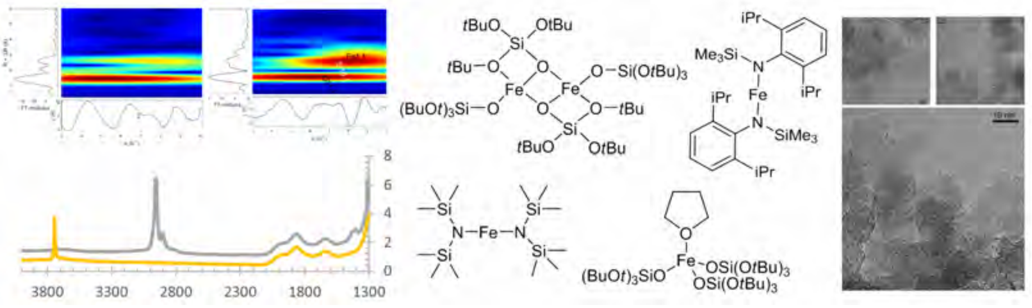
>Single iron (II) and iron (III) sites were successfully employed as catalysts in a variety of chemical reactions, including propane dehydrogenation,[1] oxidation of alkanes, alkenes and arenes and non-oxidative coupling of methane. [2,3] Nevertheless only very limited number of reports describe their nuclearity and reactivity on the surface. [1-5]

In this study siloxide based (e.g. iron(II) siloxide, iron(III) siloxide) and silylamide based materials (e. g. iron(II) bis(trimethylsilyl)amide, iron(II) bis(2,6-diisopropylphenyl)(trimethylsilyl)amide) were synthesized and grafted on the surface of partially dehydroxylated silica. Their structure was studied with variety of spectroscopic methods (X-ray absorption spectroscopy, infrared spectroscopy, electron paramagnetic resonance, etc) which indicate, that they preserve their original nuclearity even on the surface of the silica.

Such active sites show activities towards the non-oxidative dehydrogenation of propane, similarly to Co(II), Cr(III) and Ga(III) isolated sites.



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Microstructural self-regeneration of $LaSrTiNiO_{3-\delta}$: fast recovery from sulfur poisoning

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Sulfur poisoning is a problem for Ni catalysts as well as solid oxide fuel cells (SOFCs). In the case of SOFCs this is largely due to the poisoning of Ni sites active for water gas shift (WGS, $CO + H_2O \rightarrow CO_2 + H_2$), which provides additional H_2 for oxidation when the cell is operated on syngas feeds [1]. Current SOFC materials cannot easily be regenerated after sulfur poisoning. However, some perovskite type metal oxides (PMO) exhibit the remarkable reversible segregation of catalytically active metals from and reincorporation back into the PMO host lattices. This property inhibits sintering of metal particles during redox cycling [2,3]. In this work a water gas shift active and regenerable SOFC anode PMO material was developed. It can be shown that after reduction at 800 °C Ni is selectively reduced and segregated to the $LaSrTiNiO_{3-\delta}$ (LSTN) surface where it forms catalytically active, metallic Ni particles (Fig. 1-a) [3]. After reoxidation Ni is fully reincorporated into the perovskite lattice as shown by the reversibility of Ni K-edge XANES (Fig. 1-b). Catalytic data for the WGS reaction obtained over a number of redox cycles and Ni particle size analysis show the excellent redox stability of this material. For comparison, redox cycling of an impregnated material (Ni/LST) leads to Ni sintering and loss of catalytic activity (Fig. 1-c). Exposure of LSTN to H_2S caused an expected loss of catalytic activity (Fig. 1-d), which is completely restored within two redox cycles.

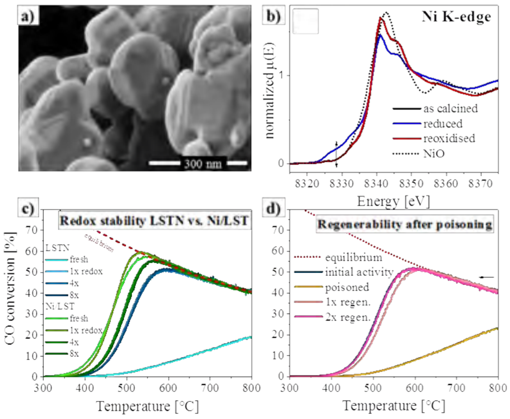

Figure 1. a) SEM image of reduced LSTN - segregated Ni particles on LSTN crystallites. b) Ni K-edge XANES of calcined, reduced and reoxidised LSTN. c) CO conversion for pre-reduced LSTN and Ni/LST over 8 redox cycles and d) after H_2S poisoning and over two oxidative regeneration cycles.

It is demonstrated that the structural reversibility exhibited by some PMOs can be exploited to regenerate S-poisoned catalysts which otherwise would suffer from deactivation by particle sintering. This function can be potentially applied to a variety of Ni catalyzed reactions suffering from similar deactivation phenomenon.

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Selective anaerobic methane oxidation into methanol over copper-exchanged mordenite

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Methane is the main component of natural gas, one of the most important fossil resources widely used in the energy section and chemical industry. However, huge amount of methane is flared resulting in the emission of large amounts of carbon dioxide. This constitutes a loss of 143 billion metric meters, currently representing a cost of about tens of billions of US dollars. [1]

Development of new approaches and technologies for methane activation and transformation under mild conditions will result in a more effective utilization of natural gas and contribute to the decreased use of fossil fuels reserves. Selective oxidation of methane into methanol – the simplest basic chemical – over solid catalysts is one of the most promising approaches, which has received significant attention over the past decade. Although significant achievements have been made towards the development of novel efficient catalysts, including copper-exchanged zeolites, further progress is limited by the lack of fundamental understanding of the process. [1-4]

In the present contribution we studied direct conversion of methane into methanol over the copper-exchanged mordenite zeolite, using water as the source of oxygen. [5] We report here that water molecules not only act as a cheap and abundant source of oxygen to partially oxidize methane and regenerate the active sites, but also facilitate desorption of the product, as well as stabilization of the reaction intermediates. The only product of the two-electron redox reaction with water is molecular hydrogen, which itself is a valuable species. Based on in situ x-ray absorption spectroscopy, infrared spectroscopy, ^{18}O isotope tracing and density functional theory calculations, we proposed a mechanism involving methane oxidation at Cu(II) oxide active centers, followed by Cu(I) reoxidation by water with concurrent formation of hydrogen. With water acting as the oxidant, no molecular oxygen is needed. This effectively anaerobic oxidation allows an efficient low-temperature activation of methane, potentially suitable for local single-reactor conversion of the off-gas, and methane in general, into one of the main precursors for chemicals synthesis.

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Quantitative depolymerization of uncondensed technical lignin under mild conditions

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Lignin is a natural amorphous polymer that provides the structural strength and integrity for plant matters. Its content in biomass is 15-30% by mass and up to 40% by energy. This component is a significant renewable source for production of bio-chemicals. Conversion of lignin to higher value added chemicals is mainly based on two steps: lignin extraction from biomass and catalytic conversion through reduction (hydrogenolysis) or oxidation.[1] Lignin condensation is a drawback in the extraction step which is caused by formation of inter-unit carbon-carbon linkages and can reduce lignin monomer yields dramatically. Furthermore, catalytic biomass deconstruction and lignin hydrogenolysis requires high temperatures (250 °C) and energy.

Based on a recent discovery, the utilization of formaldehyde during biomass pretreatment avoids lignin condensation and provides stabilized organoslv lignin monomers. Figure above represents the stabilization of lignin monomers by formaldehyde and the products after hydrogenolysis.[2] This research studies the possibility of performing hydrogenolysis under mild condition (120 °C) by considering the effect of temperature, reaction media and heterogeneous catalyst on the hydrogenolysis of biomass derived lignin.

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Bimetallic nanoparticles for the valorization of biomass. The role of the stabilizer.

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In the outlook of the replacement of petrochemicals by biomass-derived chemicals, lignin, a polymer present in the plants cell wall, is the most promising source of aromatic compounds. However, its extraction and valorization are not straightforward. Lignin, which provides the structure of plants and protects them from external aggression, is a resistant polymer that is challenging to break down. There is a need to discover efficient and selective catalysts for this purpose. Lignin is mainly bonded by diaryl ether and ß aryl ether linkages. Among the different reactions able to cleave these carbon oxygen bonds, reductive cleavage using hydrogen gas is the most appealing. In this perspective, bimetallic nanoparticles[1] coated with different cetyl trimethyl ammonium salts in water were assessed. Initial studies were made on a model compound that mimic the diaryl ether bonding motifs (diphenyl ether). The nanoparticles coated with the salts with anions of low-nucleophilicity exhibit higher catalytic activities. The efficiency of the bimetallic nanoparticle on real biomass (beech wood sawdust, dealkaline lignin and organosolv lignin) were also evaluated.

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Investigation of the relationship between ionic liquid structure and its activity for electrochemical reduction of carbon dioxide

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Since imidazolium ionic liquids (ILs) were discovered to significantly reduce overpotential for electrochemical reduction of CO_2 and suppress hydrogen evolution reaction (HER) [1], numerous attempts to clarify the mechanism of the co-catalytic activity were made [2-4]. We approach this problem from synthetic point of view, synthesizing ILs of different structures (e.g. side chains functionalities, heterocyclic backbones, heteroatoms variations) and establishing the change of their co-catalytic performance (see [5]). Some of ILs being synthesized possess much higher activity compared to the classical imidazolium ones, and some are found to exhibit higher stability. Therefore, usage of ILs provides a tunable and promising option for electrochemical reduction of CO_2.

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Asymmetric transfer hydrogenation of 1-aryl-3,4-dihydroisoquinolines using and iridium-amide complex

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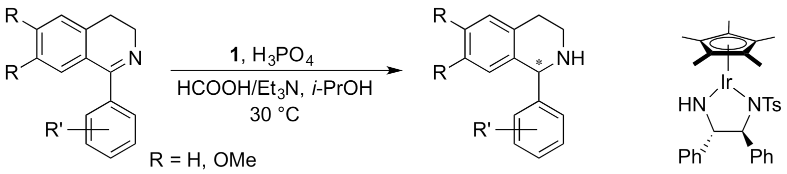
Optically pure chiral compounds are abundant among active pharmaceutical ingredients, agrochemicals, and fragrances. Efficient methods allowing the direct synthesis of single enantiomers are thus highly sought-after. The Noyori-Ikariya asymmetric transfer hydrogenation (ATH) of imines, catalysed by complexes of the [MCl(arene)(diamine)] (where M = Ru, Rh, Ir) type, belongs to a group of popular and well-established methods for the preparation of optically enriched amines [1]. However, this catalytic system still has certain limitations, one of which is the poor reactivity of 1-aryl-3,4-dihydroisoquinolines (1-Ar-DHIQs) as precursors of the chiral 1-aryl-1,2,3,4-tetrahydroisoquinoline motif present in naturally-occurring alkaloids (Cryptostylines) and drugs (*e.g.*, Solifenacin and Gantacurium). The currently used protocols are based on iridium-phosphine complexes that are oxygen sensitive and often are not readily available [2–4].

Herein, we report a simple alternative method for the ATH of 1-Ar-DHIQs. The method employs the Cp*Ir(TsDPEN) (where Cp* = pentamethylcyclopentadienyl and TsDPEN = HNCHPhCHPhNTs^{2-}) catalytic complex (**1**) that is stable and readily available, propan-2-ol and HCOOH/triethylamine mixture as the solvent and hydrogen donor, and anhydrous phosphoric acid as an additive. In total, 12 examples of substrates were hydrogenated in high yields and good to high enantioselectivity, showing tolerance for a broad spectrum of functional groups and a clear structure-reactivity pattern. Interestingly, when a 1-alkyl-DHIQ (6,7-dimethoxy-1-methyl-DHIQ) was studied for comparison, the chiral product’s *ee* was decreasing in the course of the reaction and and surprisingly, in the absence of phosphoric acid, the effect was even more pronounced as we observed a reversal of enantioselectivity at high conversions. No such decrease of *ee* was detected with 1-Ar-DHIQs, which do require the presence of the acid for hydrogenation to take place.



R = H, OMe
R' = H, OMe, Me, Br, NO_2, CF_3, CO_2Me

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Stabilization of single metal atoms on graphitic carbon nitride

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Graphitic carbon nitride (g-C_3N_4) exhibits unique properties for the preparation of single-atom heterogeneous catalysts (SAHCs) due to the presence of six-fold nitrogen-based coordination sites in the lattice.[1] Understanding how the synthesis method, carrier properties, and metal identity impact the isolation of metal centers is essential to guide their design (**Figure 1**). This study compares the effectiveness of direct and post-synthetic routes to prepare SAHCs incorporating different metals (Pd, Pt, Ag, Ir) in g-C_3N_4 carriers of distinct morphology (bulk, mesoporous and exfoliated) and composition (C/N ratio). The speciation (single atoms, dimers, clusters, or nanoparticles), distribution, and oxidation state of the supported metals are characterized by multiple techniques. SAHCs are most readily attained via direct approaches applying copolymerizable metal precursors and employing high surface area carriers. In contrast, although post-synthetic routes enable improved control over the metal loading, nanoparticle formation is more prevalent. Comparison of the impact of carrier morphology also points toward the involvement of defects in stabilizing single atoms, while tailoring the carrier composition through the introduction of carbon-rich heterocycles during the synthesis visibly affects the interaction with the metal. The distinct metal dispersions and chemical states are rationalized by density functional theory and kinetic Monte Carlo simulations, highlighting the interplay between the adsorption energetics and diffusion kinetics. Evaluation in the continuous three-phase semihydrogenation of 1-hexyne or 2-methyl-3-butyn-2-ol identifies controlling the metal–carrier interaction and exposing the metal sites at the surface layer as key challenges in designing efficient SAHCs.

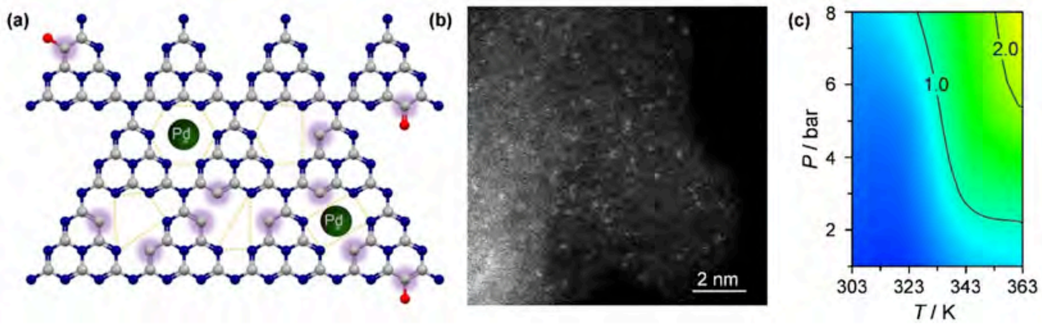

Figure 1 (a) Schematic of Pd atoms stabilized in the g-C_3N_4 structure. Doped C atoms are highlighted by a purple glow. Yellow dashed lines connect N atoms within the coordination sites. (b) AC-STEM image of the Pd dispersion on g-C_3N_4. (c) Reaction rate (in 10^3 $\mathrm{mol_{product}\ mol_{Pd}^{-1}\ h^{-1}}$) of 2-methyl-3-butyn-2-ol hydrogenation at different temperatures and pressures.

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Ostwald ripening or single atom trapping: towards understanding particle sintering

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Ostwald ripening, facilitated by the volatile species transport, is a leading cause of the platinum group catalysts degradation at high temperature in oxidizing atmosphere. However, the detailed understanding of Ostwald ripening is still missing, especially regarding the nature of volatile species, and the effect of support [1]. Recent experiments suggest that the volatile species can be trapped on ceria, forming atomically dispersed active catalytic sites instead of large nanoparticles [2], which typically form on non-reducible supports like alumina. To understand Ostwald ripening and atom-trapping phenomena at the atomic level, it is important to identify the stability and adsorption behaviour of volatile species, and their dependence on the local structure of different surfaces.

We conducted a comparative density functional theory study of the interaction of volatile species with various surfaces. PtO_2 species are the most likely volatile mobile species in the process of Ostwald ripening. Defect-free CeO_2(111) and Al_2O_3(100) surfaces have a very small binding energy towards PtO_2 compared to the platinum surface, indicative of particle growth. However, the binding energy of PtO_2 on the step site of CeO_2(111) surface is larger than that on the platinum surface. Therefore, the ceria stepped-edge could effectively trap the mobile species, generating atomically dispersed catalysts. The structure of trapped single-atom platinum-on-ceria catalysts is predicted to have a square-planar structure. A platinum atom in such a square-planar structure strongly binds to the surface, preventing the platinum atoms from aggregating into larger nanoparticles. Overall, the results indicate a mechanism of platinum particle growth in an oxidative atmosphere on defect-free alumina and ceria surfaces and of redispersion on the ceria surface with step-edges.

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Quantifying the impact of acidity on positronium formation and annihilation in zeolitic materials

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Positron annihilation lifetime spectroscopy (PALS) demonstrates unique sensitivity towards elucidating the connectivity of pore networks in zeolitic materials, which is based on the diffusional behavior of metastable *ortho*-positronium (*o*-Ps) species formed *in situ* upon positron implantation.[1] Chemical interactions between *o*-Ps and acid sites in a solid have been widely postulated to perturb the purely kinetic response.[2] However, the specific impact of the nature and amount of acid sites on the lifetime and intensity of different *o*-Ps components, and the implications for porosity analysis, have not been quantified. By studying a series of ZSM-5 (MFI structure) samples with tailored crystal size and Si:Al ratio, we map the dependence of the amount ($\mathrm{Ps_{total}}$) and fractional distribution ($\mathrm{Ps_{micro}}$, $\mathrm{Ps_{vac}}$) of *o*-Ps measured on the concentration of Brønsted acid sites and the implantation depth of positions (**Figure 1**). By modeling the possible mechanisms of interaction, we show that the presence of Brønsted acid centers most significantly affects the thermalization and delocalization of *o*-Ps, while the impact on diffusion and correspondingly on $\mathrm{Ps_{micro}}$ and $\mathrm{Ps_{vac}}$ is negligible. The study of commercial ZSM-5 samples confirms the generality of the findings and permits elucidation of the crystal size-dependent nature of kinetic and acidity effects. The impact of Brønsted acid sites can be eliminated by neutralization through exchange with $\mathrm{Na^+/K^+}$ ions. The negligible role of Lewis acid sites is confirmed from the study of a large-crystal Sn-MFI zeolite. By utilizing a controlled synthesis approach we are able to better account for the chemical interaction of *o*-Ps with acid centers, providing critical insights for the determination of pore quality in zeolites by PALS.

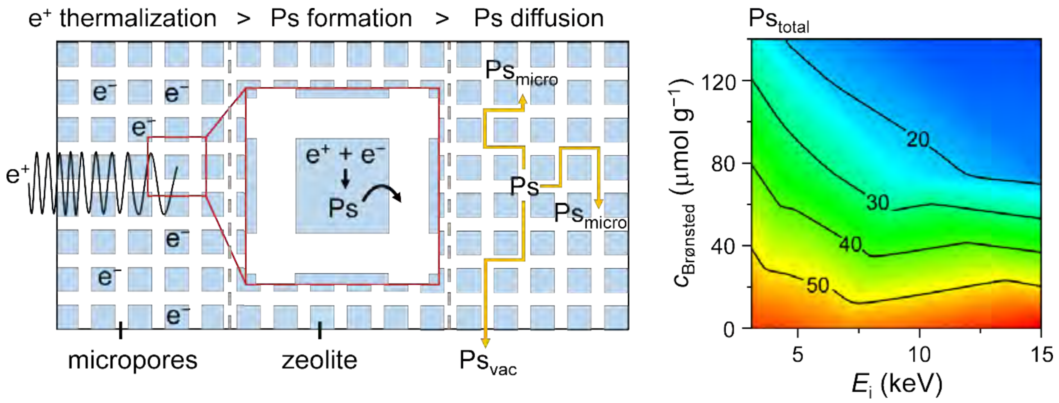

Figure 1 Schematic of the formation, diffusion, and annihilation of *o*-Ps within a zeolite and correlation of $\mathrm{Ps_{total}}$ with the concentration of Brønsted acid sites and positron implantation depth.

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Mapping the birth and evolution of pores upon thermal activation of layered hydroxides

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The porosity of layered hydroxides can be greatly enhanced by thermal activation.[1] Despite intense interest in the associated structural transformations, porosity changes have been almost exclusively described in terms of primitive bulk descriptors (surface area, pore volume, average pore size), providing limited insight into the pore architecture (*i.e.*, the geometry, location, and connectivity of the pores). Here, we map the variations in porosity upon thermal activation of well-crystallized $Mg(OH)_2$ and isostructural layered double hydroxide (LDH, $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-}_{x/n})\cdot mH_2O$) materials through novel characterization approaches as transmission electron microscopy (TEM) coupled with *in situ* heating, positron annihilation lifetime spectroscopy (PALS), and differential hysteresis scanning (DHS) by high-resolution argon sorption (**Figure 1**).[2,3] Despite exhibiting comparable surface area enhancements, arising from the formation of micro- and mesoporosity, striking differences in the structure of the developed pore networks for both materials are observed. As visualized by TEM, the substitution of trivalent metals like aluminium into the brucite-like sheets restricts the growth and improves the thermal stability of the pores, which form abundantly throughout the sample. Quantitative analysis by DHS reveals that the geometry of mesopores in the most highly porous samples is significantly constricted. Complementary insights are obtained by PALS, which evidences the asynchronous development of micro- and mesopores and readily distinguishes differences in the transport properties. The complexity of the pore evolution demonstrated by this approach illustrates the scope for improving mechanistic understanding in the design of porous materials derived from layered hydroxides.

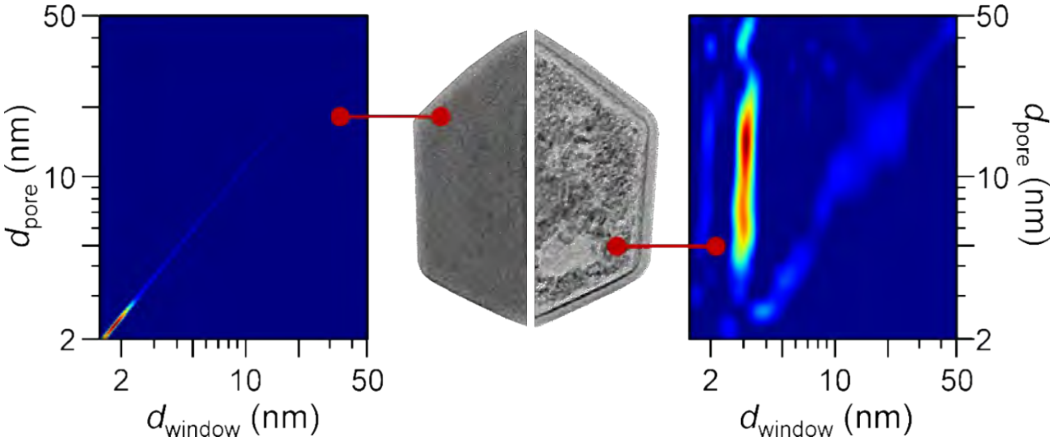

Figure 1 Multi-technique approach to track pore evolution upon thermal activation of layered hydroxides.

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Selectivity control during the one-pot conversion of aliphatic carboxylic acids to linear olefins through tandem hydrogenation/dehydration

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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. The combination of the hydrogenation properties of earth-abundant Cu and the acid sites on silica-alumina allows hydrogenation and dehydration to occur simultaneously, a process that normally calls for different reaction conditions. At 483 K and 5 bar H_2 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. We hypothesize that the presence of a small amount of hexanoic acid on the surface of the catalyst prevents overhydrogenation of the hexenes. Current efforts are targeted at reaction kinetic studies as well as surface studies using FT-IR spectroscopy to ascertain the nature of this selectivity switch. Process runs using carboxylic acids produced from biomass fermentation will also be carried out to ensure process compatibility.

Catalytic CO_2 hydrogenation to methanol over encapsulated Cu/ZnO based catalysts: Synthesis, characterization and in situ mechanism determination

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Combustion of carbonaceous fuels like coal, oil and natural gas cause atmospheric concentrations of CO_2 to continue to rise. CO_2 could be utilized as starting material in a catalytic process to produce valuable chemicals and fuels such as synthesis gas (CO and H_2 mixture), oxygenates (alcohols, ethers), or hydrocarbons. The development of an appropriate heterogeneous catalyst that will actively and selectively convert mixtures of CO_2 and H_2 to methanol as a liquid fuel additive or surrogate, can significantly contribute to a more widespread large scale utilization of CO_2 and renewable energy. The most active catalyst for methanol production is copper-zinc-based materials which are widely used for syngas transformation to methanol. These catalysts also show promising results in CO_2 hydrogenation, however, their activity value is still far from commercial utilization and further catalyst improvement is still required [1-3].

The main goal of this research project was to investigate mechanism of direct selective hydrogenation of CO_2 into CH_3OH over Cu/ZnO based catalyst. During catalyst design, attention was focused on maintaining a high dispersion and intimate contact between Cu and ZnO phases for highest possible number of active sites and consequently highest activity. For this reason nanosized Cu/ZnO clasters were encapsulated into zeolite framework. CuO and ZnO phases were introduced by ion exchange and precipitation methods. Influence of precipitation agent (Na_2CO_3/Na_2S) during preparation step was carefully investigated. It was found that precipitation with 0.05 M Na_2CO_3 results in superior catalytic properties. Furthermore, several zeolite structures (FAU and LTA) with different Si/Al ratio were investigated. Synthesized catalyst samples were further examined by a variety of relevant characterization techniques in order to determine their morphological and surface properties, as well as mechanism of CO_2 hydrogenation to methanol. Accordingly to results of *operando* XRD investigation, encapsulation of CuO and ZnO into zeolite framework prevents nano-particles sinthering and aggregation during catalytic test. It was confirmed that reducibility of ZnO (*operando* XAS) and formation of Cu-Zn alloy (*operando* XRD) play a crucial role in investigated process. The higher the amount of reduced Zn^0 species were presented in the catalyst during reaction conditions, the higher the overall activity and selectivity to methanol were.

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Olefins from natural gas via oxychlorination catalysis

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

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Ethane and propane, found in copious amounts in natural gas, comprise promising feedstocks to produce ethylene and propylene, the platform molecules for the manufacture of virtually all polymers, pharmaceuticals, and chemicals. However, the current routes to generate these pivotal olefins are (*i*) highly capital- and energy-intensive, and more alarmingly, (*ii*) unable to close the growing gap between their demand and availability.[1] Consequently, new versatile catalytic processes that can handle complex emerging feedstocks, such as shale gas, tight gas, and coalbed methane, are highly demanded. Oxyhalogenation, comprising the reaction of an alkane with a hydrogen halide (HX, X = Cl, Br) and O_2, has proven a highly effective and versatile route for alkane functionalization.[2] By investigating different families of materials, we discovered that europium oxychloride (EuOCl) provides single-pass yields to ethylene (90%) and propylene (40%) surpassing any previously reported route (**Figure 1**). Its outstanding performance was rationalized by (*i*) its balanced redox properties that enables the functionalization of the alkane while avoiding combustion, and (*ii*) its unpaired ability to dehydrochlorinate the formed alkyl chloride to the olefin, permitting the recycling of the halogen. This concept was extrapolated to mixtures of methane, ethane, and propane, achieving comparable olefin yields at >95% selectivity, respectively, demonstrating the uniqueness of the EuOCl catalyst for the selective functionalization of multiple hydrocarbon substrates at the same time without the need of highly energy intensive cryogenic pre-separation methods.

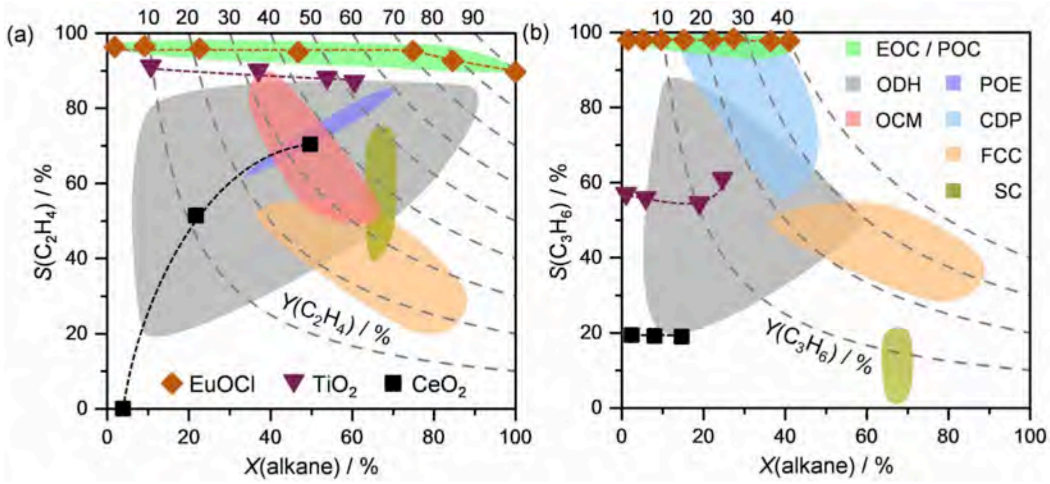

Figure 1 Alkene selectivity *versus* alkane conversion in the oxychlorination of (a) ethane (EOC) and (b) propane (POC) over EuOCl, TiO_2, and CeO_2. Dashed gray lines indicate the olefin yield, colored areas denote the single-pass molar alkane conversion and olefin selectivity achievable in EOC, POC, the oxidative dehydrogenation of ethane and propane (ODH), partial oxidation of ethane (POE), oxidative coupling of methane (OCM), catalytic dehydrogenation of propane (CDP), fluid catalytic cracking (FCC), and steam cracking (SC) of ethane and naphtha.

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Catalyst design for selective natural gas functionalization via oxyhalogenation chemistry

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

[1]ETH Zurich

The selective conversion of methane, the major component of natural gas, into value-added chemicals and fuels is one of the greatest challenges in modern catalysis research.[1] Methane oxyhalogenation is attractive for this purpose, as it enables methane functionalization into carbon monoxide or halomethanes, key chemical building blocks, under mild conditions.[1-4] However, its industrial implementation has been so far hindered by (*i*) the lack of selective and stable catalysts and (*ii*) the superficial understanding of the interplay between the specific catalyst, the type of halogen, and the operating conditions. To address these aspects, we studied methane oxychlorination (MOC) and oxybromination (MOB) and HX and CH_4 oxidation over RuO_2, Cu-K-La-X (X = Cl, Br), CeO_2, VPO, TiO_2, and $FePO_4$. The light-off points for CH_4 oxidation were shifted to higher temperatures compared to the case of methane oxyhalogenation, indicating that the presence of HX promotes methane conversion. The activity in oxyhalogenation depended on the catalyst ability to activate HX (**Figure 1a**), which was measured by the temperature required to attain 15% conversion of CH_4, $T_{15}(CH_4)$, in MOC and MOB and of HX, $T_{15}(HX)$, in the related oxidation. Almost all of the $T_{15}(CH_4)$ values in MOC and MOB were greater or equal to the corresponding $T_{15}(CH_4)$ in gas-phase methane halogenation, suggesting an important role of the latter reaction in methane activation. The distribution of the $T_{15}(CH_4)$ in MOC was also significantly broader than that in MOB. The reaction rate was primarily determined by the evolution of Cl_2 from the catalytic surface in MOC, whereas it was controlled by the gas-phase reaction between evolved Br_2 and CH_4 in MOB. The product distribution strongly depended on the type of halogen (**Figure 1b**). In addition, the halocarbon selectivity was increased by raising the inlet HX concentration, particularly over CeO_2 (**Figure 1c**), due to the (*i*) faster kinetics of HX oxidation than halocarbon combustion and (*ii*) enhanced reducing action of HX on the catalytic surface.

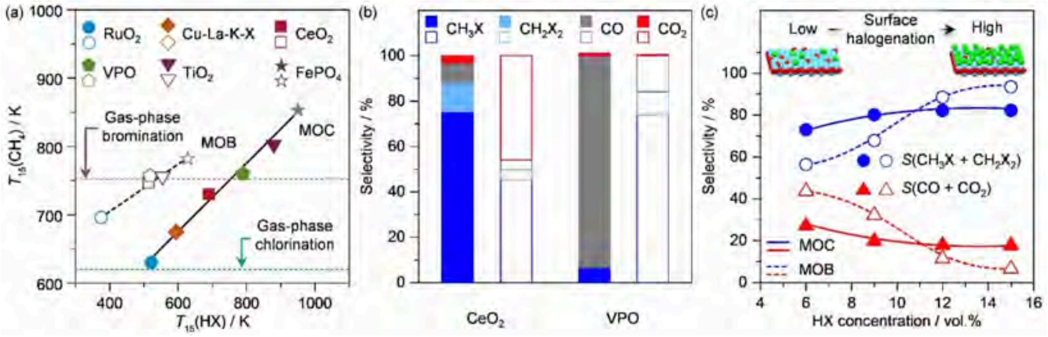

Figure 1. (a) $T_{15}(CH_4)$ *versus* $T_{15}(HX)$ over the catalysts studied. (b) Product selectivity in MOC (solid) and MOB (empty) over CeO_2 and VPO at 15% methane conversion. (c) Selectivity to products in MOC (solid line) and MOB (dashed line) *versus* the feed HX concentration over CeO_2.

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Electrochemical Hydrogen Oxidation/Evolution Kinetics – New Insights into an Old Field

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The hydrogen oxidation/evolution reaction (HOR/HER) is a central reaction in both fundamental electrocatalysis and in electrochemical energy conversion devices, viz., in H_2/air fuel cells as well as in water electrolyzers. The most active catalyst for this reaction is platinum, and in acidic electrolytes its kinetics are so large, that their quantification by the commonly used rotating disk electrode (RDE) technique turned out to be compromised by unaccounted for mass-transport resistances. This will be outlined in this presentation, showing that the true HOR/HER kinetics of Pt in acidic electrolytes are about two orders of magnitude larger than previously assumed [1]. This explains why ultra-low loadings of platinum in H_2/air fuel cell anodes or in water electrolyzer cathodes are sufficient to sustain very high rates at very low overpotentials.

A mechanistically very interesting aspect of the HOR/HER reaction is that early *ab-initio* models predicted that its kinetics on platinum are independent of pH [2], which recently was shown to not be the case, as the HOR/HER kinetics on Pt are ≈100-fold lower in alkaline compared to acidic electrolytes [3]. The so far proposed explanations for this effect are an increased H/metal bond strength [3, 4], a change of the reaction mechanism from H^+ to H_2O activation requiring more oxophilic catalyst surfaces [5], and/or a change of the water configuration at the metal/electrolyte interface [6]. The consistency of these hypotheses with the HOR/HER kinetics on different metal electrodes will be discussed. One other fundamental question of interest is whether the hydrogen oxidation/evolution reaction on palladium catalysts actually occurs on metallic palladium (as assumed in calculations [3]) or on palladium-hydride, a question which we will try to address by means of *operando* X-ray absorption studies [7].

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Magic at the interface: model multicomponent electrodes with controlled interfacial geometry for the electrocatalytic reduction of CO_2

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Combining the electrochemical reduction of CO_2 (eCO_2RR) with carbon-neutral energy sources is a potentially sustainable strategy for recycling carbon emissions. In particular, reducing CO_2 to CO would provide a versatile building block for the production of liquid fuels and plastics by well-established processes in industry. However, the application of this reaction requires the development of more efficient electrocatalysts.[1] Cu-In and Cu-Sn catalysts have shown high selectivity for CO evolution at moderate overpotentials, but their further development requires the rationalization of the synergistic effect observed in these multicomponent systems. Oxidic species that are stable under reaction conditions are crucial to the eCO_2RR over bulk In and Sn electrodes,[2,3] and recent findings indicate that the presence of $In(OH)_3$ plays a pivotal role in maintaining a high selectivity for CO over Cu-In catalysts.[4] Consequently, we hypothesize that bifunctional sites located at the interfaces between Cu surfaces and In and Sn (hydr)oxides are particularly favorable for CO evolution. In this context, we have developed a photolithography-based microfabrication process for creating model electrodes with controlled oxide-on-metal interfaces (**Figure 1**). By establishing quantitative relationships between the geometry and the CO evolution activity of the model electrodes, with further support from surface analytical techniques including operando studies, we aim to unveil the role of interfacial sites in the reduction of CO_2 to CO and to develop new descriptors for the rational optimization of this family of multicomponent catalysts.

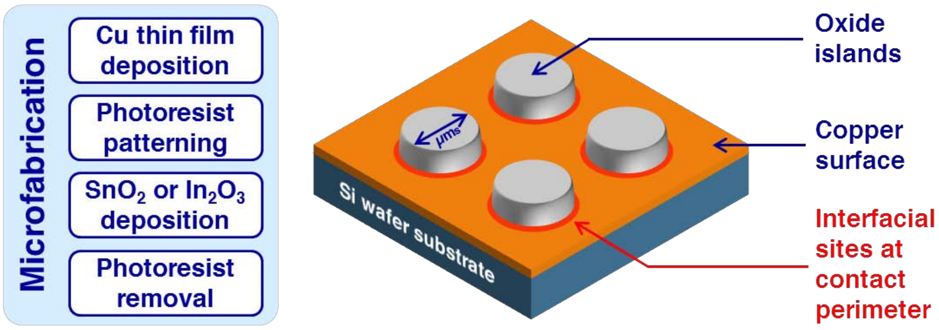

Figure 1 Main process steps for the fabrication of microstructured multicomponent model electrodes and a schematic representation of the resulting geometry. Interfacial sites are located at the contact perimeters between the circular oxide islands and the underlying smooth metal surface.

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Design of ionic polymer catalysts for the synthesis of carbonates from CO_2 and epoxides

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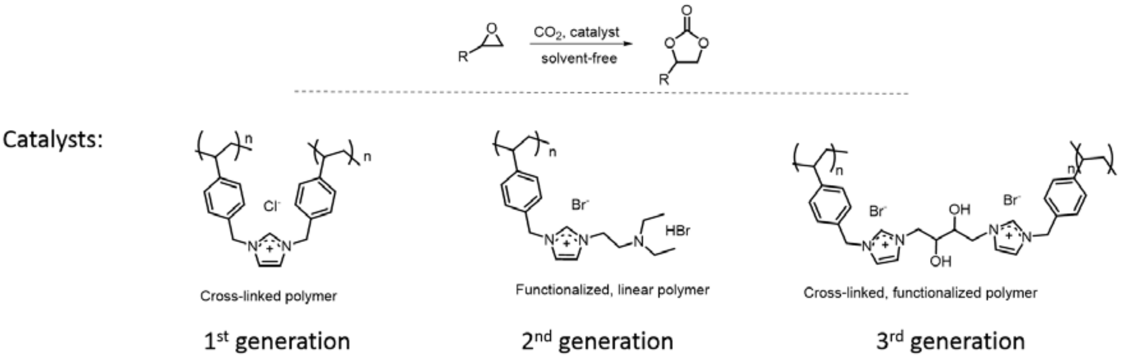
The synthesis of cyclic carbonates from epoxides and CO_2 (CCE reaction) is an atom-efficient, scalable reaction of industrial importance. It is an important example of a catalytic reaction highlighting the utilization of CO_2 as a building block. Numerous catalysts (both metallic and metal-free)[1] have been proposed for this reaction, and in particular, ionic liquids and ionic polymers have emerged as a class of potent catalysts in this transformation. In our group, we have prepared imidazolium-based polymers (Fig. 1) incorporating functional groups that are potent catalysts for the CCE reaction.[2-4]



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Surface structure and reactivity of perovskite oxynitride materials

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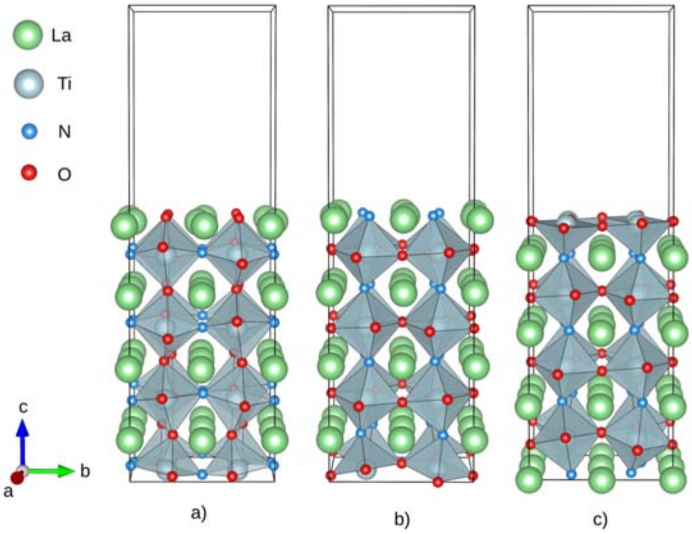
Owing to their reduced band gap compared to pure oxides, perovskite oxynitrides are a promising class of materials for photocatalytic water-splitting electrodes. While the bulk structure of these materials has been investigated both experimentally and theoretically, our knowledge about their surface structure is still very limited, despite that fact that it will dictate potential reaction mechanisms.

Based on our density functional theory (DFT) results we determine the anion arrangement in the bulk and at the surface to be different, as it is driven by bonding and electrostatic considerations respectively. From our calculations we can extract the preferred surface orientations and their terminations and will discuss them both in terms of the chosen synthesis route and as a function of their environment. We will then compare the photo-electrochemical performance of different perovskite oxynitride materials and discuss the potential of strain in thin-film configurations to induce polarity and suppress recombination losses.

Our calculations lead to a deeper understanding of the surface structure and hence the reactivity of this promising class of materials and will be instrumental in optimising them for applications in photocatalytic water splitting.



a) LaO (0.980 J/m^2), b) LaN (0.542 J/m^2) and c) TiO_2 (0.654 J/m^2) terminations of the (001) surface for the energetically most preferential bulk anion order.

Microstructural self-regeneration of $LaSrTiNiO_{3-\delta}$: fast recovery from sulfur poisoning

P. Steiger[1,3], D. Burnat[2], A. Heel[2], O. Kröcher[1,3], D. Ferri[3]*

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Poisoning by sulfur is a common problem for Ni catalysts as well as solid oxide fuel cells (SOFCs). It is widely accepted that the deactivation in SOFCs is due to the poisoning of Ni sites active for the water gas shift reaction (WGS, $CO + H_2O \rightarrow CO_2 + H_2$). This reaction provides additional H_2 for oxidation when the cell is operated on syngas feeds [1]. Current SOFC materials cannot easily be regenerated after sulfur poisoning. Some perovskite type metal oxides (PMO) exhibit the remarkable reversible segregation of catalytically active metals from and reincorporation back into the PMO host lattices. This was found to be highly efficient in inhibiting sintering of metal particles during redox cycling [2,3]. This redox stability was applied on Ni to develop a water gas shift active and regenerable SOFC anode material. It can be shown that after reduction at 800 °C Ni is selectively reduced and segregated to the $LaSrTiNiO_{3-\delta}$ (LSTN) surface where it forms catalytically active, metallic Ni particles of few tens nm in size (Fig. 1-a) [3]. After reoxidation Ni is fully reincorporated into the perovskite lattice as shown by Ni K-edge XANES (Fig. 1-b). Catalytic data for the WGS reaction obtained over a number of redox cycles and Ni particle size analysis show the excellent redox stability of this material and demonstrate inhibition of Ni particle sintering. For comparison, redox cycling of an impregnated material (Ni/LST) leads to sintering and severe loss of catalytic activity over a few redox cycles (Fig. 1-c). Exposure of LSTN to H_2S caused an expected loss of catalytic activity (Fig. 1-d), which again can be completely restored within two redox cycles.

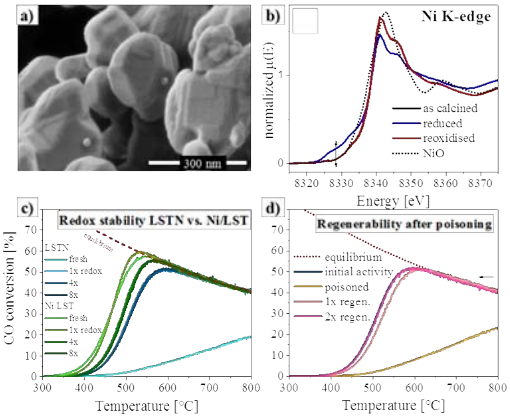

Figure 1. a) SEM image of reduced LSTN - segregated Ni particles on LSTN crystallites. b) Ni K-edge XANES of calcined, reduced and reoxidised LSTN. c) CO conversion for pre-reduced LSTN and Ni/LST over 8 redox cycles and d) after H_2S poisoning and over two oxidative regeneration cycles.

From a material and methodological point of view it is demonstrated that the structural reversibility exhibited by some PMOs can be exploited to completely regenerate S-poisoned catalysts which otherwise would suffer from deactivation by particle sintering. This function can be potentially applied to a variety of Ni catalyzed reactions suffering from similar deactivation phenomenon.

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Directed Evolution of Artificial Metalloenzymes: Genetic optimization of the catalytic activity

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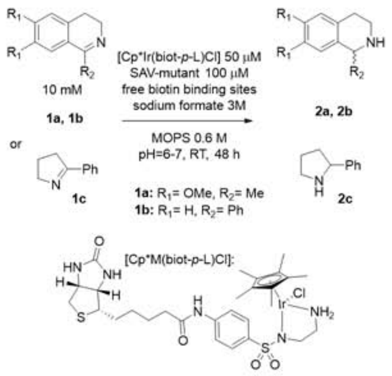
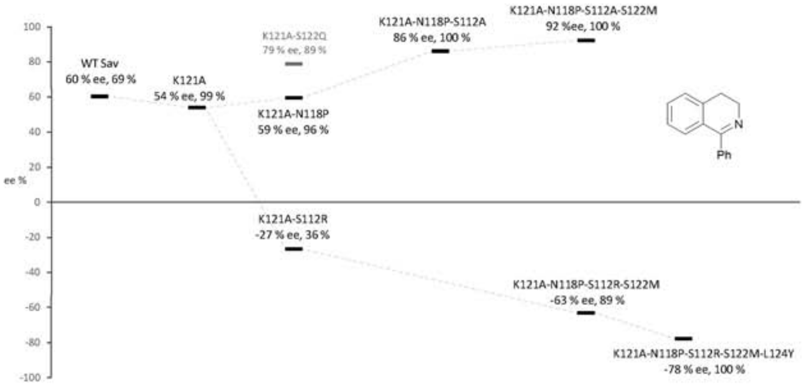
Artificial metalloenzymes (ArMs) are hybrid catalysts created by a non-covalent incorporation of an organometallic cofactor within a host protein scaffold.[1,2] This system, based on biotin-streptavidin technology, combines attractive features both of enzymatic and organometallic catalysis under near physiological conditions.[3,4] With the aim of performing catalysis *in vivo*, we have selected the transfer hydrogenation of cyclic imines as a model reaction.Herein we demonstrate the potential of directed evolution of artificial transfer hydrogenases (ATHase). Building upon a streamlined protocol[5], Sav mutants contained in *E. coli* cell free extracts were treated with diamide[6] and screened in the presence of the iridium cofactor. After identification of a successful "hit", the results were reproduced; the corresponding mutant was overexpressed, purified using an iminobiotin column and confirmed by screening.





This simplified process significantly speeds up the screening protocol and allows for the identification of improved Sav mutants for ATHase of cyclic imines. Guided by the protein crystal structure, we have performed four rounds of mutation and selection. As a result, two Sav isoforms with improved activities and yielding opposite enantiomers in the reduction of 1-phenyl-3,4-dihydroisoquinoline were obtained. X-ray analysis confirmed the presence of introduced mutations, namely K121A-N118P-S112A-S122M (96 % ee, full conversion) and K121A-N118P-S112R-S122M-L124Y (-82 % ee, full conversion). These mutants also show improved reaction rates in comparison with the use of Sav wild type.

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Zeolites for Clean Air

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The use of zeolites as adsorbents and catalysts in petrochemical processes is well established now for several decades. More recently, spurred by developments in automotive catalysis (DOC, SCR), their unique properties including temperature stability and hydrophobicity, combined with tailored pore geometries have been exploited in numerous environmental applications as catalysts, adsorbents and as exceptional support materials. Examples of these include: decomposition of N_2O from nitric acid tail gas by Fe-zeolites, adsorption of VOCs in composite matrices and as novel oxidation catalysts in conjunction with platinum group metals that can operate in high dust environments. These unique materials, used alone or combined with other chemical functionalities enable a large scope of end uses. The utility of such zeolite properties can be rationalized and explored leading to high performance materials by design.

Supported Crystalline Monodisperse Ga_2O_3 Nanoparticles with Tunable Size for the Catalytic Dehydrogenation of Propane

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[1]ETH Zurich

Crystalline colloidal monodisperse Ga_2O_3 nanoparticles with tunable sizes ranging from 2.5 to 5.2 nm have been prepared from gallium acetylacetonate and oleylamine. Concentrated toluene solutions of these nanoparticles were impregnated onto various supports to give catalysts active for propane dehydrogenation (PDH) with selectivities and activities higher than those of a benchmark catalyst prepared from gallium nitrate. Importantly, this synthesis method allows characterizing Ga_2O_3 nanoparticles prior to their deposition on supports and it leads to active, well-defined supported Ga_2O_3 PDH catalysts amenable for a more direct evaluation of support and particle size effects on catalytic properties.

Conventional synthesis routes for gallium oxide-based catalyst catalysts typically use aqueous gallium nitrate solutions for impregnation of supports, followed by calcination.[1] This approach usually gives ill-defined catalysts with a broad distribution of metal sites. Identification of the catalytically active sites in such systems is very challenging, if not impossible. Here, we report the synthesis of crystalline, ligand-capped Ga_2O_3 nanoparticles with controllable size that form a stable colloidal solution in an organic solvent (toluene). The synthetic methodology to such size-tunable nanoparticles has been developed previously for the preparation of solution-processable gallium oxide quantum dots for optoelectronic applications.[2] We demonstrate that this method serves as a convenient entry to establish a structure-activity relationship for Ga-based catalysts that includes particle-support interactions, particle size effect and the nature of Ga sites.

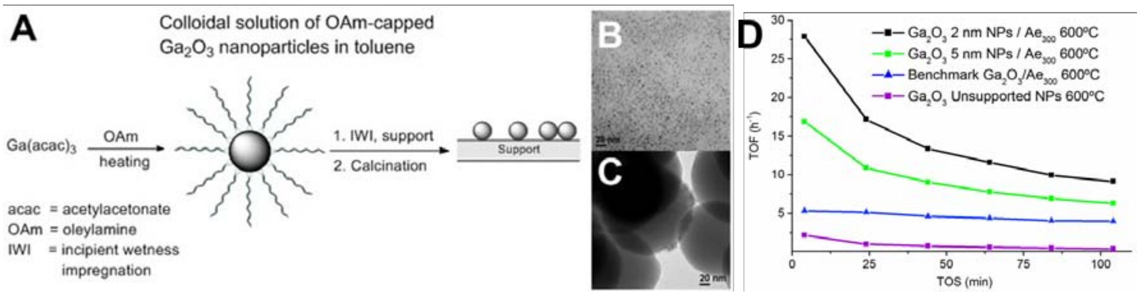

Figure 1. *Synthesis of ligand-capped colloidal Ga_2O_3 nanoparticles and their impregnation onto supports (A). TEM images show Ga_2O_3 nanoparticles in a colloidal solution (B) and the same NPs after impregnation and calcination onto silica nanospheres (C). Catalytic performance for propane dehydrogenation at 550 ºC (WHSV= 7.2 h^{-1}) (D).*

By introducing synthetic protocols from quantum dots chemistry to catalysis, we have successfully produced stable colloidal solutions containing crystalline gallium oxide nanoparticles with controllable sizes. Depositing these nanoparticles onto various supports gives catalysts that are active for propane dehydrogenation. Our results show that colloidal routes allow to prepare catalysts with higher activity and selectivity per total gallium when compared to the benchmark systems obtained through a *conventional* route, i.e. the impregnation of aqueous solutions of $Ga(NO_3)_3$ on the support. The colloidal approach uses pre-formed, well-defined gallia NPs and therefore allows for a more direct and systematic evaluation of the catalyst performance, an important step towards the development of structure-activity relationships in gallia systems.

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Rational design of Pd/Na-ZSM-5 catalysts for complete methane oxidation

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

Stabilization of metal nanoparticles in a constrained internal space of a support has attracted considerable attention in the recent years [1], allowing to reduce the production costs by decreasing the amount of the active metal. In this work, we have exploited this approach in order to prepare active and stable methane oxidation catalysts, which currently lack low-temperature activity and long-term stability due to metal nanoparticle sintering [2], for possible utilization in catalytic converters to treat the exhaust of natural gas fueled vehicles. Moreover, we defined the activity and stability descriptors for the novel fully sodium exchanged Pd/Na-ZSM-5 catalysts using various zeolite post-modification techniques.

Dealuminated ZSM-5 zeolites were obtained by leaching the parent material (Clariant SM-27, Si/Al=12) with HCl, HNO_3 and oxalic acid. Mesoporous ZSM-5 was obtained by consecutive base and acid leaching. The thus treated zeolites were then exchanged with salts of Pd and Na to achieve 1 wt. % palladium and to fully exchange the acid sites of the zeolite. The stability of the catalysts was evaluated in a quartz glass plug-flow reactor with a feed of 1 vol.% CH_4, 4 vol.% O_2 and 5 vol.% H_2O (bal. N_2) at 420°C and GHSV = 80,000 h^{-1}.

Transmission IR spectra (Fig. 1b) of acid washed Pd/Na-ZSM-5 revealed different Al extraction mechanisms by the acids. Whereas HCl caused unselective surface and bulk dealumination of the framework (as evidenced by the increase of the peaks corresponding to the terminal Si-OH at 3743 cm^{-1} and H-bonded Si-OH groups at 3520 cm^{-1}), oxalic acid caused only surface dealumination [3]. Both HNO_3 and oxalic acid significantly reduced the amount of extra-framework aluminum (EFAL, 3664 cm^{-1}). The better performance of the samples washed by HNO_3 and oxalic acid (Fig. 1a) suggests that EFAL species passivate Pd/Na-ZSM-5 catalysts. Generation of a small amount of mesopores (nanocages) by desilication together with the control of aluminum speciation yielded a highly active and stable catalyst. Microscopic investigation confirmed that this was achieved by trapping palladium particles within the nanocages of the zeolite (Fig. 1c,d).

The results show that achieving high performance of Pd/Na-ZSM-5 requires, besides the complete Na exchange, control of Al speciation and pore structure of the zeolite.

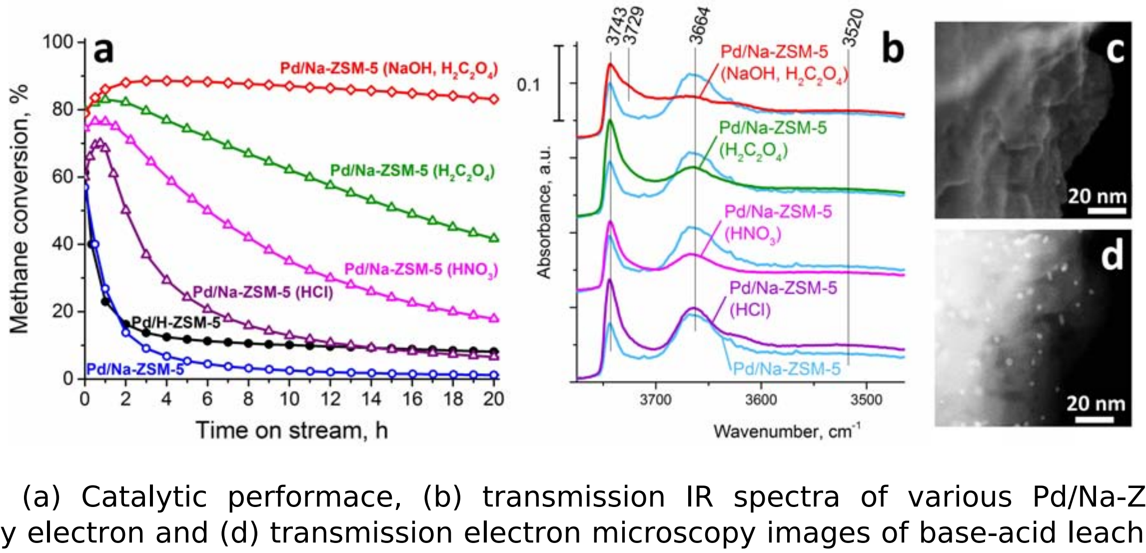

Figure 1. (a) Catalytic performace, (b) transmission IR spectra of various Pd/Na-ZSM-5. (c) Secondary electron and (d) transmission electron microscopy images of base-acid leached Pd/Na-ZSM-5.

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Deactivation of Fluid Catalytic Cracking Catalysts, a Three-Dimensional View of Structural Changes

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[1]Paul Scherrer Institut, [2]W. R. Grace Refining Technologies, [3]European Radiation Synchrotron Facility, [4]ETH Zurich

Since its commercial introduction three-quarters of a century ago fluid catalytic cracking has proven to be one of the most important conversion processes in the petroleum industry. In this process porous composites composed of zeolite and clay crack the heavy fractions in crude oil into transportation fuel and petrochemical feedstocks. Yet, over time the catalytic activity of these particles decreases. Here we report on resonant ptychographic and fluorescence tomography measurements complemented by electron microscopy to elucidate the structural changes that lead to catalyst deactivation. In combination, acquired tomograms reveal zeolite amorphization and distinct structural changes to the particle exterior as the driving forces behind catalyst deactivation. Amorphization of zeolites, in particular, close to the particle exterior results in a reduction of catalytic capacity. A concretion of the outermost particle layer into a dense amorphous silica-alumina shell further reduces the mass transport to the active sites within the composite. The results provide a complementary explanation to currently suggested deactivation mechanisms driven by feed and reactor impurities.

Rational design of sulfur-tolerant ruthenium catalysts for dry biomass derived CO methanation

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The process of methane production from dry biomass, called wood-to-Synthetic Natural Gas (SNG), consists of 4 main steps: biomass gasification, syngas cleaning to remove catalyst poisons such as H_2S, COS and C_4H_4S using "cold" gas cleaning technologies, methanation and upgrading to remove H_2O and CO_2.[1] To make SNG cost-competitive, the concept of integrating gas cleaning with methanation, which utilizes the ability of ruthenium-based catalysts to be regenerated under oxidizing atmosphere after sulfur poisoning is explored.[2]

However, a complete recovery of the catalytic activity after the regeneration cannot be achieved so far, probably because of a combination of several reasons. Firstly, Al_2O_3 support of the nanoparticles can "store" some of the sulfur poisons in the form of sulfate, which prevent efficient regeneration.[2] Secondly, TEM and XAS analysis evidences particle sintering upon recycling of originally 1 nm particle in Ru/Al_2O_3.

Here, we show that silica largely improve the regeneration process, because it is less prompt to sulfur storage (Fig. 1a). *Operando* XAS at the sulfur K-edge (Fig. 1b) and DRIFTS (Fig. 1c) showed that sulfate species formed on SiO_2 are unstable and could be removed by subsequent treatment with H_2. However, sintering still remains an issue. In addition, DRIFT spectroscopy revealed altered CO adsorption profile for the regenerated catalyst, implying that structural and/or electronic properties of the catalyst are changed after a poisoning-regeneration cycle.

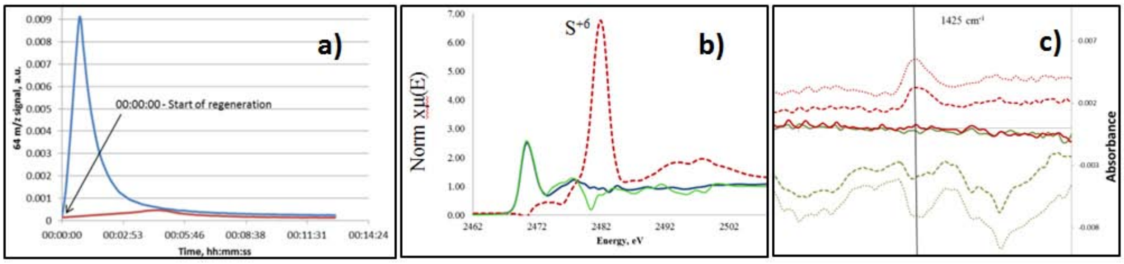

Figure 1: a) SO_2 detected at the reactor outlet for Ru/Al_2O_3 (red) and Ru/SiO_2 (blue) b) Sulfur K-edge XAS spectrum of Ru/SiO_2 catalyst taken during methanation with poisoning (blue), regeneration in 1% O_2 (red) and subsequent methanation (green); c) DRIFTS spectrum of Ru/SiO_2 showing sulfate (ca. 1425 cm^{-1} band)[4] formation (1% O_2 regeneration after catalyst poisoning, red) and decomposition (1% H_2, green) onSiO_2 surface

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Development of Coke- and sintering-resistant Ni/SiO_2-based dry reforming catalyst by depositing a thin layer of Al_2O_3 via ALD

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The dry reforming of methane, DRM ($CH_4 + CO_2 \rightarrow 2CO + 2H_2$), is a promising process to convert two greenhouse gases into a synthesis gas (H_2/CO), that is a key intermediate for liquid fuels synthesized via the Fischer-Tropsch process [1]. Due to its comparatively low price (when compared to noble metals) and high activity, Ni-based catalysts are attractive for DRM. The main deactivation mechanisms of Ni-based dry methane reforming (DRM) catalysts are sintering and coke deposition, the extent of coke deposition being critically affected by the size of the Ni particles [2, 3]. Thus, by controlling and stabilizing the Ni particle size Ni-based DRM catalysts that possess a high and stable activity can be realized. In this work, we have developed Al_2O_3-coated, SiO_2-supported Ni DRM catalysts using atomic layer deposition (ALD). Catalysts with different Al_2O_3-shell thicknesses were prepared. Coating of Ni nanoparticles with an Al_2O_3 shell increases appreciably the catalysts' resistance to sintering and coke formation when compared to unmodified SiO_2-supported Ni.

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