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Selectivity Control in CO_2 Electroreduction through Rational Catalyst and Electrolyte Design

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The utilization of fossil fuels as the main energy source gives rise to serious environmental issues, including global warming caused by the continuously increasing level of atmospheric CO_2. Recently, the electrochemical conversion of CO_2 (CO_2RR) to chemicals and fuels driven by electricity derived from renewable energy has been recognized as a promising strategy towards sustainable energy.

In my talk I will provide examples of recent advances in the development of highly active plasma-modified single crystals, nanostructured thin films and nanoparticle (NP) electrocatalysts (Cu, Ag, Zn, and Cu-M with M = Zn, Sn) and how their structure (crystal orientation, atomic arrangement, size, shape, defects), oxidation state and composition influence their selectivity in CO_2RR. I will also discuss how important morphological motives and chemical sites can be created and regenerated in pulsed electrochemistry experiments. Additionally, the determining role of the electrolyte in the surface restructuring, reaction activity and selectivity will be illustrated.

The importance of *in situ* and *operando* characterization methods (e.g. EC-AFM, Liquid-TEM, XAS, XPS) to gain in depth understanding on the structural and chemical transformations of CO_2RR catalysts under working conditions will be demonstrated. Our results are expected to open up new routes for the reutilization of CO_2 through its direct selective conversion into higher value products such as ethylene and ethanol.

Enhancement of power-to-gas via multi-catalyst reactors tailoring reaction rate and heat exchange

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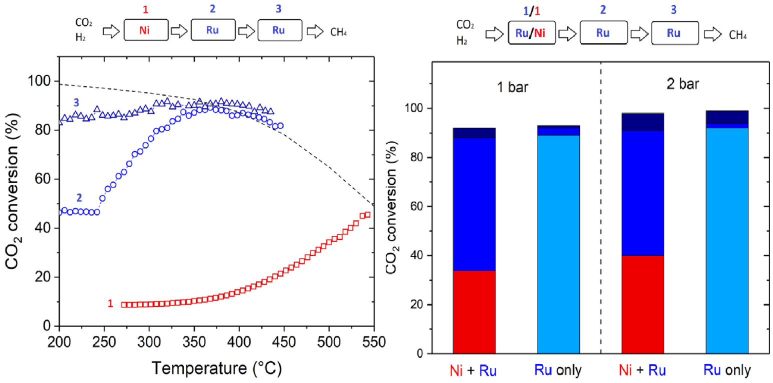
The methanation reactor, key of Power-to-Gas (PtG) systems, is a catalytic reactor with different requirements according to the advancement of the reaction. In fact, the reaction rate can be limited by thermodynamics or kinetics depending to temperature and conversion. With an appropriate model-based optimization routine[1], it is possible to determine the requirements of the system in term of heat transfer properties to minimize the residence time needed to reach the target CO_2 conversion (99.5% due to grid injection regulations). We reported that three different cooling zones are sufficient to optimize the reactor: first an adiabatic section, followed by a zone with large cooling and a final section with low heat transfer [1]. According to these findings, we targeted the coupling of PtG with a natural gas expansion station, where low temperature heat is required to keep the gas temperature constant during expansion from 60 to 5 bar. This specific reactor is an important breaktrough for PtG, as it allows the direct valorization of process waste heat, improving the economic performance of the system. The manufactured reactor operates with Ru/Al_2O_3 as catalyst and includes three different cooling areas: an adiabatic preheater, a cooled section operated with the cooling water from the gas expansion station and a final area with low heat exchange properties. The reactor was operated in field and the gas quality and temperature profile were recorded. According to the experimental results of the tests, the concept is further refined by changing the catalyst in the three zones, operating the first two with Ni/Al_2O_3 and only the last section with Ru/Al_2O_3. Consequently, a new system tailoring the catalyst properties is designed and operated [2,3]. First, the reaction is activated over the Ni-based catalyst, therefore reducing the amount of noble metal required for the operation. This change changes the concentration profiles in the system, but not the final conversion. As shown in figure 1a, initially Ni can be used for the adiabatic part of the reactor, reaching a hotspot of 550 °C. Afterwards the reaction can be continued quickly cooling the reactor to lower temperature over Ru. In this part of the reactor, the cooling is adapted to ensure the maximum reaction rate and reach high conversion. Figure 1b shows the comparison between the Ru-based and the hybrid (Ru+Ni) reactor. The total CO_2 conversion is the same in the two cases, confirming that an important part of the reactor can operate over Ni, without losses in productivity.



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Methanol synthesis *via* hydrogenation of hybrid CO_2-CO feeds

T. Pinheiro Araújo[1], A. H. Hergesell[1], D. Faust Akl[1], S. Buchele[1], J. A. Stewart[2], D. Curulla-Ferré[2], C. Mondelli[1], J. Pérez-Ramírez[1]*

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The thermocatalytic conversion of carbon dioxide and hydrogen into methanol is regarded as an attractive approach to combat climate change while producing a valuable energy carrier. Although carbon monoxide will comprise up to half of the carbon feedstock, depending on CO_2 origin and process configuration, the impact of CO on CO_2-to-methanol catalysts has been scarcely investigated.[1-3] Herein, Cu-based catalysts, $ZnO-ZrO_2$, and In_2O_3-based systems were assessed in cycle experiments with hybrid CO_2-CO feeds and their CO sensitivity compared (**Fig. 1**). All catalysts were promoted upon CO addition. Cu-based materials are intrinsically more active in CO hydrogenation and profit from exploiting this carbon source for methanol production, whereas CO induces a surplus formation of oxygen vacancies, *i.e.*, the catalytic sites, on $ZnO-ZrO_2$ and In_2O_3-based systems. Mild-to-moderate deactivation occurred upon re-exposure to CO_2-rich streams due to water-induced sintering for all catalysts except $ZnO-ZrO_2$, which responds reversibly to feed variations likely owing to its more hydrophobic nature and the atomic mixing of its metal components. Our study categorizes catalytic systems for operation in hybrid CO_2-CO feeds, emphasizing the significance of catalyst and process design to foster advances in CO_2 utilization technologies.

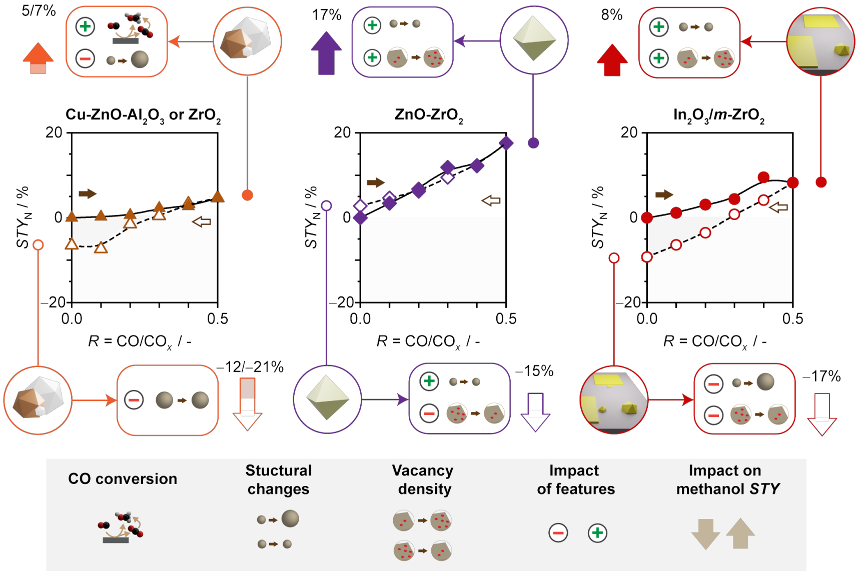

Fig. 1. Structural features and performance of Cu-based catalysts, $ZnO-ZrO_2$ and In_2O_3 supported on monoclinic (*m*) ZrO_2 in methanol synthesis upon step-wise replacement of CO_2 by CO in the CO_2+H_2 feed. Conditions: 513 K for Cu-containing, 593 K for $ZnO-ZrO_2$, and 553 K for $In_2O_3/m-ZrO_2$, 50 bar, H_2/CO_x (CO_2+CO) = 4, and *WGSV* = 24,000 and 48,000 (Cu-based catalysts) $cm^3\ h^{-1}\ g_{cat}^{-1}$.

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Following the structure of copper-zinc-alumina across the pressure gap in carbon dioxide hydrogenation

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The central position of heterogeneous catalysis in the chemical industry makes it the enabling technology for a sustainable society. Rational catalyst design requires understanding of the structure of the catalyst in its working state. Such understanding is made possible by *in situ* and *operando* characterization. Such tools are now central to the majority of current scientific catalysis literature and research. The wealth of new insights that these methods provide into catalysis has, at the same time, created numerous strong controversies and often studies on the same catalytic system have reported contradictory results.

Copper-zinc-alumina (CZA) catalysts are the industrially-used formulation for methanol synthesis from carbon monoxide and carbon dioxide. The superior performance develops from synergies between its components. This important catalytic system has been intensively investigated, however, no comprehensive agreement has emerged as to the fundamental source of its high activity. One potential source of the disagreements is the considerable variation in pressure used in studies to understand a process that is industrially performed at pressures above 20 bar. Here, a systematic X-ray absorption spectroscopy study of the catalyst state during temperature-programmed reduction and under carbon dioxide hydrogenation is presented. The evolution of the catalyst over four orders of magnitude in pressure (1 mbar – 10 bar) shows how the state is defined by its environment [1]. In the light of the new systematic findings, existing controversies on the copper-zinc-alumina catalysts can be explained by considering the pressure regimes under which many previous studies have been conducted. As pressure gaps are a general problem in catalysis, these observations have wide-ranging ramifications.

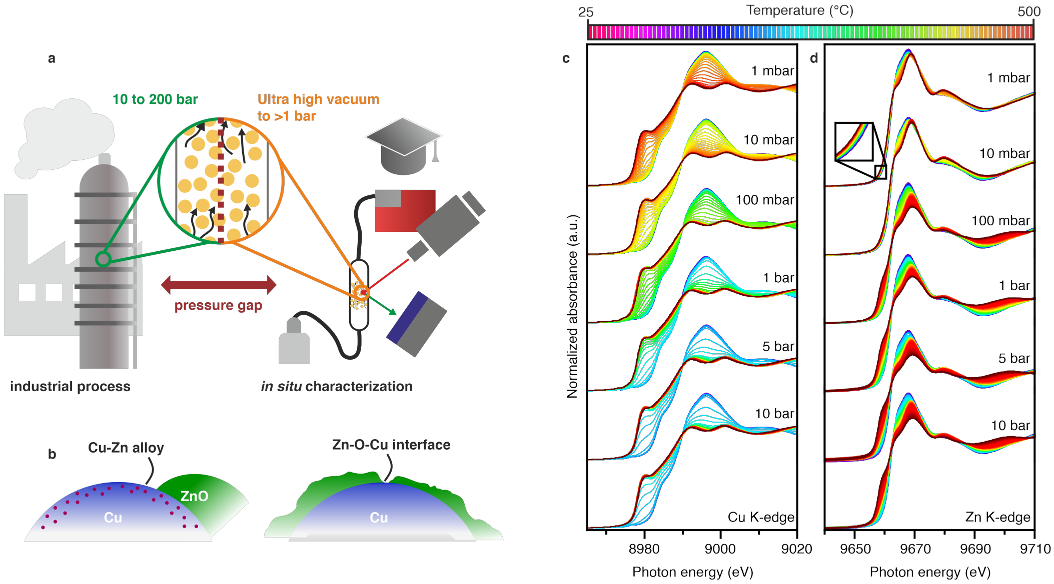

Figure 1: (**a**) The pressure gap existing between research and industrial conditions. (**b**) Proposals for the active site of copper-zinc catalysts.(**c**, **d**) XANES obtained during reduction.

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The Role of Alloying in Highly Selective and Stable Propane Dehydrogenation Catalysts based on Silica-Supported Pt-Mn Particles Prepared via SOMC

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Light olefins, e.g. ethene/propene, are key intermediates for the production of a large number of bulk and fine chemicals as well as polymers. While these olefins were mostly produced from cracking of naphtha, the increasing availability of shale gas led to changes in cracking technology, resulting in decreased propene production despite an increased demand.[1] Thus, the direct dehydrogenation of the corresponding alkane has become the dominating alternative approach for the production route of olefins in recent years. Two classes of catalysts are currently used industrially, based on either Cr or Pt. Both of them suffer from fast deactivation requiring constant regeneration and necessitate additional promoter metals to achieve high selectivity at high conversion as well as stability.[2] The Pt-based catalysts, used in the Olefex (PtSn) and Dow Fluidized Catalytic Dehydrogenation (PtGa), are bimetallic, where the two metal components generate an alloy, improving the selectivity and the stability of the catalysts towards sintering and coke formation.[3] Other metal dopants have also been investigated, where the formation of alloys has be shown to a key to high selectivity in Pt-based catalysts.

Here we report the preparation and characterization of a highly selective and stable silica-supported, Pt-Mn based Propane dehydrogenation catalyst using Surface Organometallic Chemistry.[4] This involves a two-step approach with first the generation of Mn(II) single sites on the support surface and second, grafting of a Pt precursor followed by a reduction treatment under a flow of H_2. Detailed multi-technique characterization, including microscopy, *in-situ* XAS, XPS and EPR show that this particularly robust and highly selective catalyst is best described as Pt-rich nanoparticles – resembling Pt_3Mn – with a majority of Mn(II) sites on the support surface.

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Suppression of water inhibition and thermal deactivation on Pd/Al_2O_3 during lean methane oxidation using oxygen dithering

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The growing interest in natural gas as transportation fuel arises from its lower CO_2 and particulate matter emissions together with its higher energy density. However, unburnt CH_4 is a severe greenhouse gas and has to be removed from the exhaust. Because this is challenging[1], important efforts must be undertaken to improve CH_4 abatement either through material development or by optimization of the operating conditions. Previous studies[2,3] have demonstrated that by repeatedly applying short reducing pulses (SRP), which are implemented by periodic removal of O_2 from the gas feed, a significant increase in activity could be achieved for lean CH_4 oxidation and NG exhaust treatment over a Pd-based zeolite[2] and a three-way catalyst[3], respectively.

In this study[4], the beneficial effect induced by short reducing pulses were studied over a Pd/Al_2O_3 catalyst for wet lean CH_4 oxidation. By applying SRP, we were able to activate the catalyst and bring it to a highly active state compared to static conditions ($T_{50\%}$ from 428 °C to 370 °C; Figure 1a). In line with this observation, the $E_{A,app}$ under SRP conditions dropped by ca. 20 kJ/mol. This strategy also allowed reversing the structural effects induced by thermal treatments and therefore to recover the degraded activity of these materials. Consequently, under isothermal conditions (435 °C), SRP suppressed the fast deactivation of Pd/Al_2O_3 (fresh and aged), observed under static conditions in the presence of water, and allowed to maintain the catalyst active (> 99%) for over 16 h (Figure 1b). Combination of time-resolved operando X-ray absorption spectroscopy (XAS) at the Pd K-edge and fit of oxidation kinetic models revealed that only moderately active PdO species were present under static conditions while under SRP operation an amorphous PdO_x shell around a Pd metallic core was formed and maintained for long periods (Figure 1c). This study demonstrates that high activity can be achieved in presence of water as long as a Pd metallic core is present, but when this is fully consumed, PdO_x is believed to densify and crystallize causing a decrease of CH_4 conversion. Based on these results we propose a practical range of Pd oxidation degree that allow maintaining high CH_4 conversion levels.

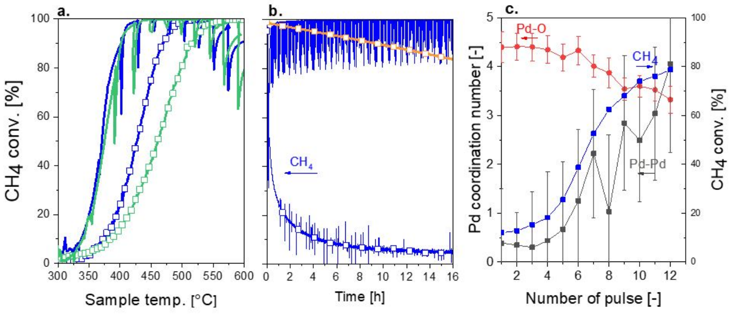

Figure 1. CH_4 conversion of fresh catalyst (blue) and thermally aged catalyst (green) (a) during heating ramp and (b) stability test under static (-□-) and SRP (-) lean conditions. Panel b. includes data collected for the fresh sample in dry static conditions (green). Conditions: 1 vol% CH_4, 4 vol% O_2, 10 vol% H_2O; WHSV = 2,550 h^{-1} mg^{-1}.

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Catalysis and Engineering: From Academia to Industry

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Casale can trace its origins to the pioneering age when the ammonia industry was born, at the beginning of the XX century. At that time, ammonia was only industrially produced in Germany by Badische Anilin and Soda Fabrik (“BASF”) using its proprietary Haber-Bosch process.

In this process, owing to the relatively low synthesis pressure, water scrubbing of the reacted gases was used to capture the product ammonia as an aqueous solution, which would then undergo subsequent steps of purification in order to obtain pure ammonia.

Luigi Casale, an italian chemist, devised an innovative scheme deciding to operate the ammonia synthesis at a much higher pressure than BASF’s one, thus obtaining directly liquid ammonia.

Ammonia Casale, the original company’s name, was therefore established in Lugano (Switzerland) in 1921 with the purpose to license the newly patented process.

Lugi Casale’s flair of innovation has been preserved and continuously nurtured over the decades-long history of his Company and still deeply permeates the culture of today’s Casale. Drawing upon its creativity and thanks to significant investment in the development of core technologies and know-how for the production of **Ammonia**, **Urea**, **Melamine**, **Methanol**, **Syngas**, **Nitrate fertilizer** and **Phosphates fertilizers** Casale is nowadays able to provide, for plant retrofits and new plants, a comprehensive range of proven and efficient solutions, services and products as summarized below:

- know-how and licensing of core technologies
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- equipment and materials supply
- site assistance and site construction services
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Titanium hydride surfaces for ammonia synthesis

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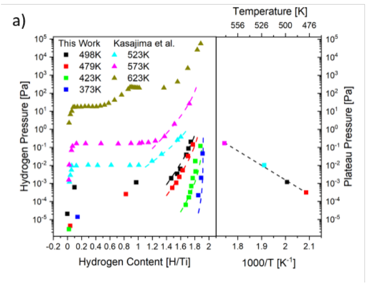
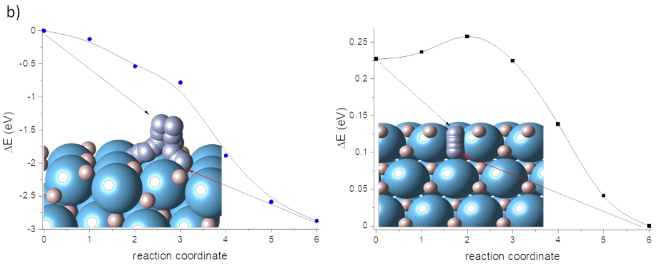
Because of its relevance in catalysis, the interaction of hydrogen with metallic surfaces is generally well studied. However, knowledge on surface properties is limited when it comes to the class of metals, which form bulk hydrides, such as titanium. Hydride surfaces have peculiar properties for their application as heterogeneous hydrogenation catalysts, e.g., they may have even less hydrogen on the surface than their metallic counterparts resulting in lower catalytic yields [1]. Titanium dihydride TiH_2 has been recently shown to catalyze the ammonia synthesis under Haber-Bosch conditions while titanium metal shows no activity [2].
The key to understanding the catalytic properties of hydrides is their electronic structure. The standard electron spectroscopy methods are incompatible with hydrogen pressures needed to form hydrides, therefore these kind of experiments are usually restricted to post-mortem analysis. We have developed a method to hydrogenate thin films *in-situ* under UHV conditions compatible with electron spectroscopy measurements. We can measure pressure-composition isotherms (pcT) of the Ti-H system by electron energy loss spectroscopy (EELS) (see Fig. a) and investigate different titanium hydrides by electron spectroscopy methods. Furthermore the UHV system allows for introduction of nitrogen gas and the spectroscopic study of the resulting surfaces. The findings are supported by DFT calculations of the titanium hydrogen interactions (see Fig. b).





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Piano-stool N-heterocyclic carbene iron complexes and the impact of ligand variation on hydrosilylation activity

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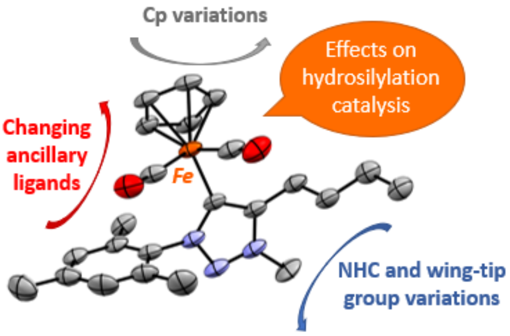
Hydrosilylation of alkenes and carbonyls is an important catalytic transformation both in bulk and fine chemical industry, however this transformation is normally catalyzed by precious metals such as platinum rhodium and iridium.[1,2] In the past two decades iron catalysts have emerged as attractive complexes for this transformation, offering a cheaper and more benign option. While NN and NNN type ligands dominate the hydrosilylation of alkenes, N-heterocyclic carbenes (NHCs) have demonstrated efficiency as ligands for iron-catalyzed hydrosilylation of carbonyls.[3,4,5]



In this work we present a new synthetic method to prepare NHC iron piano-stool complexes and we evaluate effects emerging from variations of wing-tip groups, NHC scaffold, cyclopentadiene (Cp) unit and ancillary ligands on catalytic hydrosilylation activity. Our data reveal a clear trend in catalytic activity which depends strongly on the NHC scaffold as well as the steric bulk imparted by the NHC wing-tip groups. We will also discuss mechanistic insights obtained by ^{1}H NMR and *in situ* spectroscopies, which support a substrate-dependent catalyst activation.[6]

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Single-Atom Substitution in Two-Dimensional Molybdenum Carbide: Implications for Electrocatalysis

D. Kuznetsov[1], Z. Chen[1], P. Kumar[2], P. Abdala[1], A. Fedorov[1]*, C. Müller[1]*

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Two-dimensional carbides and nitrides (MXenes) represent an excellent platform for the fundamental catalysis studies due to their well-defined and tunable structure and theoretically predicted high activity in numerous catalytic reactions.[1] However, the scope of metals capable of forming thermodynamically stable MXenes is limited mostly to early transition metals, making the investigation of properties inherent to mid or late transition metal carbides/nitrides challenging. Here, we present the synthesis and structural characterization of the Mo_2CT_x:M phases[2,3] (M = Co, Fe; T_x = O, OH, F surface terminations), where M substituents occupy molybdenum positions in the Mo_2CT_x lattice, providing isolated Co/Fe sites. Our studies demonstrate that metal M substitution imparts Mo_2CT_x:M carbides high catalytic activity in the hydrogen evolution and oxygen reduction reactions. An examination of the electrode materials after catalytic tests proved high stability of Mo_2CT_x:M (M = Co) carbide under reductive conditions (hydrogen evolution) and complete decomposition of Mo_2CT_x:M (M = Fe) under oxygen electrocatalysis conditions. The latter has proven to be a common phenomenon for MXene family applied to oxygen electrocatalysis.

Overall, our work expands the compositional space of the MXenes by introducing materials with isolated metal sites incorporated into the matrix of Mo_2CT_x. Our results highlight the general applicability of the developed synthetic approach and illustrate that tailoring the properties of MXenes for a specific application can be achieved via targeted substitution of the host metal, as well as showcases the intrinsic stability ranges for the use of MXenes in electrocatalysis.

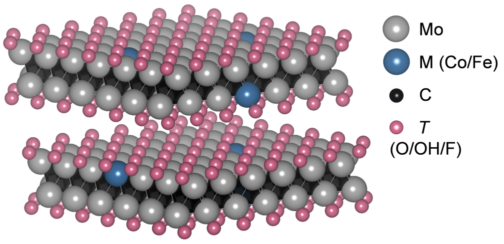

Figure 1. Structure of Mo_2CT_x:M.

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Photo- and Electrocatalysis with a Polymerised Water Reduction Catalyst

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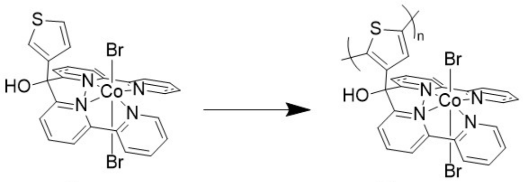
During the last years our group was working on the improvement[1] and immobilisation of water reduction catalysts (WRC). Polymerisation of the WRC allows for immobilisation, recycling and the introduction of further functionalities in the backbone such as proton shuttling or conductivity. A variety of monomers containing catalytically active units were synthesised, polymerised and tested in photo- and electrocatalysis for the hydrogen evolution reaction (HER). Here we present results of our thiophene derivative **1**.



1 **P1**

Monomer **1** was synthesised in an analogous way to established WRCs[1]. Polymerisation was done in a mixture of MeCN and water with persulfate. Photocatalysis of polymer **P1** with $[Ru(bipy)_3]Cl_2$ as photosensitiser and ascorbate as sacrificial electron donor was performed to test for HER activity. Surprisingly, **P1** showed good photocatalytic activity equal to the one of the monomer **1**, independent of chain length. Even copolymerisation with thiophene (Th) in different ratios gave polymers with comparable photocatalytic properties (Fig. 1a).

Electrocatalysis was performed on a glassy carbon (GC) rotating disc electrode. The polymer was immobilised in a blend with NaPSS on PEDOT:PSS. The GC/PEDOT:PSS/**P1**:PSS electrode showed good stability and electrocatalytic activity in cycled potential studies (Fig. 1b).

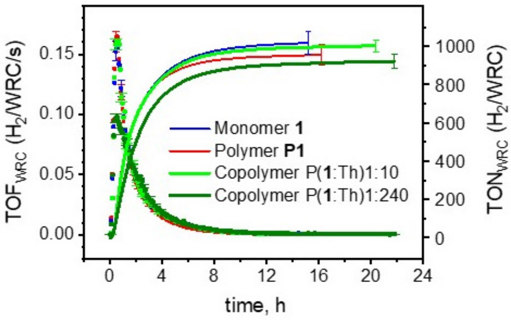


Fig. 1a: Photocatalysis in aqueous solution (10 mL) at pH 5 with 5 μM WRC 500 μM $[Ru(bipy)_3]Cl_2 \cdot 5\ H_2O$, 1 M sodium ascorbate. The light source is a 453 nm LED.

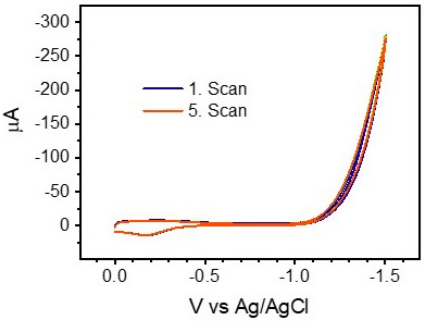


Fig. 1b: 5 CV scans from 0 to -1.5 V vs Ag/AgCl at pH 5 in 0.2 M acetate buffer with a rotating GC/PEDOT:PSS/**P1**:PSS electrode at 600 rpm.

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Mn(I) Phosphine-Amino-Phosphinites: A Highly Modular Class of Pincer Complexes for Enantioselective Transfer Hydrogenation of ketones

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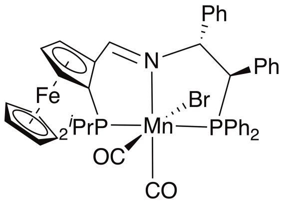
Despite manganese being cheap and non-toxic, the first Mn(I) catalysts for the asymmetric hydrogenation of ketones were reported only in 2017. Complex **1** is active under hydrogen transfer conditions (ATH), whereas **2** and **3** operate under H_2 (AH),[1] and all contains pincer ligands.



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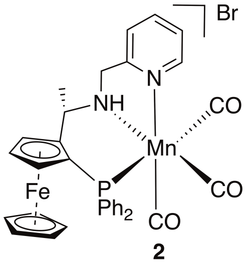

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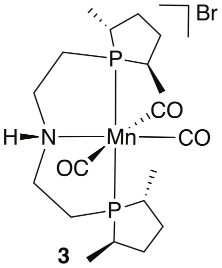

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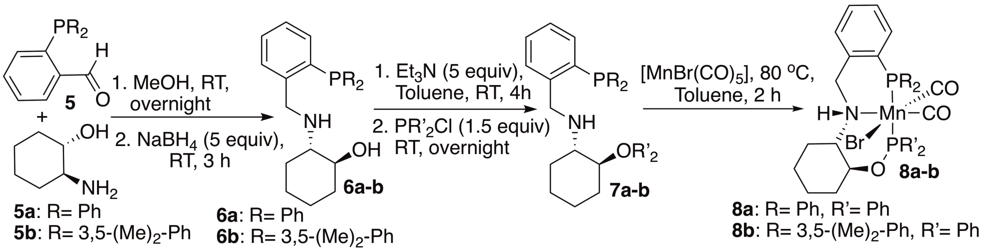
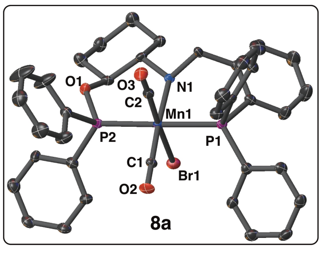
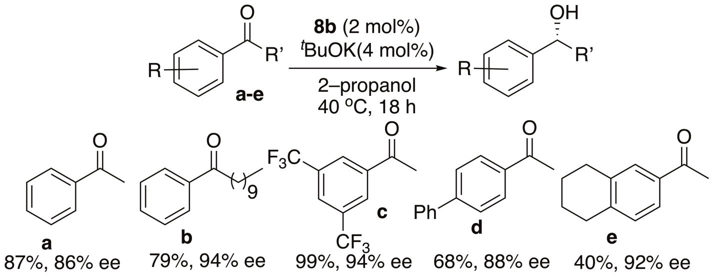
We report here, a new class of chiral phosphine-amino-phosphinite pincer ligands (P'(O)N(H)P) (**7a-b**) and their Mn(I) complexes (**8a-b**) that are prepared from cheap (1S,2S)-2-aminocyclohexanol. Complexes **8a-b** are active only under ATH conditions. Catalyst **8b** (2 mol%, ^{t}BuOK (4 mol%), 2-propanol, 40 °C, 18h) hydrogenates aromatic ketones to their corresponding alcohols with enantiomeric excess and conversion up to 97% ee and 99%, respectively (selected examples given below).







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Unravelling the aging phenomena of Diesel oxidation catalysts

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Fossil fuels are expected to continue playing a relevant role in heavy-duty transportation, but the related noxious emissions require mitigation by the use of exhaust aftertreatment systems. In case of Diesel engines, this measure includes a Diesel oxidation catalyst (DOC) to oxidise CO, unburned hydrocarbons and NO. Supported noble metal nanoparticles are typically the active phase of the DOC, which is then washcoated onto a monolith substrate [1].

To meet current and future emission regulations, it is essential to understand and predict the long-term durability of DOCs. To this end, characterization and activity measurements were performed on a DOC monolith extracted from a truck with 288,000 km. The study allowed the identification of two main deactivating agents: 1) chemical poisoning (due to accumulation of P and S compounds from oil and fuel impurities) and 2) noble metal sintering. An in-depth analysis on different segments along the monolith revealed that P accumulation takes place preferentially in the inlet and in the top region of the washcoat, while S exhibits a reversed distribution [2]. The poison distribution is believed to influence the size and redox properties of noble metal particles along the monolith. The results evidence that aging leads to radial and axial gradients on the DOC and that a strong cross influence exists between the different deactivating parameters. Such poison distribution can be replicated at lab scale by exposing an unused DOC to increasing amounts of P precursor by spraying, while impregnation leads to a homogenous and unrealistic poison distribution on the catalyst. The activity tests under simulated diesel exhaust evidenced that poisoning by spraying was more detrimental and caused a more severe decrease in NO oxidation performance, which is in agreement with the behaviour of the truck aged DOC. Sequential treatments comprising exposure to P, thermal treatment and exposure to S were also performed to better understand the catalyst deactivation mechanism.

The results can be used to draw recommendations for DOC formulations with enhanced poison resistance and build the basis for the prediction of catalyst durability.

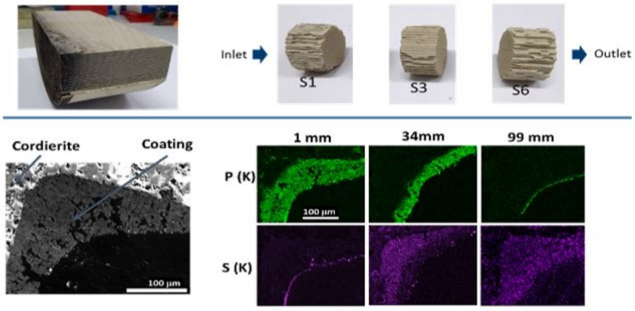

Figure 1. *Truck aged DOC with 288,000 km and the different segments extracted for analysis (top). SEM-EDX microscopy results of the segments showing the inhomogeneous P and S distributions in the coated catalyst layer (bottom).*

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Ga^0-Cu ratio as the main descriptor of the catalytic activity of Ga promoted Cu nanoparticle based catalysts for CO_2 hydrogenation to Methanol.

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The hydrogenation of CO_2 to methanol has gathered substantial interest as a potential key reaction in a renewable fuel cycle of the future[1]. Catalysts investigated for this reaction are usually based on supported Cu nanoparticles along with promoter(s). Recent reports show that Cu nanoparticles, supported on Ga single site decorated silica, which were synthesized via surface organometallic chemistry (SOMC), exhibit excellent activity and selectivity for this reaction. In this system, denoted Cu-Ga@SiO_2, Ga is partially reduced to Ga^0 during pre-treatment in hydrogen (precatalyst state) and forms an alloy with Cu[2]. Under reaction conditions however, Ga is reoxidized to Ga^{III}. However, when a catalyst with identical Cu and Ga weight loadings is prepared by introducing Ga_2O_3 via incipient wetness impregnation, followed by introduction of Cu via SOMC, the resulting catalyst, denoted Cu-Ga_2O_3/SiO_2, is inactive despite comparable particle sizes.

Here we show that the activity of Ga promoted Cu catalysts for CO_2 hydrogenation is directly determined by the Ga^0-Cu ratio in the precatalyst. X-Ray absorption near edge structure (XANES) and Multivariate curve resolution (MCR) analysis of the Cu-Ga_2O_3/SiO_2 and Cu-Ga@SiO_2 precatalysts reveals that they mainly differ in fraction of the Ga^0 component. Supported Ga_2O_3 is shown to be more reducible than the Ga single sites, resulting in a higher Ga^0/Cu ratio in the precatalyst. To further interrogate this, we developed a cografting approach to directly synthesize supported, alloyed $Cu_{1-x}Ga_x$ nanoparticles prepared by grafting Ga_2OtBu_6 on SiO_2 and subsequently Cu_4OtBu_4 and containing only Ga^0 in the precatalyst state. Using these materials, we showed that the strong promotional effect of Ga on the CO_2 hydrogenation is observed up to x=0.1 ($Cu_{0.9}Ga_{0.1}$); at x>0.1 the catalysts get poisoned; and at x=0.2 they become fully inactive.

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Electrochemical Reduction of CO_2 on Au Electrocatalysts Under Commercially Relevant Condition

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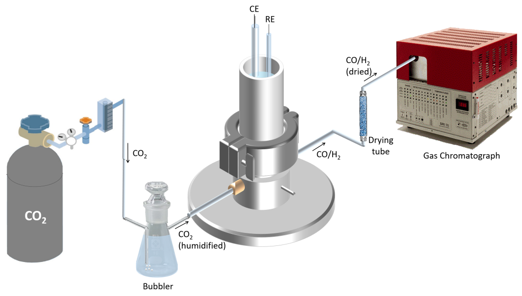
Much effort has been devoted for development of effective catalysts for the electrochemical reduction of CO_2 (ECO_2RR). For ECO_2RR, performing H-cell experiments is the most common catalyst screening method where the reactant CO_2 gas is usually dissolved in an aqueous bicarbonate-based electrolyte[1]. However, the low solubility of CO_2 in aqueous solutions (~35 mM at 298 K and 1 atm pressure) causes mass transport limitations when using dissolved CO_2 as the reactant. Recently introduced screening methods for ECO_2RR based on gas diffusion electrode (GDE) setups can be categorized primarily from a microfluidic design with a flowing catholyte to polymer electrolyte membrane (PEM) electrolyzers, which a gas diffusion layer, catalyst and polymer exchange membrane are combined as one unit without presence of a flowing electrolyte between the catalyst layer and polymer exchange membrane[2]. Therefore, PEM electrolyzers are also known as catholyte-free or gas-phase electrolysis. The advantage of PEM electrolyzers over the microfluidic designs, is that it is relatively easy to pressurize the reactant and product flows. In addition, the similarity of these devices to PEM water electrolyzers, makes it easier to scale up to the commercial scale and construct the large sized stacks[3]. However, due to the lack of a solid-supported electrolyte between the catalyst layer and polymer exchange membrane in PEM electrolyzers, they suffer from CO_2 reduction selectivity[2]. Here we performed same experiments in GDE setup and H-cell configuration by holding all parameters constant. Observations confirmed that not only H-cell configuration suffers from mass transport limitation of the reactant gas but also it cannot differentiate between different ionomer content in the catalyst layer. However, GDE setup could successfully show these differences. Furthermore, we showed that the presence of Nafion ionomer improves the selectivity of the gold (Au) electrocatalyst towards CO formation.



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The structural and kinetic signatures of the copper sites in mordenite for methane oxidation to methanol

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The interest in one-step methane valorization processes is continuously growing, and the direct methane oxidation to methanol over copper-exchanged zeolites is one of the major research directions in this field [1]. Significant progress has been achieved in the design of the novel copper-containing materials for direct methane oxidation [2,3], however, the exact structures and especially the spectroscopic and kinetic characteristics of the active sites remain debated [4]. We showed that copper mono-μ-oxo dimers and $CuOH^+$ monomers are the active sites in copper-exchanged mordenite, while Cu^{2+} ions are inactive in methane oxidation.

As a first step, we studied the reaction of methane with copper-exchanged mordenite by means of *operando* time-resolved UV-vis spectroscopy and simultaneously measured the absolute methane consumption. Prior to the reaction, UV-vis spectra contain a band at 26100 cm^{-1} due to copper mono-μ-oxo dimers. The intensity of this band decreases in the course of reaction with methane, and the decay can be fitted within a single first-order reaction model. However, the reaction of copper mono-μ-oxo dimers cannot completely describe overall methane consumption kinetics. Instead, an additional parallel first-order process was detected, apparently due to another type of the active species contributing to methane consumption. Notably, the second process is slower compared to the copper dimers conversion indicating lower reactivity towards methane of the corresponding active sites. To establish the nature of these active sites, we employed *in situ* EPR spectroscopy and found signals from two different copper monomeric species. The first one is characterized by $g_{||}$=2.33 and $A_{||}$=480 MHz and corresponds to Cu^{2+} ions located in the 6MR of mordenite, with charge compensation by two aluminium atoms. The second signal has $g_{||}$=2.27 and $A_{||}$=550 MHz and is due to $CuOH^+$ species having one aluminium atom from the zeolite framework compensating of the positive charge. Importantly, the reaction of activated copper-exchanged mordenite with methane leads to a decrease of intensity of the signals due to the $CuOH^+$ species, while the signal corresponding to Cu^{2+} ions persists. Based on this, we concluded that $CuOH^+$ species are prone to oxidize methane, while Cu^{2+} ions are inactive in such a reaction. The kinetic analysis of the overall methane consumption also reveals activation energies of 60 and 33 $kJ\cdot mol^{-1}$ for methane reaction with mono-μ-oxo dimers and $CuOH^+$ monomers, respectively.

To summarize, the combination of kinetic measurements and *in situ* spectroscopic methods enabled identifying copper species in copper-exchanged mordenite and determining their spectroscopic signatures and intrinsic activity towards methane oxidation. This is an important step in understanding the reaction mechanism of methane activation over copper-exchanged zeolites aiding the design of novel materials for this process.

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Ultrahigh permeance metal coated porous graphene membranes with tunable gas selectivities

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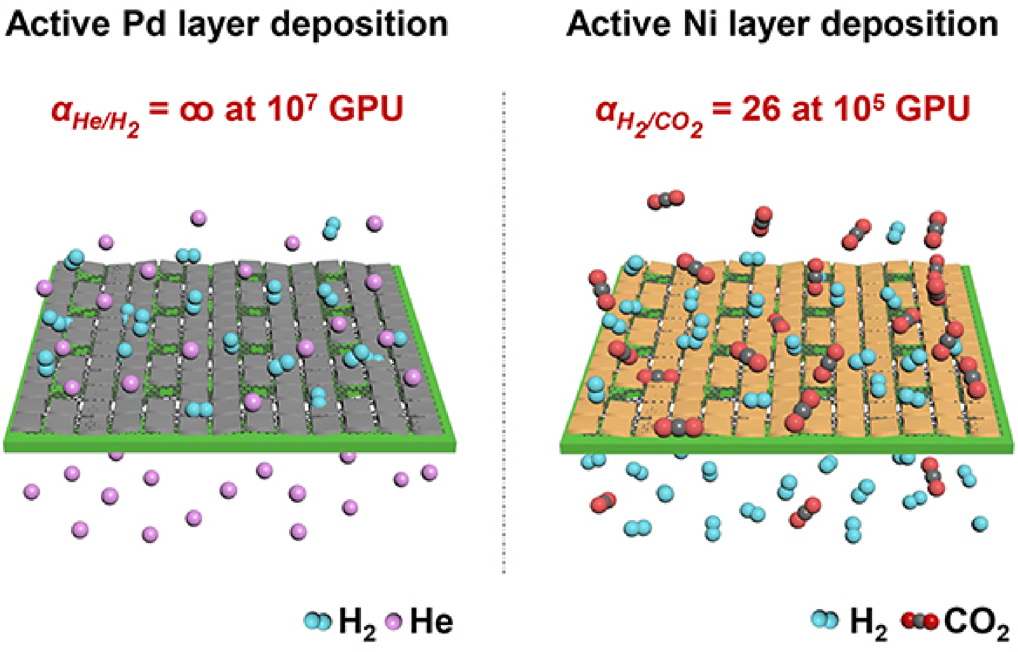
Membranes are important in gas separation applications due to their high energy efficiency, low operational costs, and durability. They are, however, subject to a permeability-selectivity trade-off i.e., membranes with high permeability (fast flow rate) have low selectivity (low separation capability) and vise-versa. In order to simultaneously achieve high selectivity and permeance, membranes that do not obey a simple trade-off rule would be required. In this direction, the concept of adsorptive separation can enhance membrane selectivity by individually targeting a single gas in a mixture while retaining high permeance. In this study we demonstrated highly efficient adsorptive separation of He/H_2 and steady-state separation of H_2/CO_2 with the highest H_2/CO_2 separation factor of 26 within the ultrahigh permeance range by depositing microislands of Pd and Ni to target H_2 and CO_2, respectively, thus offering promising alternatives for energy-efficient, cost-effective gas separation.
Tuning the transport properties of an individual gas in a binary gas mixture
Highly efficient steady-state H_2/CO_2 and adsorptive separation of He/H_2 gas mixtures using metal-coated graphene-based membranes
Broad applicability for the separation of various gas mixtures using a suitable metal layer
The highest steady-state H_2/CO_2 separation factor of 26 in the 10^5 GPU permeance range.

We demonstrate the template-assisted, uniform deposition of microislands of Pd and Ni onto the porous double-layer graphene in order to selectively target H_2 in He/H_2 and CO_2 in a CO_2/H_2 gas mixtures. These membranes enabled highly selective gas separation in the ultrahigh permeance range, thus offering promising alternatives for membrane gas separation applications.



Correlating Lewis Acid Activity to Extra-Framework Aluminum in Zeolite Y Introduced by Ion-Exchange

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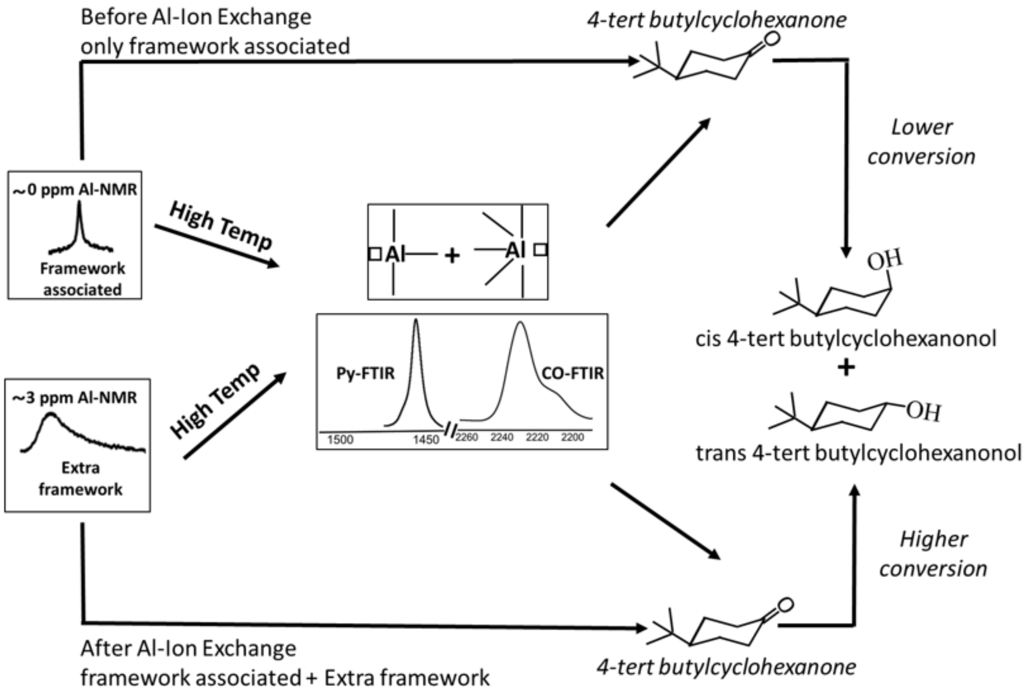
Lewis acidity was introduced in zeolite Y (Si/Al=30) in a controlled manner by ion-exchange of aluminum cations. X-ray diffraction and nitrogen physisorption suggest the retention of the zeolitic framework after successful incorporation of ions at extraframework positions. With an increase in total extraframework aluminum content of the modified zeolites, a pronounced increase in the amount of Lewis acidity was illustrated by FTIR spectroscopy of adsorbed pyridine and carbon monoxide whereas no significant change in amount of Brønsted acidity was observed. Likewise, the catalytic activity i.e. conversion and rate of reaction of zeolite catalysts for the Meerwien-Ponndorf Verley reduction of 4-tert butylcyclohexanone using isopropanol was highly improved after ion-exchange. ^{27}Al-MAS-NMR spectra show a broad asymmetric resonance at ~3 ppm after ion-exchange that suggest the presence of extraframework aluminum in octahedral coordination, present in small clusters. A quantitative agreement between the concentration of these aluminum species with the total Lewis acid content from pyridine-FTIR and with the initial catalytic rates illustrates that the newly introduced aluminum species adopt an octahedral coordination under the conditions of NMR measurement and are responsible for the Lewis acid activity.



Activity and initiation of silica-supported Mo olefin metathesis catalysts in the liquid phase

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[1]Department of Chemistry and Applied Biosciences, ETH Zürich, [2]Applied Sciences, bp Innovation & Engineering, BP plc

Olefin metathesis is a key technology for the formation of C-C bonds by rearrangement of alkylidene fragments among olefins, with applications ranging from petrochemicals to pharmaceuticals. Extensive development of transition-metal-based molecular systems has led to homogeneous catalysts with exceptional room temperature activity and selectivity that are widely used in organic and polymer syntheses. Though likely operating via analogous mechanisms, heterogeneous catalysts based on supported Mo or W oxides, used industrially for light olefin conversion, require high temperature activation and/or reaction conditions, and typically exhibit ill-defined surface structures with low (<5%) quantities of active sites.[1] The initiation routes of metal oxo sites remain largely unknown, in part because the complex distributions and low quantities of active sites complicate analysis of reaction properties and spectroscopic features. Correspondingly, understanding the structure and improving the catalytic performance of supported metathesis catalyst is still an on-going and highly active research area, with the goal to develop detailed structure-activity relationships towards rational design of new, improved catalysts.

Here, we compare metathesis activity for a series of well-defined molecular and supported Mo-based catalysts, establishing the influences of olefin-surface interactions on reactivity. Tailored metal-organic molecular oxo precursors are grafted onto partially dehydroxylated silica followed by thermal treatment to remove organic ligands,[2] yielding isolated surface metal oxo species identified by X-ray absorption and solid-state NMR spectroscopies. These exhibit low-temperature (less than 100 °C) metathesis activity for metathesis of linear alpha olefins after activation under reducing conditions, with catalytic properties that depend on synthetic route and corresponding local structures of the precatalytic species as well as chain length of the linear olefin substrate.

The supported Mo oxo metathesis catalysts are systematically compared to molecular and supported organometallic catalysts comprised of highly active Mo alkylidenes, which require no pre-activation,[3] as well as catalysts prepared via conventional impregnation approaches. Despite different intrinsic reactivities, the supported catalysts all show reaction rates that depend on linear alpha olefin substrate chain length due to adsorption of reaction products at surface -OH sites, as established by solid-state NMR analyses of post-reaction catalysts supported by molecular dynamics simulations. This is in contrast to the homogeneous catalysts, which show little dependence of metathesis activity on substrate chain length. The analyses provide guideline principles to design and improve heterogeneous metathesis catalysts.

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Solid catalysts aerobically catalyze the conversion of methane to methyl derivatives in high yields under improved conditions

A. N. Blankenship[1], M. Ravi[1], J. A. van Bokhoven[2,1]*

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A direct methane valorization process that achieves high product yields in a scale-flexible manner would provide numerous opportunities in the sustainable production of fuels and high-value chemicals; however, a commercial process has yet to emerge due to numerous challenges. Studies on the heterogeneously catalyzed partial oxidation of methane to methanol have revealed a selectivity-conversion paradigm, independent of the catalyst, which arises from the facile over-oxidation of methanol that restricts achievable yields to impractical levels [1-3]. In order to break out of this limit, a product protection strategy that prevents the over-oxidation of the primary oxygenates is essential. A successfully demonstrated example of product protection involves the derivatization of produced methanol to an oxidation-resistant methyl ester in concentrated acid solvents [4, 5]. Despite unprecedented yields, these approaches typically rely on extremely aggressive conditions, economically impractical oxidants, and homogeneous catalysts, all of which pose issues for catalyst/product recovery and basic process economics [6].

Through targeting conventional shortcomings of methane-to-methyl-ester chemistry, we demonstrate an approach that uses a solid catalyst, air as an oxidant source, and a diluted acid solvent (< 25 wt%). The methyl ester is subsequently recovered from the reaction medium through a liquid-liquid extraction with a polar solvent at ambient conditions. In this work, we summarize the methane conversion activity of transition metals (Mn, Co, Cu) deposited onto silica and alumina supports in this system. We find that the performance of these catalysts on the basis of turnovers and average production rates is competitive even to previously-reported homogeneously-catalyzed methane-to-methyl-ester systems that employ stronger oxidants and higher methane partial pressures. The improved performance of the supported transition metal catalysts combined with the advantages in catalyst/product recovery signify a promising advancement in direct methane partial oxidation technologies.

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Testing supported IrO_x and $IrRuO_x$ nanocatalysts for the acidic oxygen evolution reaction in a novel gas diffusion electrode setup

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Hydrogen production *via* acidic electrochemical water splitting is a valuable and sustainable alternative to fossil fuels. While the catalyst for the cathodic reaction is already well established, the materials for the anode reaction still need to be optimized to overcome the sluggish kinetics of the oxygen evolution reaction (OER). Hereby, we present two highly active OER catalysts, IrO_x and $Ir_{0.4}Ru_{0.6}O_x$ nanoparticles (NPs), prepared by a straightforward colloidal synthetic route.[1] The metallic NPs are ~ 2 nm in diameter and were deposited on carbon Ketjen Black (C_{KB}) as well as on commercial antimony doped tin oxide (ATO) to investigate the active phase as well as potential influences of the support material. After the colloidal synthesis and supporting, the catalysts were activated, and their performance benchmarked in terms of activity and stability using our recently developed gas diffusion electrode (GDE) setup.[2] This novel approach allows closing the experimental gap between the two most common methods, namely rotating disk electrode (RDE) and membrane electrode assembly (MEA). Independently from the support, $Ir_{0.4}Ru_{0.6}O_x$ shows a higher activity towards OER than IrO_x at three tested temperatures, *i.e.* 30, 40, 60 °C. The performance of IrO_x catalyst was also used to compare the two different support materials. NPs deposited on C_{KB} showed slightly higher activity at low current densities (< 40 mA mg_{Ir}^{-1}) than those deposited on ATO. At mild current densities (40 to 100 mA mg_{Ir}^{-1}), the activities of IrO_x NPs on the two different supports converged. We hypothesize that this phenomenon is due to an improved ATO conductivity at higher current densities. Accelerated potentiostatic stability test reveals a rapid degradation of the IrO_x/C_{KB} (within the first minutes of the test), while IrO_x/ATO exhibits improved stability.

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Highly Selective Pd-P-MOF-catalyzed mild Suzuki Reactions

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Cross-coupling reactions are important tools in the synthesis of complex organic molecules. Homogeneous palladium complexes are predominantly used in large-scale production of fine chemicals as well as in pharmaceuticals and agrochemicals[1]. The development of robust and versatile heterogeneous catalysts offers the potential to recycle the catalyst as well as to simplify the purification of the final product from metal residue contaminations[2]. Heterogeneous palladium catalysts based on metal nanoparticles are often applied under conditions that promote a high mobility of the metal species[3]. The use of heterogeneous catalysts may also promote the hydrodehalogenation of the starting material[4]. In this contribution, we present a molecularly defined heterogeneous palladium catalyst based on the phosphine-functionalized metal-organic framework (P-MOF) LSK-15[5].

We studied the catalytic performance of various palladium catalysts in Suzuki cross coupling reactions of 3-bromoanisole with phenylboronic acid under mild conditions. Thereby, we have demonstrated that the presence of a phosphine ligand and the stoichiometry between metal and ligand play a critical role for the product selectivity and the activity of the catalyst. Catalysts based on LSK-15 gave the highest selectivity among all the homogeneous and heterogeneous systems studied when the ratio between palladium and phosphine species was 1:2. XAFS (X-ray Absorption Fine Structure) characterization at the P and Pd K-edges shows a correlation between the nature of the active site and the selectivity of the system. Our experiments suggest that palladium–phosphine sites promote cross coupling, whereas metal particles are negatively affecting the selectivity via hydrodehalogenation side reaction.

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Mapping the hydrocarbon pool formation and coke generation in C_1 coupling over zeolite catalysts

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C_1 reagents like methanol or methyl halides are strategic building blocks for the sustainable production of chemicals and fuels. They are readily transformed into longer-chain hydrocarbon products over zeolite catalysts, but controlling the selectivity and stability remains challenging. In the methanol-to-hydrocarbons reaction, where several commercial processes exist, the formation and degradation of active species have been the subject of intensive investigation.[1]Methyl halide coupling, in particular methyl chloride (MCTH) due to its low toxicity and easier handling compared to the other halides, is gaining relevance for natural gas upgrading *via* halogen-mediated route but has so far received much less attention. To improve understanding of the complex reaction networks, here we combine kinetic studies with *operando* photoion photoelectron coincidence (PEPICO),[2] and *ex-situ* electron paramagnetic resonance (EPR)[3] spectroscopies (**Fig. 1**) comparing MTH and MCTH under equivalent conditions. This approach provides new insights into the distinct mechanisms of chain propagation from the first C-C bond formation to the generation of coke species deposited in the zeolite pores.

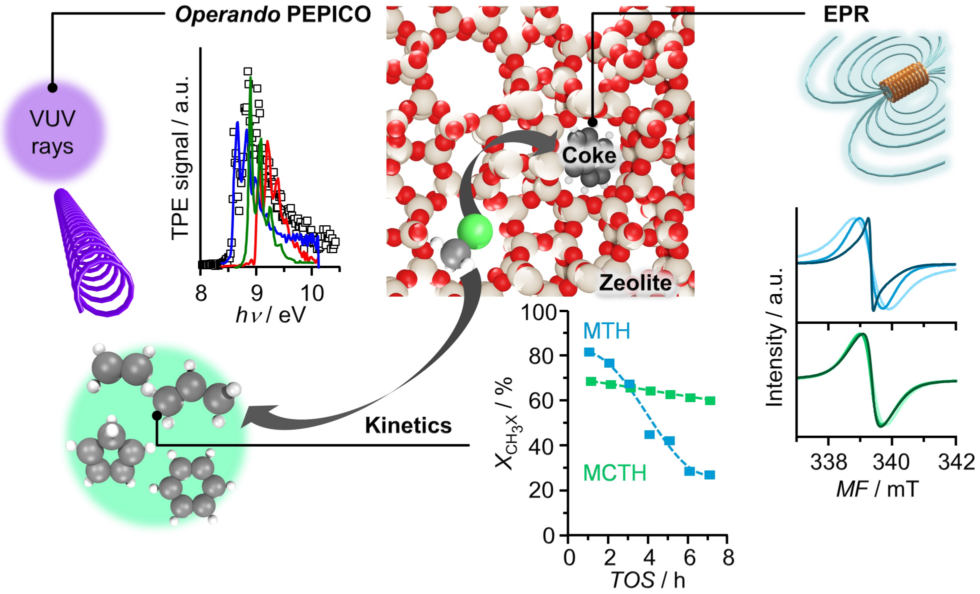

Fig. 1. Approach to map the hydrocarbon pool formation and evolution in MTH and MCTH, combining kinetic analysis with advanced techniques including *operando* PEPICO and *ex-situ* EPR spectroscopies.

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Understanding and fine-tuning of lignin fast pyrolysis towards phenolics and aromatics

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style="text-align: justify;">Lignin is one of the main components of lignocellulosic biomasses and the most abundant natural source of aromatics. It can be depolymerized into fine chemicals and fuels. Recent advances in lignin extraction methods provide lignins with a preserved native structure.[1] This allows the conservation of important functional groups present in natural lignin, which can be retained in the depolymerization products. However, a control of undesired side reactions is crucial to improve depolymerization with enhanced selectivity. For this, an effective strategy is the protection of reactive groups such as the alpha, gamma-diol group in the aliphatic chains of lignin.

For fast pyrolysis, selective acetylation of lignin in its aliphatic hydroxyl groups shows an improved performance in which an important increase in selectivity towards phenolics is obtained.[2] Furthermore, zeolites such as H-USY and H-ZSM-5 are suitable and well-known catalysts to fine-tune the product distribution of this type of thermochemical processing.[3,4]

Herein, lignin model compounds having the most abundant type of linkages present in native lignin (beta-O-4 substructures) and aliphatic protections are investigated. Fast pyrolysis in a batch-type reactor coupled with GC/MS detection (py-GC/MS) is carried out to analyze product distribution under process-like conditions. Results of non-catalytic and catalytic fast pyrolysis are compared to provide insights in the process, allowing the understanding of fine-tuning the selectivity towards phenolics and aromatics. Further mechanistic insights are obtained from experiments performed under collision-reduced environment with analysis of pyrolysis products using vacuum ultraviolet synchrotron photoelectron photoion coincidence tools available in the VUV beamline of the Swiss Light Source (Paul Scherrer Institute).

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In-situ SEM investigation on the active state of nickel catalyst in dry reforming of methane

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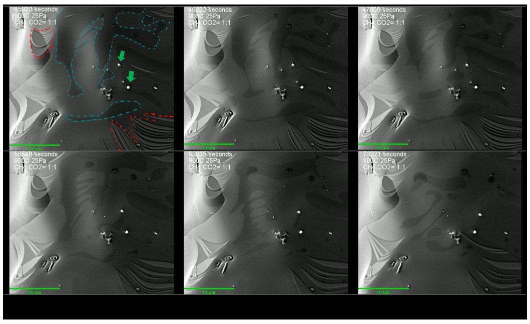
Our generation is already facing the drastic consequences of climate change. As scientists, we have the responsibility to pave the way towards developing a sustainable economy that is based on renewable natural resources and to mitigate the emission of greenhouse gases. Concerning the second point, dry reforming of methane (DRM) has recently gained much attention.
The advantage of converting methane from natural gas to valuable products is twofold: first, it prevents carbon dioxide emissions from methane flaring, and second, it produces highly exploitable syngas mixtures. Amongst the most studied technologies for converting methane to syngas are the reforming techniques (steam, dry and autothermal) which differ in the oxidant used, final hydrogen to carbon monoxide ratio, and the kinetics and energetics of the reaction. In the case of dry reforming of methane (DRM), carbon dioxide is used as oxidant [1]. Although DRM is a highly endothermic reaction, it is attractive because of the high selectivity that can be achieved when operating at low pressure and high temperature. The main barrier that still prevents its industrial implementation is related to a fast deactivation of the catalyst through sintering and carbon coking [2].

The objective is to obtain insights on gas-phase and temperature-induced processes that are related to the emergence of catalytic activity in dry reforming of methane, and to reveal mechanisms that lead to catalyst deactivation.

In order to achieve the ambitious goal, suitable model systems are essential for providing a fundamental understanding of the complex mechanisms of a working catalyst under relevant conditions. Therefore, poly-crystalline foils and nickel foams are employed for the detection and investigation of reaction-induced processes. While high-surface-area nickel foams are most suitable for the detection of catalytic conversion inside the SEM chamber, polycrystalline foils will provide insights into the relationship between surface structure and dynamics, which can then finally be studied in more detail on selected single crystal surfaces. A suitable platform for *in-situ* observation of active catalysts resides at the core of this study. A commercially available Thermo Fisher Scientific Quattro S SEM was modified to meet the prohibitive requirements for assessing the mechanisms of catalytic act. The specialty of this dedicated setup resides in the high precision and exceptional stability of the experimental parameters.

We have discerned the active species of a Ni catalyst that are implied in the dry reforming of methane, as well as the spectator structures that exist alongside carbon forming species. We have studied the surface morphology as a function of operation parameters and encountered a stable active regime in non-stoichiometric environments.



Our unique in-situ SEM set-up allows us to visually observe the state of the active catalyst under reaction conditions in real-time, at high spatial resolution using a combination of dedicated secondary electron, high-temperature 3D backscatter- and an electron-beam absorbed current detectors. Direct observation combined with on-line mass-spectroscopic analysis of the gas-phase

Pt-based Nanocomposite Catalysts for the Oxygen Reduction Reaction in Rotating Disk Electrode and Gas Diffusion Electrode measurements

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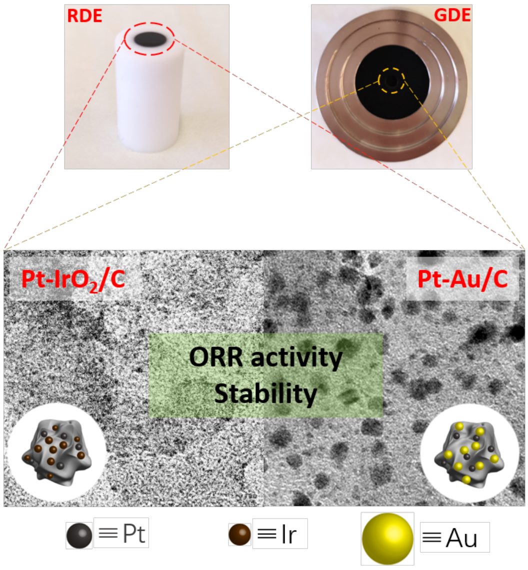
Conventional optimization of PEMFC cathode catalysts is achieved by alloying of Pt with one or more components such as Co, Ni, Au, etc,[1,2] which leads to the development of several different types of highly active catalysts. More recently, catalyst stability and performance under high mass transport conditions have gained increasing attention.[3] In the present study, we develop the concept of nanocomposites consisting of supported Pt and activated Ir NPs (Pt-IrO_2/C) and supported Pt and Au NPs (Pt-Au/C) for potential ORR electrocatalyst application (Graphics 1). The performance is investigated in conventional rotating disk electrode (RDE) measurements as well as in gas diffusion electrode (GDE) measurements which provide realistic catalyst loadings and mass transport conditions. The measurement results indicate that both the introduction of IrO_2 and Au NPs alleviate the degradation of the Pt NPs in RDE condition. In case of IrO_2, the improvement in stability is at the expense of a decrease in ORR activity. By comparison, Au NPs seem to boost stability and ORR activity of the Pt NPs likewise. At more realistic condition, i.e., in a GDE setup, the performance improvement of the Pt-Au/C nanocomposite is limited to very low current densities and cannot be sustained at high current density. However, the boosted stability of Pt-Au/C leads to improved ORR performance after degradation test, which can be assigned to a reduced Pt particle growth due to the adjacent Au NPs. The GDE measurements indicate that the improved stability might lead to an improved ORR performance over the lifetime of the fuel cell, by comparison, the stabilization of fuel cell catalysts by IrO_2 might not be a promising approach as the stability improvement is at the expense of Ir dissolution, and therefore more likely a short-term effect.



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SynFuel: Development of a new synthetic pathway for the production of renewable jet-fuels from methanol

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Despite the context of energy transition currently operated in order to reduce the society environmental impact, the global demand for carbon-based transportation fuels is still increasing from year to year. Aviation fuel (jet-fuel) demand follows this trend. Jet-fuel consists in kerosene petroleum fraction composed of branched alkanes mostly in the C_{10} to C_{18} range. Their production is however still entirely dependent on petroleum distillation, the corresponding kerosene distillation fraction being almost ready-to-be-used as it is. Following the most recent interests, we propose a new synthetic route towards the production of “green/renewable kerosene” obtained from methanol. Methanol is an important chemical intermediate acting as a renewable carbon source; it can be synthesized from CO_2, biomass, synthetic gas, or natural gas. Consequently, the main idea of this work is to combine two industrially relevant processes and ultimately integrate into one: (i) methanol to olefin and (ii) oligomerization processes, in order to develop a “green kerosene” production unit. First, C_2 to C_8 light olefins are formed in the methanol to olefin (MTO) process. After removal of water and unreacted alcohols (if needed), the as obtained light olefin mixture is then used as a feed for a subsequent oligomerization step where the goal consists in adjusting the selectivity towards C_{10} to C_{18} alkenes (jet-fuel range products). A simple hydrogenation step will then be sufficient to convert the products into ready-to-use jet-fuel. In this approach, the oligomerization step is the most challenging: it needs to be finely tuned and its selectivity adjusted so as to yield mostly jet-fuel range products. However, the oligomerization reaction is known as being difficult to control due to the occurrence of a Shultz-Flory type product distribution, favoring the formation of either only lighter products with correct selectivity, or heavier products with very poor selectivity. Our approach for improving the C_{10} to C_{18} yield is to tune the oligomerization unit feedstock using the methanol to olefin process, and to work under relatively high pressure and low temperature. The properties of the catalysts are also going to be tuned (density and strength of acid sites, presence or not of Ni, catalyst pre-treatments, etc.), so that the selectivity towards jet-fuel range product can be maximized.

Scalable two-step annealing method for preparing ultra-high-density single-atom catalyst libraries

D. Faust Akl[1], S. Mitchell[1], X. Hai[2], J. Pérez-Ramírez[1]*, J. Lu[2]*

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The stabilization of transition metals as isolated centers on suitably tailored carriers with high density is crucial to exploit the technical potential of single-atom heterogeneous catalysts (SACs), enabling their maximized productivity in industrial reactors.[1] Wet-chemical methods are best suited for practical applications due to their high amenability to scale up. However, achieving single-atom dispersions at high metal contents (>2 wt.%) remains challenging. We introduce a versatile approach combining impregnation and two-step annealing to synthesize ultra-high-density (UHD-)SACs with metal contents up to 23 wt.% for 15 metals and combinations thereof, on chemically-distinct carriers (**Fig. 1**). Translation to an automated protocol demonstrates its robustness and provides a path to explore accessible catalyst libraries. At the molecular level, experiments and simulations to understand the synthesis mechanism show that controlling the bonding of metal precursors with coordination sites in the carrier *via* stepwise ligand removal prevents their thermally-induced aggregation into nanoparticles, ensuring monodispersity in the resulting UHD-SACs.

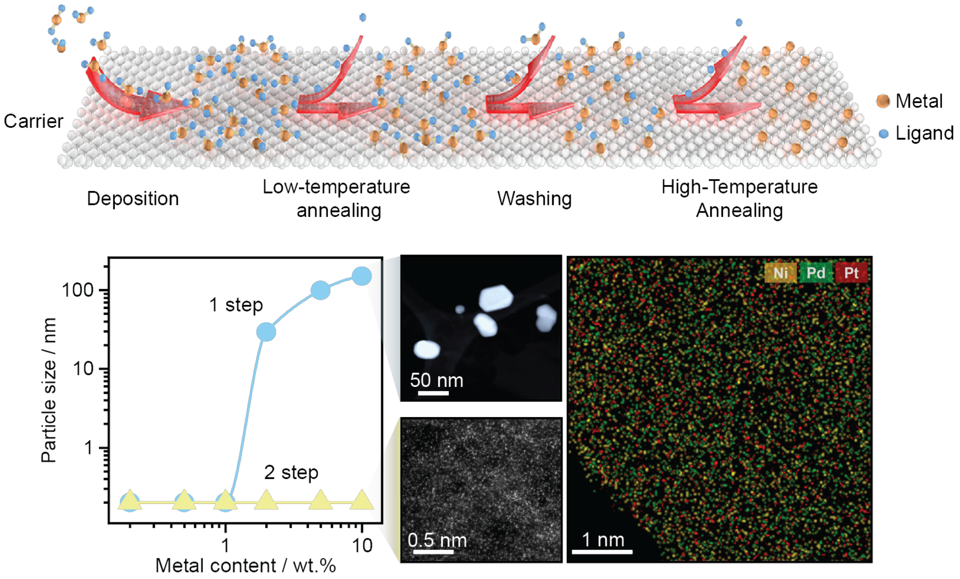

Fig. 1. Two-step annealing approach introduced for the synthesis of mono or multimetallic UHD-SACs (top). Compared to the conventional one-step approach, single-atom dispersions can be obtained up to much higher metal contents. EDX mapping confirms the homogeneous distribution of simultaneously supported Ni, Pd and Pt.

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SynFuels - an ETH initiative for the production of synthetic jet fuels - Thermochemical routes

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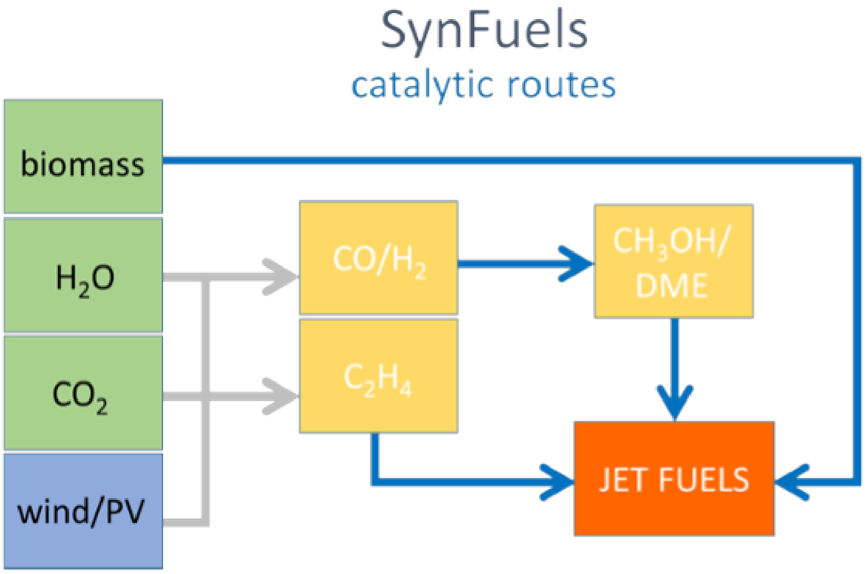
Air traffic grows continuously worldwide despite occasional declines such as during the current pandemic. The only viable option to significantly decrease the CO_2 emissions of aviation and thus impact on environment is the use of sustainably produced jet fuels that are compatible with current technology and fuel systems. Sustainable jet fuel production for example from CO_2 requires development of novel chemical processes and of heterogeneous catalysts to enable these. A research initiative between PSI and Empa funded by the ETH-Board tackles this challenging research. The production of carbon-neutral jet fuels was selected because it leads research already present at PSI and Empa beyond synthetic natural gas and H_2. An important section of the initiative deals with the thermochemical production of methanol and DME intermediates from CO_2 and CH_4 into jet fuels as well as with the direct hydrothermal liquefaction of biomass into long-chain hydrocarbons. An alternative route is proposed to start from ethylene intermediate of electrocatalytic processes.

CO_2 hydrogenation is the most investigated route for methanol synthesis but routes from CH_4 and H_2O_2 from renewable production of H_2 are also appealing. Discovery and continued development of process as well as of catalysts are needed.

Commercially available processes exist to convert methanol into olefins and hydrocarbons that can be upgraded to aviation fuel. However, methanol/DME can be used directly as well, but require further process optimization and catalyst development that are targeted in the initiative. Because of the advantages of DME over methanol for the production of olefins and hydrocarbons, direct conversion of CO_2 to DME will be also investigated.

Biomass liquefaction is technologically advanced and yields a broad range of hydrocarbons and oxygenates. Attempts will be made to steer selectivity towards hydrocarbons in the jet fuel range.

Existing technical solutions on the selective oligomerization of C_2H_4 to alkanes of defined chain length rely on technically pure reactants, which is not the case when using intermediates produced by electrochemical CO_2 reduction. Thus, new efficient processes and catalysts are needed enabling the selective oligomerization of C_2H_4 in the presence of CO and H_2.



Following the sintering behavior of Platinum by *in-Situ* STEM aided by artificial intelligence.

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The stability of noble metal particles exposed to harsh conditions is of paramount interest for catalysis as their size, form and number are crucial parameters that dictate catalyst performance. Particle sintering leads to loss of active surface area and hence activity, whereas particle dissipation into single atoms may lead to loss of total metal volume via leaching and/or change of catalyst selectivity. We apply *in-Situ* Scanning Transmission Microscopy (STEM) and a neural network-based particle recognition algorithm that enables tracking the faith of a statistical meaningful number of particles simultaneously and in real time. Electron beam dose during the experiment is hereby carefully managed by automizing the image acquisition featuring long beam blank periods between image acquisition and automized focus and drift control. Combining the unmatched spatial resolution of STEM with the prediction power of a convolutional neural network the evolution of particle size, shape, and position of thousands of particles can be tracked simultaneously. Here, we show results for platinum particles that where sputter deposited on either on a SiN_x membrane as a template for a non-interacting support and on a TiO_2 thin film, deposited by electron beam evaporation. Both samples were exposed for extended times (12 h) to oxidative environments at high temperatures (400 °C - 800 °C). In both cases, particle sintering via the Ostwald ripening route took place. The titania support effectively slowed down and limited the extent to which particle sintering progressed. The rate determining steps during sintering processes can thus be identified.

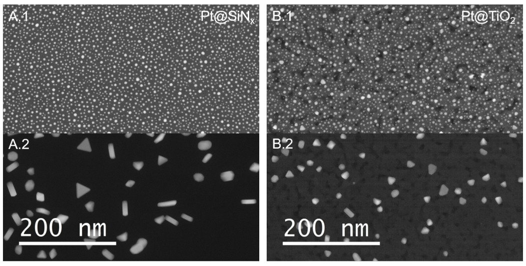

Figure 1. ADF-STEM micrographs of $Pt@SiN_x$ (A) and $Pt@TiO_2$ (B) before (.1) and after (.2) exposure to an oxidative atmosphere at 600 °C for 12 h.

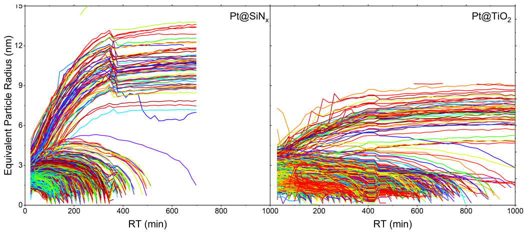

Figure 2. Particle radius of individually tracked particles of the course of the experiment for $Pt@SiN_x$ (l) and $Pt@TiO_2$ (r).

Adsorption Effects of Zn-MOF-74 in Cobalt-Catalyzed Hydroformylation

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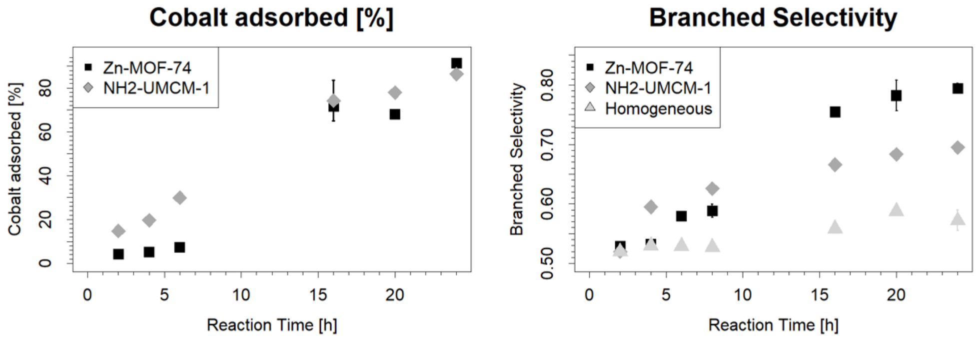
Hydroformylation is an industrially important, homogeneously catalyzed reaction. Olefins react with a 1:1 mixture of H_2 and CO, promoted by cobalt or rhodium catalysts, to form branched and linear aldehydes [1]. Our research showed that the addition of MOFs with certain properties enhances the branched selectivity by adsorption-driven kinetic modulation (AKM) [2]. To get a deeper insight into the mechanism, we analyzed the impact of the MOF on the product distribution through a conversion vs selectivity study. The branched selectivity increased at higher conversion of the olefin, contradicting the published rate laws [3]. The selectivity curve is rationalized by the slow adsorption of the cobalt catalyst within the MOFs (Figure 1). Based on that finding, we investigated several approaches to increase the adsorption kinetics to aiming to enhance the branched selectivity.



Additionally, Zn-MOF-74 plays an important role in promoting aldol condensation of the aldehyde products. Our data and simulation [2] suggest that the MOF increases the local concentration of the aldehyde and thus enhances the reaction rate. Zn-MOF-74 therefore promotes aldol condensation by AKM. The understanding of AKM will drive the development of even more selective MOF-promoted reactions.

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Controlled formation of dimers and spatially isolated atoms in Au-Ru single-atom catalysts *via* carbon-host functionalization

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

Modifying the electronic structure in single-atom catalysts (SACs) by adding a foreign metal to the active site coordination environment has recently emerged as a new research front in the field of catalysis, generating bimetallic SACs with unique electronic properties.[1] To date, the study of intermetallic coordination in bimetallic SACs has been thwarted by the lack of (*i*) synthetic techniques capable of controlling intermetallic bonds, and (*ii*) suitable characterization techniques, as they exclusively rely on X-ray absorption spectroscopy (XAS), requiring distinguishable scattering paths for the two metals to assess intermetallic coordination.[2] In this contribution, we present a novel synthetic strategy with control over intermetallic bonds in Au-Ru SACs on carbon supports *via* host functionalization, tailoring anchoring sites to deliver dimers (D) or spatially isolated atoms (**Fig. 1a**), as corroborated by XAS. Their distinct electronic features are unveiled *via* the electrocatalytic hydrogen evolution reaction, herein proposed as a proton-adsorption sensitive probing tool. Not only does Au exhibit a pronounced promotional effect on Ru in dimers, but also in spatially isolated atoms, increasing the H_2 evolution rate by 3.2- and 1.5-fold compared to Ru SACs, respectively (**Fig. 1b**). In both configurations, Au is speculated to bring the proton adsorption strength of Ru closer to neutrality, switching the rate determining step from proton adsorption to proton coupling (**Fig. 1c**). For the first time, different intermetallic coordination in bimetallic SACs is achieved and validated by XAS, altering the catalyst adsorption properties, and leading to distinct catalytic fingerprints. This exemplifies control over intermetallic coordination as a means to modulate electronic features in bimetallic SACs.

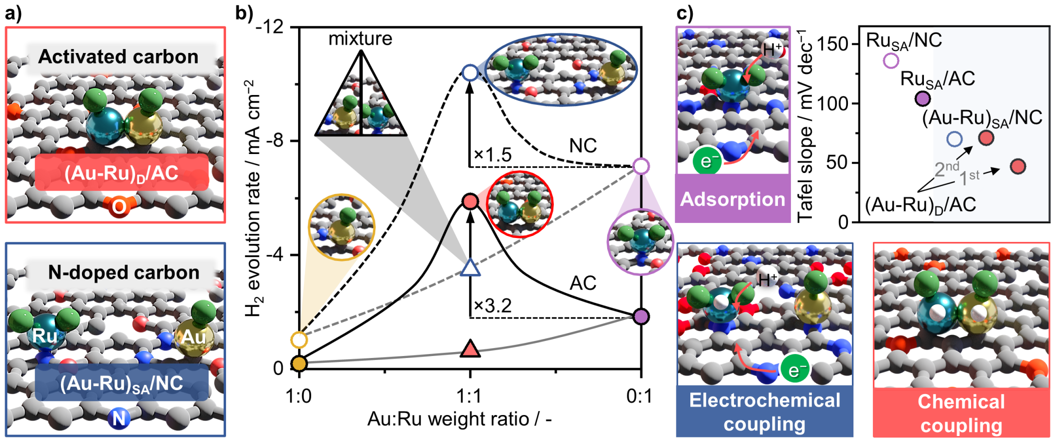

Fig. 1 a O-functionalities in AC deliver dimers, while N-functionalities in NC deliver spatially isolated atoms. **b** H_2 evolution rates at −0.27 V *vs* RHE in 0.5 M H_2SO_4 of SACs on NC (open symbols) and AC (solid symbols), with physical mixtures of Au and Ru SACs (triangles, no promotional effect). **c** Tafel slopes indicate SAC rate determining steps. The (Au-Ru)$_D$/AC slope shifts from low (L) to high (H) overpotentials.

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Selective conversion of polypropylene into motor oil on carbon-supported platinum catalysts

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Despite polypropylene (PP) constituting *ca.* 30% of plastic waste generation, its catalytic processing has received very modest attention in recent years, being typically linked to poorly controlled product distributions.[1] Here, we present carbon-supported platinum nanoparticles for its highly selective conversion (*ca.* 80%) into motor oil range (C_{21}–C_{45}) with stable selectivity for, at least, four consecutive runs (**Fig. 1a**). The metal and carrier phases are found to operate synergistically. The C–C bond cleavage activity increases as particle size reduces until *ca.* 2 nm, resulting in shorter chain products for the same reaction time (**Fig. 1b,c**). The carbon carrier enables selective product distribution by modulating the adsorption of hydrocarbons on its surface. The adsorption strength of the hydrocarbon chains, assessed using temperature programmed desorption of a surrogate hydrocarbon molecule (*n*-heptane), was found to have an inverse correlation with the concentration of oxygen groups on the carbon surface (**Fig. 1d**), corroborating observations developed for petrochemical processes.[2] As a result, varying the concentration of oxygen groups allows control over the selectivity. The use as carrier of the activated carbon with the largest oxygen content (AC1) maximized the production of motor oil range (**Fig. 1e**), as it disfavored the adsorption of shorter chain species. This is in agreement with the inactivity of catalysts comprising non-adsorbing carriers such as alumina or silica. Through investigation of nanostructuring and support effects, this works provides inceptive guidelines for catalyst design towards the conversion of polyolefins.

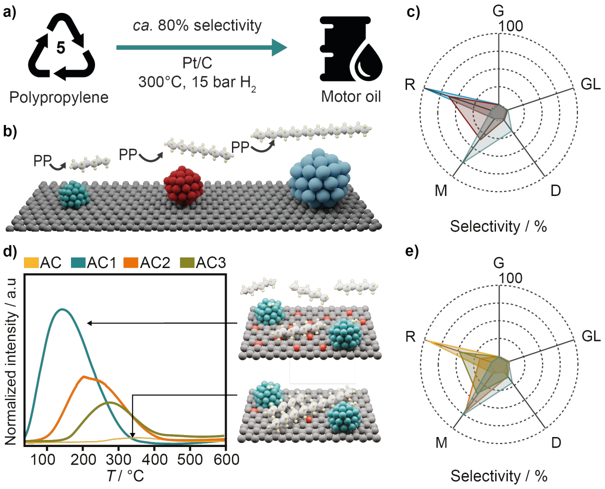

Fig. 1 a Selective conversion of PP into motor oil at 300°C and 15 bar hydrogen pressure over 24 h in the presence of 5 wt.% Pt/AC1. **b** Scheme showing the trend in product length with nanoparticle size and **c** selectivity towards various fraction with the different nanoparticle sizes. **d** Temperature-programmed desorption of *n*-heptane from various activated carbons with surface oxygen concentrations following the order AC<AC2<AC3<AC1. **e** Selectivity resulting from their use as carriers for platinum. Radar plot legends: G = gas (C_1-C_5), GL = gasoline (C_5-C_{12}), D = diesel (C_{12}-C_{21}), M = motor oil (C_{21}-C_{45}), R = residue (C_{45+}).

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^{15}N NMR Chemical Shift Tensor as Acidity Descriptor for Al-O(H)-Al sites in Molecular Aluminosilicate Models and Link to Reactivity

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Zeolites have attracted great interest in industry and academia as they are used to catalytically convert both petrochemical and biomass derived compounds. Their catalytic activity is commonly ascribed to Brønsted and/or Lewis acidic sites that originates from the presence of aluminium and silicon in the framework. Brønsted acidity arises from tetrahedrally coordinated aluminium with four –O–Si linkages, where the negative charge is balanced by a proton, leading to the formation of acidic hydroxyl moieties.[1] The formation of related Al_{IV}–(OH)–Al_{IV} motifs incorporated into the framework is prohibited in accordance with Löwenstein’s rule. Yet, such sites can be formed during dealumination processes. The catalytic relevance of such sites has been debated, in particular because their acidity is assumed to be low based on ionic bond strength considerations.

One tool to gain further insight on the fundamental reactivity of such species is the synthesis of suitable well-defined molecular model complexes. However, compounds featuring –Al–O(H)–Al– moieties embedded in siloxide ligand environments are scarce and their reactivity towards organic substrates has hardly been investigated. To overcome these limitations, a well-defined cluster, that contains that structural motif, was recently developed, $[Al_3(\mu_2\text{-OH})_3(THF)_3(PhSi(OSiPh_2O)_3)_2]$ (**1**).[2,3] In this work, we further explore the catalytic activity of **1** in alcohol dehydration reactions and determine the acidity of these OH groups. More specifically, we demonstrate that the Al_{IV}–(OH)–Al_{IV} unit of **1** reacts with a variety of different alcohols to form an Al–(OR)–Al species and secondly, that the formed alkoxy species undergoes dehydration at elevated temperatures to afford the corresponding olefin. To further probe the Brønsted acidity of **1**, we investigated the ^{15}N solid-state NMR signature of the corresponding pyridine adduct $[Al_3(\mu_2\text{-OH})_3(py)_3(PhSi(OSiPh_2O)_3)_2]$ (**2**), with the goal to extract the ^{15}N chemical shift tensor of the formed pyridine adducts and to obtain a semi-quantitative evaluation of acidity from the ^{15}N chemical shift. Overall, analysis of the ^{15}N chemical shift tensor shows that one of the bridging hydroxyl groups is characterized by a remarkable acidity, much higher than typically observed for pyridine adducts of hydroxyl groups in oxide materials such as alumina.[4] The chemical shift of this site can be explained through the interaction of the emerging N-H σ-bond with the π*-orbital of the pyridine ring, thus providing a direct link to acidity and the observed reactivity.

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Structure-activity evolution of platinum species supported on ceria exposed to different reaction environments

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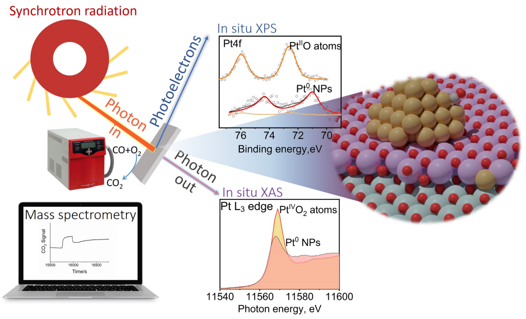
Catalytic systems based on supported noble metals are extensively studied because of their widespread application. Discussions remain about the nature of the active species, whether they are atomically dispersed or nanoparticles, and their reactivity. In this work, combining in situ/operando spectroscopies with theoretical modelling, we propose a phase diagram of atomically dispersed platinum on ceria, demonstrating that it reversibly changes from $Pt^{IV}O_2$ to $Pt^{II}O$ as a function of temperature and oxygen partial pressure. The phase diagram helps identifying the stability domain of each species, while spectroscopy provides a quantitative evaluation depending on the reaction conditions. Finally, our results show that a high-temperature activation in the presence of steam of supported atomically dispersed platinum enhances the activity toward low temperature carbon monoxide oxidation, because it promotes aggregation into nanoparticles. This work highlights the structure-activity relationship in supported metal catalysts, and proposes a suitable approach to determine the amount of each species before investigation of the reaction mechanism.



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Oxidative Dehydrogenation of Ethane with *in-situ* Oxygen Production *via* Chemical Looping with Oxygen Uncoupling

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Chemical looping for air separation (CLAS) represents an energy-efficient and cost-effective method for producing oxygen [1]. So far, CLAS has been mostly investigated as a standalone process or coupled with combustion processes for power generation.

Our work demonstrates that the chemical looping (CL) approach for producing gas-phase oxygen can be combined efficiently with catalytic oxidation processes. Consequently, the use of oxygen derived from a separate, costly and energy-intensive production process, e.g. cryogenic rectification, is avoided. Here a proof of concept has been carried out using the oxidative dehydrogenation (ODH) of ethane to ethylene as a sample reaction. Previously investigated CL-ODH processes use the lattice oxygen of an oxygen carrier (or redox catalyst) to selectively combust hydrogen produced from the dehydrogenation of ethane at temperatures of 700 – 850 °C [2]. Here, we utilise molecular oxygen released from an oxygen carrier to undertake the ODH reaction simultaneously in the presence of a dehydrogenation catalyst in the same reactor, at 500 °C. The lattice oxygen-depleted oxygen carrier is subsequently regenerated in air to complete the reaction cycle.

A highly selective dehydrogenation catalyst based on MoTeVNb mixed oxides is used together with a $NaNO_3$-doped $Sr_{0.8}Ca_{0.2}FeO_{3-\delta}$ perovskite as the oxygen carrier [3, 4, 5]. We show that the addition of the alkali metal dopant to the oxygen carrier is an effective strategy to avoid the deep oxidation of ethane to CO_2, that is typically observed in conventional ODH processes [6], hence enabling a high selectivity of the catalyst-oxygen carrier system towards the product ethylene.

The experiments are performed in a U-shaped quartz tube reactor in a layered bed configuration, at 500 °C and space time W/F_{ethane} (W is the mass of catalyst and F_{ethane} is the molar flow rate of ethane) of ~ 13 g_{cat} h $\mathrm{mol}_{\mathrm{ethane}}^{-1}$. Ethylene yields of ~ 25 % are obtained through this novel chemical looping configuration, compared to ~ 21 % in the conventional process without *in-situ* oxygen generation, i.e. by co-feeding oxygen. The cyclic performance stability is assessed over 30 consecutive cycles and shows no significant decay in activity. The oxygen carrier is thoroughly characterised by means of electron microscopy and X-ray techniques to elucidate the role of $NaNO_3$ on preventing the deep oxidation of ethane.

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Planetary footprints of low-carbon ammonia

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At present, the synthesis of ammonia through the Haber-Bosch (HB) process accounts for roughly one fourth of the global fossil consumption from the chemical industry, which creates a pressing need for alternative low-carbon synthesis routes. Analyzing nine indicators quantified following the planetary boundaries (PBs) methodology related to the safe operation of our planet,[1] we find that the standard HB process is unsustainable as it vastly transgresses the climate change PB. In order to identify more responsible strategies from this integrated perspective, we assess the absolute sustainability level of 34 alternative routes for low-carbon ammonia synthesis where hydrogen is supplied by methane steam reforming with carbon capture and storage, biomass gasification, or water electrolysis powered by various energy sources (**Fig. 1**). Some of these scenarios could substantially reduce the impact of fossil HB on climate change, yet they could critically exacerbate other Earth system impacts. Furthermore, we identify that reducing the cost of electrolytic H_2 is the main avenue towards the economic appeal of the most sustainable routes. Our work highlights the need to embrace global impacts beyond climate change in the assessment of decarbonization routes of fossil chemicals. This approach identified prominent challenges towards environmental and economically attractive ammonia synthesis.

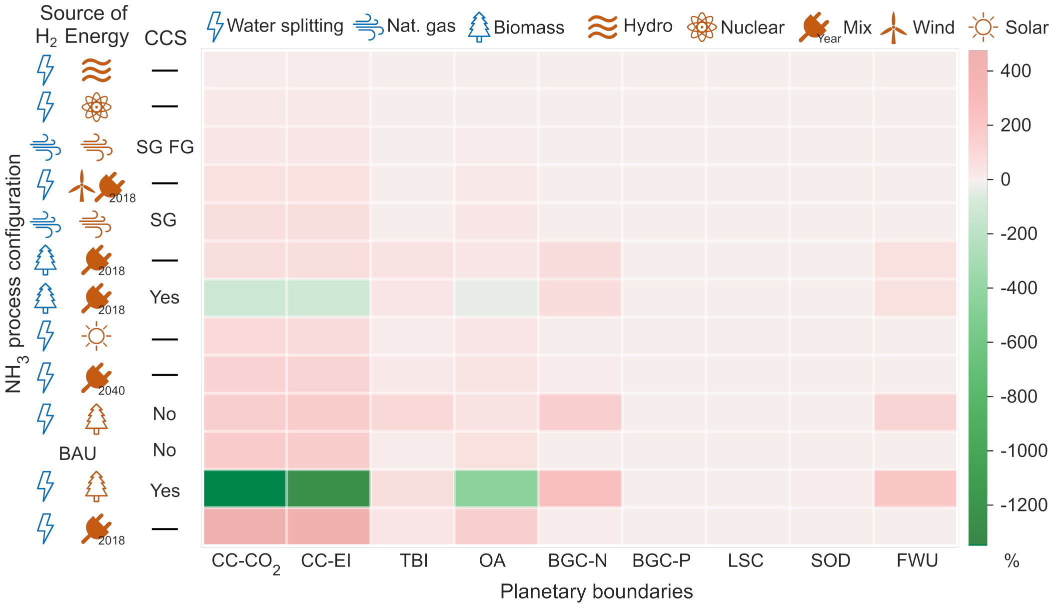

Fig. 1 Level of transgression as percentage of the safe operating space assigned to the chemical industry for representative scenarios for nine planetary boundaries. CC CO_2: climate change, CO_2 concentration; CC-EI: climate change, energy imbalance; TBI: terrestrial biosphere integrity; OA: ocean acidification; BGC-N: biogeochemical flows, nitrogen; BGC-P: biogeochemical flows, phosphorus; LSC: land system change; SOD: stratospheric ozone depletion; FWU: freshwater use. CCS: carbon capture and storage from steam reforming of syngas (SG) and of flue gas from natural gas combustion (FG). BAU: natural gas-based HB process

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Copper Nanoparticles under CO_2 Hydrogenation Conditions - Shape and Surface Morphology from First Principles and Variation due to Promoter Inclusion

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Cu-based catalysts can selectively hydrogenate CO_2 into methanol. One of their key advantages is the absence of the overreduction of CO_2 to hydrocarbons. However, the catalytic performance (activity and stability) of pure Cu-based catalysts is rather low. Introducing interfacial sites with metal oxide supports increase significantly both methanol reaction rates and selectivity [1]. XAS measurements have shown that Cu remains metallic and fully reduced under reaction conditions, but the exact nature of the active sites is still being debated. It is also known that adding reducible promoters (Prom = Zn, Ga) can radically improve their catalytic properties. While Cu is shown to alloy under reducing conditions, partial or full de-alloying is observed under reaction conditions, and such process is reversible. The addition of both Ga and Zn as promoters increases the intrinsic methanol formation rate and selectivity by suppressing the competing Reverse-Water-Gas-Shift reaction [2]. These results raise several questions regarding the state of Cu in these complex system and reaction conditions: What is the surface coverage of Cu under these conditions, how does it depend on the partial pressure of the involved gases, how are these properties modified by introducing different contents of promoters such as Ga and what is the influence of their distribution (alloyed vs. surface layers)?

Here, we used static DFT calculations and *ab initio* thermodynamics to model the stability of different Cu and CuGa bulk and surface structures with different Ga contents and distributions over a large range of conditions relevant to CO_2 hydrogenation. As a result, we evaluate the surface coverage as a function of gas phase chemical potential (and thus individual partial pressures). We show that the (111)-facet of pure Cu dominates due to its low surface energy, while acting as a hydrogen reservoir for the CO_2 hydrogenation reaction to methanol [3]. Adding Ga to the surface models has several effects: While alloyed Ga inside the particle barely influences the surface coverage of the particles, adding Ga surface sites or surface layers strongly affects both oxygen and hydrogen adsorption. Ga on the surface significantly decreases hydrogen adsorption while it also increases oxygen adsorption by forming Ga (sub-)oxide on the particle surface, showing the inherent differences of the Cu and CuGa system under reaction conditions.

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Reversible phase transitions in novel Ce-substituted perovskite oxide composites for solar thermochemical CO_2 redox splitting

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Thermochemical CO_2 and H_2O splitting via two-step metal oxide redox cycles is a promising approach to generate large-scale quantities of carbon-neutral liquid fuels. Solar thermochemical pathway utilizes the enitre spectrum of solar radiation as a source of high-temperature process heat to split CO_2 and H_2O into CO and H_2 (*syngas*), a precursor for synthetic liquid hydrocarbon fuels.[1] The two-step thermochemical temperature-swing cycle involves an endothermic reduction step of a redox metal oxide at high temperatures (1300–1500 °C), generating lattice oxygen vacancies, followed by an exothermic re-oxidation step with CO_2 and H_2O at low temperatures (800–1000 °C).[2] Perovskite-type ($ABO_{3-\delta}$) oxides are being considered as an attractive redox material class alternative to the state-of-the-art material ceria ($CeO_{2-\delta}$), due to their high structural and thermodynamic tunability. We identified a novel Ce-substituted perovskite manganite oxide composite, $La^{3+}{}_{0.48}Sr^{2+}{}_{0.52}(Ce^{4+}{}_{0.06}Mn^{3+}{}_{0.79})O_{2.55}$ (LSC25M75), aiming to overcome individual thermodynamic limitations of ceria and perovskite oxide-based materials. Thermochemical CO_2 redox splitting and long-term cyclability of LSC25M75 were evaluated with a thermogravimetric analyzer and an IR furnace reactor over 100 consecutive redox cycles. The results demonstrated a two-fold higher CO_2 conversion extent than the current state-of-the-art perovskite oxide, $La_{0.60}Sr_{0.40}MnO_{3-\delta}$ (LSM). The reasons for this high performance were elucidated for the first time with complementary diffraction techniques. Based on in situ high temperature neutron, synchrotron X-ray and electron diffraction experiments, we obtained an unprecedented structural insight into thermochemical perovskite oxide materials. Furthurmore, we proposed a novel CO_2 splitting reaction mechanism involving a reversible temperature induced phase transition from the $n = 1$ Ruddlesden-Popper phase $(Sr_{1.10}La_{0.64}Ce_{0.26})MnO_{3.88}$ (*I4/mmm*, K_2NiF_4-type) at reduction temperature (1350 °C) to the $n = 2$ Ruddlesden-Popper phase $(Sr_{2.60}La_{0.22}Ce_{0.18})Mn_2O_{6.6}$ (*I4/mmm*, $Sr_3Ti_2O_7$-type) at re-oxidation temperature (1000 °C) after the CO_2 splitting step.[3]

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Hydrogen spillover in hydrogenation catalysts by neutron imaging

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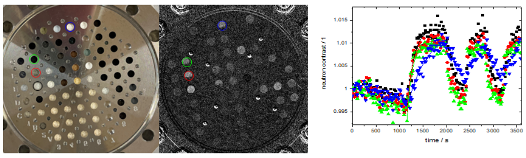
Hydrogenation reactions are crucial in a renewable energy scenario, notably to facilitate the production of hydrocarbons from hydrogen. The reactions are catalyzed by specific catalysts consisting of metal nano-particles on an oxide support, which functions is known to be more than that of a support [1]. Hydrogen after dissociative chemisorption may migrate over the oxide surface and thereby promote the transport to and from the reactive sites [2]. Verification of this so-called hydrogen spillover and particular its effect on the reaction kinetic is an analytical challenge, because the quantitative detection of dynamic hydrogen at relatively low concentrations ($c_H \ll 1$ at.%) is difficult. We developed a combinatorial setup for neutron imaging, capable of measuring up to 69 samples simultaneously under identical conditions (temperature/pressure) to quantify the amount of hydrogen in different methane and methanol catalysts. Hydrogen/deuterium exchange measurements at temperatures between 20 to 300°C and at a pressure of 1bar were performed on Ni deposited on reducible and non-reducible supports. Hydrogen spillover on the Al_2O_3 support proceeds via natural hydroxy groups on its surface in contrast to TiO_2 and SiO_2. On zeolites, spillover is observed only at sufficiently high water partial pressure.



Left: optical micrograph of the combinatorial sample stage. Middle: Neutron image during H-D exchange. Right: Kinetics of H-D exchange as measured by neutron contrast. Samples: Al_2O_3 (blue); Ni 0.5%-at on Al_2O_3(black); Ni 5%-at on Al2O3 (red); Ni 40%-at on Al_2O_3(green)

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Investigation of HCN formation from formaldehyde during the selective catalytic reduction of NO_x with NH_3 over V_2O_5/WO_3-TiO_2

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Selective catalytic reduction (SCR) is the technology of choice for NO_x reduction in diesel-powered vehicles and thermal power plants. Although modern catalyst formulations and process engineering measures have greatly hampered the occurrence of side reactions during SCR, some reactions can still occur in parallel. One of the most unwanted ones is the reaction of NH_3 with formaldehyde, a noxious compound that is formed due to the incomplete oxidation of hydrocarbons. This parasitic reaction not only decreases the SCR efficiency by as much as 13% (Fig. 1a), but also produces significant amounts of toxic hydrogen cyanide (HCN) (Fig. 1b). HCN selectivity and formaldehyde conversion was found to decrease with increasing water concentration while CO_x selectivity increased. This suggests that water competes for adsorption sites, and that formaldehyde requires close proximity with the active sites for HCN production.

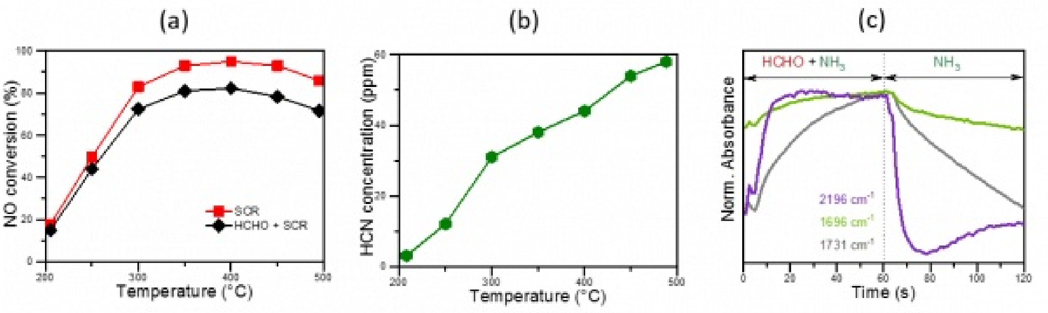

Fig. 1. (a) NO_x conversion over V_2O_5/WO_3-TiO_2. (b) HCN concentration. (c) Time-resolved IR signals of surface species during formaldehyde cut-off at 300 °C.

Operando IR spectroscopic experiments revealed the presence of adsorbed cyanide (2196 cm^{-1}) and amide (1696 cm^{-1}) species, which are key intermediates in HCN formation. Although formate species were also present on the catalyst surface, they were not responsible for the observed HCN emissions. Instead, formaldehyde reacted directly with adsorbed NH_3. Upon formaldehyde cutoff, the signal of the cyanide species decreased sharply but recovered again at the expense of formaldehyde (1731 cm^{-1}) and amide (Fig. 1c), suggesting that HCN production can be sustained through the reaction of the persisting surface species. TiO_2 alone was sufficient to catalyze the side reaction, but the presence of VO_x and/or WO_x sites increased HCN formation by preventing the formation of inactive polyamide species.

The formation of HCN under SCR conditions should be avoided by all means because of its toxicity. Therefore, our studies should serve as a basis for the development and implementation of technical measures to prevent HCN emissions.

Potassium Magnesiate Catalysed Hydrophosphinylation of Styrenes

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Organophosphorus compounds are an important class of compound because of their wide range of applications spanning organo-electronics and catalysis, as well as being ubiquitous moieties within the agrochemical and pharmaceutical chemistry.[1] Common methods for preparing organophosphorus compounds typically rely on hazardous halogenated precursors such as PCl_3. A more atom-economical and sustainable strategy is the direct addition of suitable P-H precursors to unsaturated precursors, however general methods for this transformation are still lacking. Specifically, the hydrophosphinylation reaction (Figure 1) has received little attention and current methods exploit rare earth metal catalysts under harsh reaction conditions and are limited to activated substrates.[2]

Recently, simple alkali metal pre-catalysts have been shown to facilitate hydrophosphinylation reactions under mild conditions, however these methods still suffer from low functional group tolerance.[3] In this work we show that a heterobimetallic potassium magnesiate co-complex is an efficient pre-catalyst for the hydrophosphinylation of stryenes and other unsaturated substrates (Figure 1). These studies illustrate a marked alkali metal and donor effect, highlighting the cooperative action of the heterobimetallic catalyst

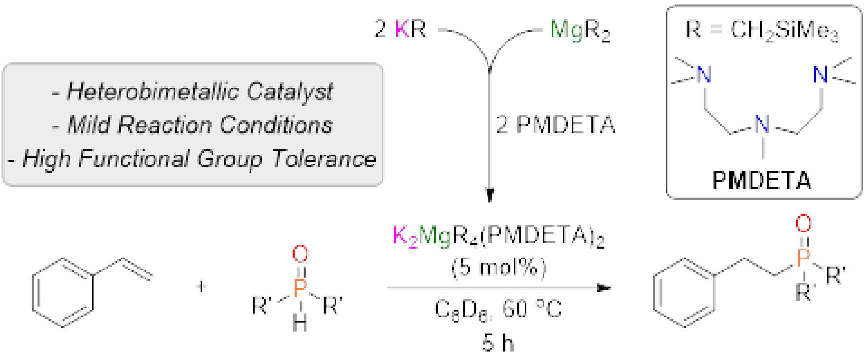

Figure 1: Potassium Magnesiate Catalysed Hydrophoshinylation of Stryenes.

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Palladium single-atoms supported on nitrogen doped carbon for Sonogashira cross-coupling

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Among the transition-metal catalyzed cross-coupling reactions, the Sonogashira-Hagihara reaction presents a cornerstone in today's synthetic chemists toolbox to access complex arylalkynes and enynes.[1] Attempts to replace homogeneous palladium catalysts with solid-supported, mostly nanoparticle-based counterparts have failed to compensate for inferior activity or severe metal leaching. Heterogeneous single-atom catalysts (SAC) are promising approach to maximize the control over the palladium site, while displaying favorable metal-efficiency and facile recoverability.[2] We explore the use of palladium atoms supported on nitrogen-doped carbon (Pd/NC) to catalyze the coupling of arylhalides and arylacetylenes on its own (Figure 1) as well as in the presence of copper co-catalysts. Advanced characterization techniques are used to relate structure properties with catalyst activity and stability. Although for now, lower activity was observed compared to homogeneous benchmarks the SAC stands out with its stable performance. A more holistic and process-centered assessment of the investigated catalysts is obtained through life cycle analysis (LCA), unveiling the sustainability of heterogeneously catalyzed Sonogashira coupling.

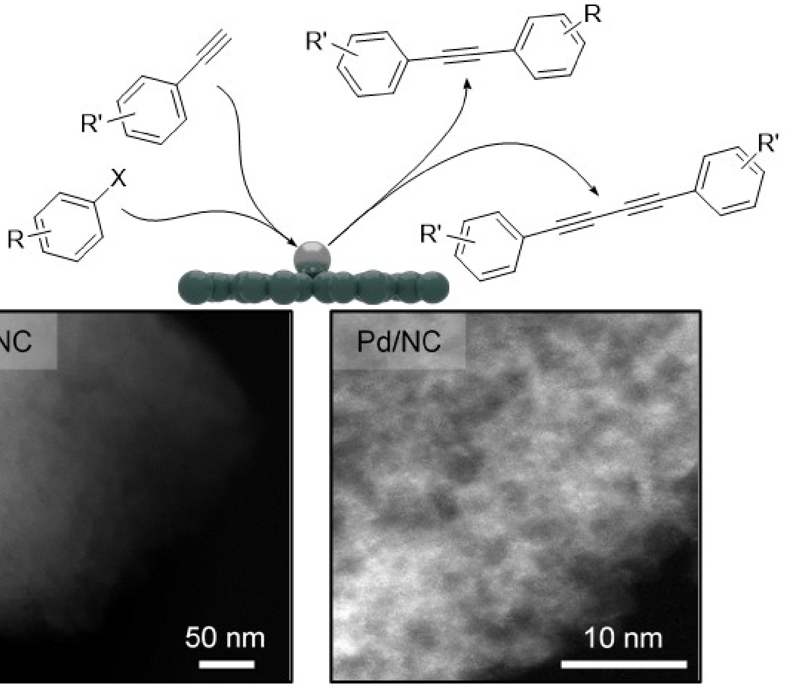

Figure 1 Basic idea of the coupling reaction catalyzed by a supported Pd single-atom (top) and electron microscope images of the freshly prepared SAC (bottom).

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Molecular Transformer-aided Biocatalysed Synthesis Planning

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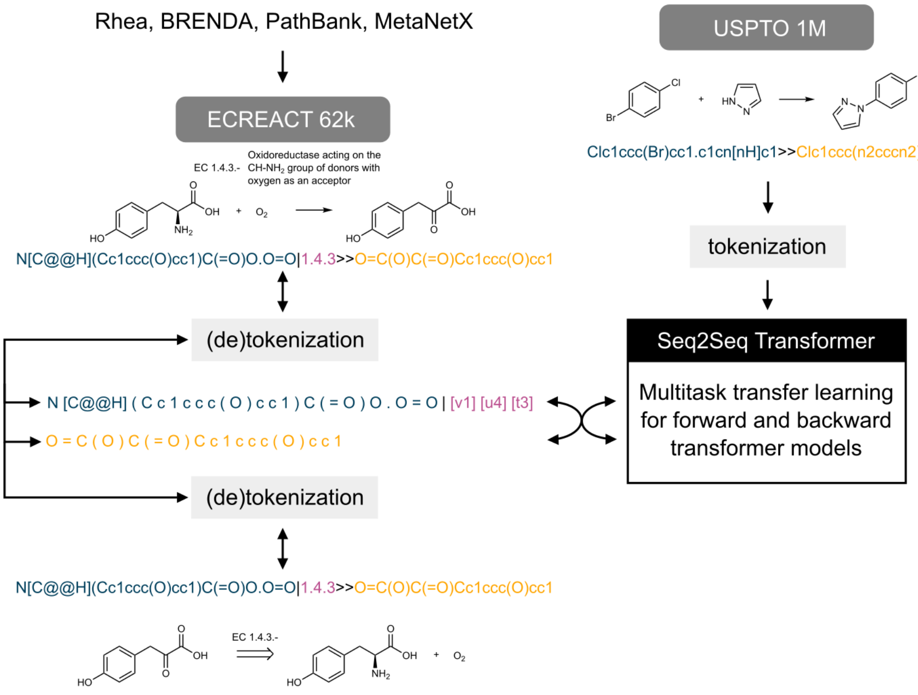
Enzyme catalysts are an integral part of green chemistry strategies towards a more sustainable and resource-efficient chemical synthesis. However, the retrosynthesis of given targets with biocatalysed reactions remains a significant challenge: the substrate specificity, the potential to catalyse unreported substrates, and the specific stereo- and regioselectivity properties are domain-specific knowledge factors that hinders the adoption of biocatalysis in daily laboratory works. [1,2]



Here, we use the molecular transformer architecture [3] to capture the latent knowledge about enzymatic activity from a large data set of publicly available enzymatic data, extending forward reaction and retrosynthetic pathway prediction to the domain of biocatalysis. We introduce a class token based on the EC classification scheme that allows to capture catalysis patterns among different enzymes belonging to same hierarchical families. The forward prediction model achieves a top-5 accuracy of 62.7%, while the single step retrosynthetic model shows a top-1 round-trip accuracy of 39.6%. The enzymatic data and the trained models are available through the RXN for Chemistry network (https://rxn.res.ibm.com and https://github.com/rxn4chemistry).

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Mechanistic insights on the conversion of methane under non-oxidative conditions over iron-modified silica

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Methane is a valuable chemical feedstock that can be transformed into useful chemical products. Its direct conversion under non-oxidative conditions is an interesting method due to its simplicity and capacity to produce C_{2+} hydrocarbons and hydrogen.[1] Even being the focus of scientific research for many decades, its advance has been hampered by inherent kinetic and thermodynamic limitations, and by catalyst deactivation via coke formation, both contributing to low yields.[2] Recent reports have pointed out remarkable performance for iron-modified silica catalysts for this type of methane conversion.[3-4] Yet, comprehensive mechanistic understanding remains elusive, which is of significant importance to improve the performance of the process towards feasible methane conversion under practical reaction conditions. Herein, we report a thorough mechanistic study of the direct conversion of methane under non-oxidative conditions over iron-modified silica catalysts. Using vacuum ultraviolet synchrotron photoelectron photoion coincidence tools available in the VUV beamline of the Swiss Light Source (Paul Scherrer Institute) for downstream analysis,[5] elusive intermediates and products were detected, enabling the unique description of the complex gas-phase reaction network. Our experiments identified different C_{2+} radical species that allow for a stepwise growth of the hydrocarbon products and revealed that propargyl radicals are essential for the formation of benzene, which contributes to the production of heavier products via hydrogen abstraction - acetylene addition pathways.

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Exploiting resonant X-ray powder diffraction at the Al K edge to locate aluminum in zeolite frameworks

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The position of aluminum in a zeolite framework structure defines the accessibility and geometry of the catalytically active sites, so a crystallographic determination of the Si-Al ordering would enable a better understanding and fine-tuning of a zeolite catalyst. However, there is currently no general method that can identify directly which T sites in a zeolite framework structure are occupied by aluminium. Recognizing T-site dependent reactivity of zeolites is a long-standing question in zeolite science that to date remains unanswered, because the aluminum substitution for silicon is usually only partial (typical zeolite catalysts have Si:Al ratios larger than 5) and the scattering power of these two elements is very similar.

To address this problem, we have exploited the properties of resonant (anomalous) X-ray powder diffraction (AXRD) across the Al K edge (1.56 keV), where the aluminum scattering factor changes drastically while that of silicon remains unchanged. Those changes in the scattering power highlight aluminum in the structure. While the well-established X-ray absorption methods exploited at the Al edge are short-range probes and can report only on local environment around the aluminum position, AXRD can collect information of the long-range structural order of Al:Si distribution and consequently unambiguously pinpoint aluminum's position in the framework. Because the diffraction limit at 1.56 keV corresponds to a *d* spacing of only 3.98 Å, the data from a conventional measurement were combined with those at energies near the X-ray absorption edge to quantify the aluminum concentration at all T sites in the refined zeolite structure.

In this way, two **FER**-type zeolites with identical chemical compositions but the different distributions of aluminum and different catalytic properties could be determined quantitatively and unambiguously. One sample was more active and selective in the isomerization of *n*-butene to *i*-butene than the other, but it also deactivated much faster.(*1*, *2*) This could be better understood from the aluminum ordering found. The higher activity and faster deactivation was due to the higher proportion of active sites in the accessible 10-ring channels. The results are in line with previous studies performed on the same samples, but are also quantitative.

These analyses demonstrate that the method can be applied even for zeolites with Si:Al ratios as high as 15. The method yields a quantitative characterization of the catalytically active sites in a zeolitic material, and that, in turn, allows the activity of that zeolite to be understood and fine-tuned. This constitutes a major advance in our fundamental understanding of the relationship between zeolite structure and catalytic activity. We believe that AXPD at the Al K edge could become the technique of choice for zeolite scientists interested in locating the active catalytic sites in their materials.

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Iron-associated active oxygen species are responsible for low-temperature catalytic activity of Pt-FeO_x /Al_2O_3 catalyst

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Reducible oxides are effective aerobic oxidation catalysts being able to activate molecular oxygen.[1] This ability is generally attributed to the high concentration of oxygen vacancies serving as oxygen activation sites.[2] At the same time, the mechanism of oxygen activation remains unclear since specific surface sites cannot be easily detected using conventional methods.[3] In this work, we unraveled the mechanism of oxygen activation over iron sites of Pt-FeO_x/Al_2O_3 during carbon monoxide oxidation using a combination of *in situ* FTIR and *operando* time-resolved X-ray absorption spectroscopy. This experimental strategy provided insight into the highly debated catalytic mechanism of low-temperature carbon monoxide activation over supported Pt-FeOx catalyst. We quantitatively demonstrated that the Fe^{2+}/Fe^{3+} redox couple is responsible for oxygen activation during carbon monoxide oxidation, while carbon monoxide activates on metallic platinum (**Fig. 1**). Our experiments also indirectly allude to a catalytic cycle involving electrophilic oxygen species adsorbed on iron centers as reaction intermediates. A similar oxygen activation mechanism might be expected for other catalytic oxidation reactions over cationic iron of both chemical and biological importance, where iron-associated active oxygen radical species are proposed intermediates responsible for low-temperature oxidation activity.

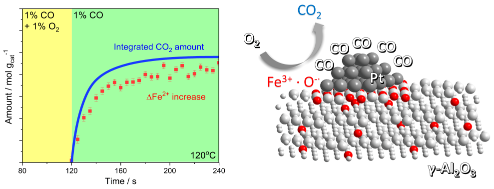

Figure 1. Left: correlation between the amount of carbon dioxide vs. that of produced Fe^{2+} after oxygen cut-off obtained from *operando* Fe K-edge XAS and MS data. Right: reaction scheme.

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Design of carbon supports for metal-catalyzed acetylene hydrochlorination

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[1]ETH Zurich, [2]University of Alicante, [3]Paul Scherrer Institut

For decades, carbons have been the catalyst support of choice for acetylene hydrochlorination, a key industrial process for polyvinyl chloride manufacture.[1] However, no unequivocal design criteria could be established to date, due to the complex interplay between the carbon host and the metal nanostructure.[2-3] Herein, we disentangle the roles of carbon in determining activity and stability of platinum, ruthenium, and gold-based hydrochlorination catalysts and derive descriptors for optimal host design, by systematically varying the porous properties and surface functionalization of carbon, while preserving the nanostructure of the active metal sites. The acetylene adsorption capacity is identified as central to superior activity (**Fig. 1a,b**), while the density of acidic oxygen sites determines the coking tendency and thus catalyst stability (**Fig. 1c**). With this understanding, a platinum single-atom catalyst is developed that withstands two-fold accelerated deactivation conditions compared to the state-of-the-art system (**Fig. 1d**), marking a step forward towards sustainable PVC production.[4]

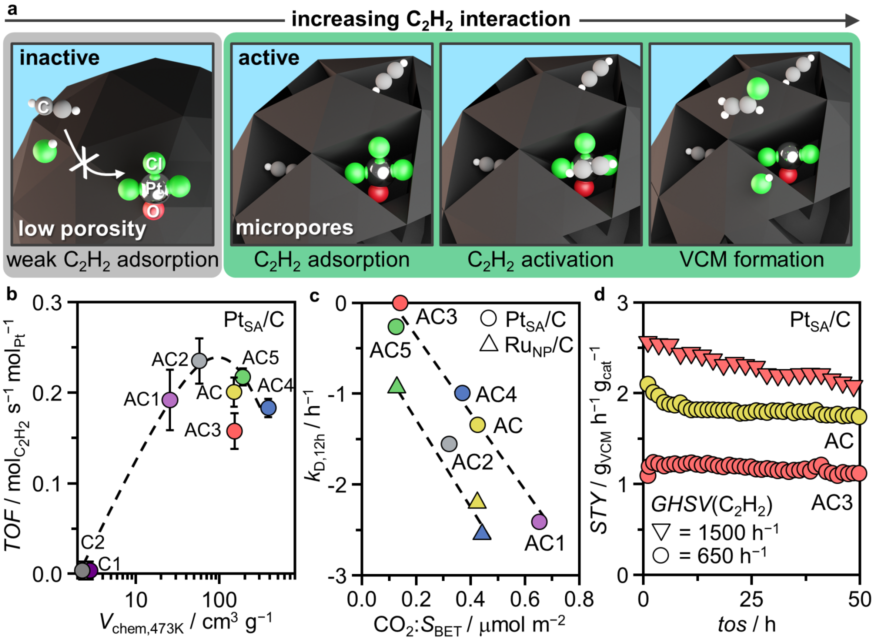

Fig. 1 a Effect of acetylene adsorption properties of the carbon support on the performance of Pt_{SA}/C catalysts. Correlation between **b** catalytic activity and acetylene adsorption capacity and **c** deactivation constants of Pt_{SA}/C and Ru_{NP}/C catalysts and density of acidic oxygen functionalities. **d** Time-on-stream performance of the state-of-the-art Pt-based system (yellow) and the newly designed Pt_{SA}/C catalyst (red). Sample codes: $M_{SA\text{ or }NP}$/support, SA = single atom, NP = nanoparticle. AC*X* and C*X* supports with varying porous properties and surface functionalization.

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Gold supported on ceria as a superior catalyst for nitrous oxide production *via* direct ammonia oxidation

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Nitrous oxide, a mild, green oxidant, has been of interest to chemical industry for decades due to its ability to directly convert hydrocarbons into value-added oxygenates.[1] However, it is prohibitively expensive due to the lack of an efficient and economic route for its large-scale manufacture. Herein, we report gold nanoparticles supported on ceria (**Fig. 1a**) as a highly selective and active catalyst for low-temperature direct ammonia oxidation to nitrous oxide, far surpassing the productivity of the state-of-the-art Mn-Bi catalyst (**Fig. 1b**).[1] The unprecedented catalytic footprint is attributed to the synergistic metal-support interaction, highlighted both by the inertness of pure ceria and by the low activity of gold nanoparticles hosted on other metal oxides. The oxygen transfer ability of ceria,[2] which is significantly enhanced *via* deposition of gold (**Fig. 1c**), in tandem with the $Au^{\delta+}$ and Au^0 species, found at the metal-support interface and on the nanoparticle surface, respectively, are speculated to be the key factors governing the catalytic performance of the system. These findings are of fundamental and practical relevance to the development of a new generation of catalysts for direct ammonia oxidation holding prospects towards industrial viability.

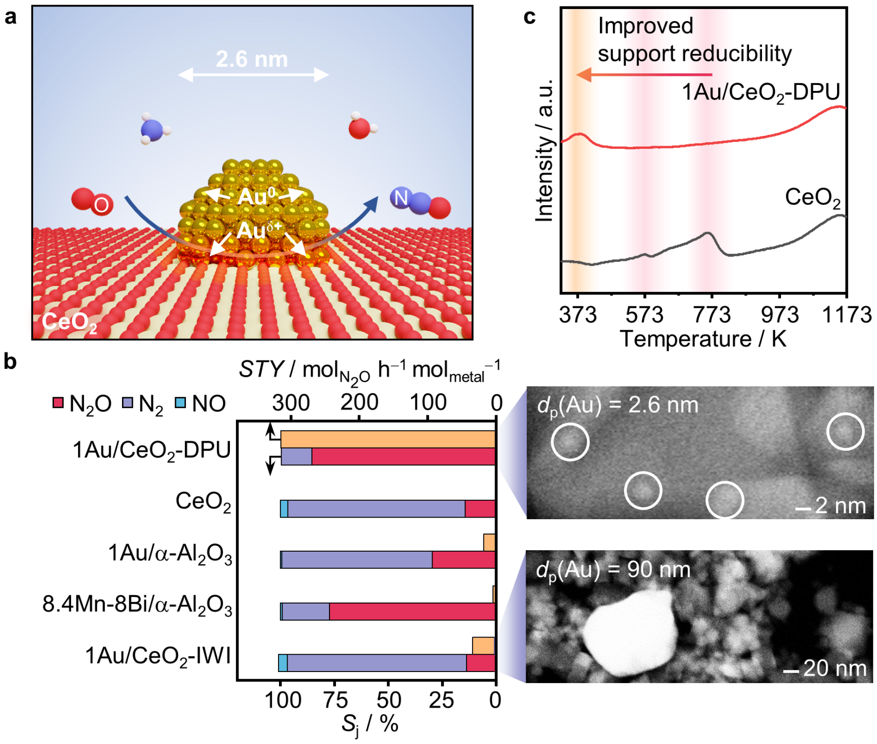

Fig. 1 a Schematic representation of the surface of the $1Au/CeO_2$-DPU catalyst. **b** Catalytic performance of selected ammonia oxidation catalysts (left) and STEM images (right) of Au/CeO_2 systems prepared *via* deposition precipitation with urea (DPU) and incipient wetness impregnation (IWI). **c** H_2-TPR profiles of $1Au/CeO_2$-DPU and the pure ceria support. Sample code: (metal loading in wt.%)M/support-(synthesis method).

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Hydrogen Dissociation Sites on Indium-Based ZrO_2-Supported Catalysts for Hydrogenation of CO_2 to Methanol

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[1]Department of Mechanical and Process Engineering, ETH Zürich, Switzerland, [2]N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, Russia

In_2O_3-based materials have emerged as promising catalysts for the direct conversion of CO_2 into methanol.[1,2,3] Our recent *operando* X-ray absorption spectroscopy – X-ray powder diffraction (XAS-XRD) studies showed that the exceptionally high activity and stability of the In_2O_3/m-ZrO_2 catalyst is due to the dissolution of In_2O_3 into the high surface area nanocrystalline m-ZrO_2 support, i.e. the actual catalyst is a m-ZrO_2:In solid solution. This material features active In–V_o–Zr sites that avoid deactivation by over-reduction to oxidation states of indium below In^{2+}. In contrast, In–V_o–In sites in In_2O_3, In_2O_3/t-ZrO_2 and In_2O_3/am-ZrO_2 catalysts undergo such undesired over-reduction.[4,5] Yet the nature and abundance of sites for the heterolytic dissociation of H_2 in these In_2O_3/ZrO_2 catalysts or the activation of CO_2 remain understudied. Here, we apply infrared (IR) spectroscopy to investigate surface sites that dissociate H_2 at room temperature (RT) in the catalyst systems mentioned above. Subsequently, we study the interaction of the formed In–H species with CO_2.

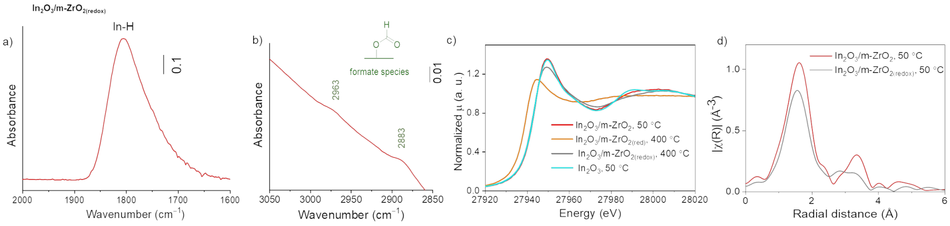

Figure 1. FTIR spectra of a) In–H species formed via the dissociative adsorption of H_2 on the four catalysts after redox treatment; b) formate species formed at RT by the reaction between CO_2 and In–H species of In_2O_3/m-$ZrO_{2(redox)}$ and m-ZrO_2:$In_{(redox)}$; c) In K-edge XANES spectra of calcined, reduced (red) and re-oxidized (redox) In_2O_3/m-ZrO_2 along with the In_2O_3 reference and d) FT of the k^2-weighted EXAFS of In_2O_3/m-ZrO_2 and In_2O_3/m-$ZrO_{2(redox)}$ at 50 °C.[6]

The phase of the ZrO_2 support influences the nature and the relative abundance of In–O sites for the dissociative adsorption of H_2.[6] While H_2 dissociates at RT on In_2O_3/m-ZrO_2 and m-ZrO_2:In catalysts, a redox pretreatment is required to form sites for hydrogen dissociation in In_2O_3/t-ZrO_2 and In_2O_3/am-ZrO_2. The reaction between CO_2 and the In–H species of redox-treated catalysts gives formate species, i.e. intermediates of the methanol synthesis pathway, only on In_2O_3/m-$ZrO_{2(redox)}$ and m-ZrO_2:$In_{(redox)}$. This indicates a more favorable reactivity of In–H species and carbonates on the m-ZrO_2 support. In situ XAS at the In K-edge on In_2O_3/m-ZrO_2 confirms the formation of a m-ZrO_2:In solid solution after the redox pretreatment. Thus, H_2 dissociation on the most active catalyst, i.e. m-ZrO_2:In, proceeds on In^{3+}–O–Zr^{4+} sites with the formation of In–H and Zr–OH sites.

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Toward reliable and accessible ammonia quantification in the electrocatalytic reduction of nitrogen

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The electroreduction of nitrogen may alleviate the large fossil energy requirements to produce fertilizers.[1] However, the lack of rigorous and accessible ammonia quantification tools hampers catalyst development. Ultraviolet-visible (UV/Vis) spectrometry and the ion-selective electrode (ISE) are convenient techniques for first catalyst screening. 1D proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy is the technique of choice in more rigorous testing protocols,[2] because it allows for a clear distinction between adventitious ammonia ($^{14}NH_4^+$) and catalytically produced ammonia ($^{15}NH_4^+$) in experiments with isotopically labelled species. However, it is scarcely applied due to the high expertise required from the analyst and expensive apparatuses demanded. This work assesses UV/Vis spectrometry and ISE to maximize their reliability (**Fig. 1a**). As for ^{1}H-NMR, we introduce a protocol encompassing sample preparation, acquisition, optimization and post processing, accessible to catalyst practitioners displaying 10 ppb detection limit using 30 min analysis in a 500 MHz spectrometer. High quality spectra arise from the high selectivity of the water suppression method, the use of non-deuterated samples, and the identification of optimal line broadening factors. Its transfer to a widely available 300 MHz analogue retained excellent spectrum quality at relevant concentrations (**Fig. 1b**). By making ^{1}H-NMR quantification more accessible, this study foster the broader application of state-of-the-art catalytic assessments.

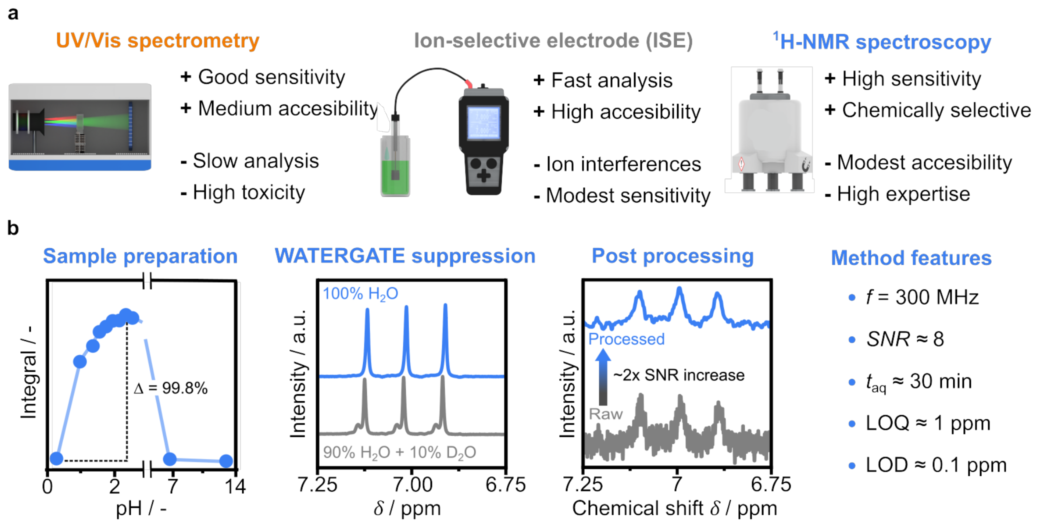

Fig. 1. a Ammonia quantification tools UV/Vis spectrometry, ISE, and ^{1}H NMR and their pros and cons. **b** ^{1}H NMR method developed, listing the pH range for sample preparation, optimized acquisition by the use of WATERGATE suppression method, effect of signal post processing, and its main features. SNR = signal-to-noise ratio.

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Catalytic activity of cobalt sulfide for alkene epoxidation

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Transition metal sulfides have recently gained significant attention due to their promising catalytic properties for bifunctional water splitting, i.e. both for hydrogen evolution (HER) and oxygen evolution reactions (OER).[1] Under OER conditions transition metal sulfides form oxidized surfaces that outperform corresponding metal oxide and sometimes even noble metals in OER catalysis.[2,3,4] The ability of transition metal sulfides to oxidize water under electrochemical conditions could be indicative of a more general catalytic potential for oxidative transformations, in particular for reactions involving oxygen transfer. However, this catalytic potential has not been broadly explored. Development of earth-abundant metal sulfides in new catalytic applications would pave the way towards more sustainable catalytic processes.

Here, we present thermal catalysis by mesoscale cobalt sulfide (Co_xS_y) for alkene epoxidation with stoichiometric oxidants. Co_xS_y was prepared by hydrothermal synthesis and characterized by pXRD, XPS, SEM, and EDX. The prepared material oxidizes under reaction conditions and displays higher activity for the epoxidation of cyclic alkenes than the corresponding cobalt oxide. This highlights surface oxidized cobalt sulfide as a catalyst for further applications in oxidative transformations. We discuss the oxygen transfer ability of cobalt sulfide and the observed reaction selectivity, and analyze the role of the *in situ* oxidation with respect to catalytic activity and stability.

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Elucidating the mechanism of oxidative dehydrogenation of ethanol over V_2O_5/TiO_2 by transient XAS

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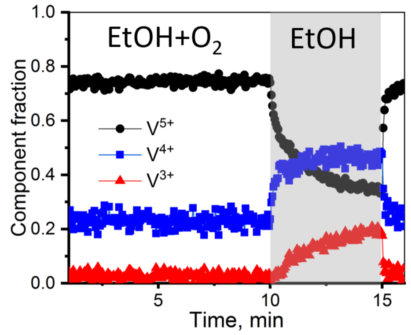
Titania supported vanadia catalysts exhibit outstanding activity in a number of catalytic redox reactions. In spite of the numerous investigations, the redox state of the vanadium intermediate and the involvement of the titania support remain a matter of debate. In this work, we used operando time-resolved V K-edge and Ti K-edge XANES under transient conditions to investigate the redox transformations of metal sites during ethanol oxidative dehydrogenation (ODH). Ethanol ODH proceeds via a Mars-van Krevelen mechanism, which consists of two consecutive processes: ethanol oxidation by lattice oxygen coupled with catalyst metal reduction and re-oxidation of the catalyst by molecular oxygen. For efficient probing of the catalyst by V K-edge and Ti K-edge XAS, we used a bilayer 5 wt%V_2O_5/15 wt%TiO_2/SiO_2 catalyst. This catalyst has several advantages for kinetic and mechanistic studies since (i) both the vanadia and titania are present at the surface allowing the use of XAS that is a bulk-sensitive technique; (ii) all the vanadia sites are in direct contact with the surface titania sites; and (iii) the bilayer catalyst exhibits TOF values comparable to supported VO_x/TiO_2 catalysts [1].

A series of dedicated transient experiments were performed in an *operando* reactor to probe the activity of V and Ti sites. These experiments showed the formation of V^{4+} and V^{3+} species upon oxygen switch off experiments. The quantitative analysis, however, showed that the formation of acetaldehyde is kinetically coupled to formation of V^{4+}: the formation of 1 mol of acetaldehyde is accompanied by reduction of 2 mol of V^{5+} to V^{4+}. Very subtle changes of the titanium during ethanol ODH were tracked using modulation excitation Ti K-edge XAS experiments, which allowed us to detect a slight reduction of titanium and adsorption of ethanol. Semi-quantitative estimation showed that the extent of titanium reduction is about 20 times lower than that of vanadium. This suggests that titanium does not change its oxidation state significantly during ethanol ODH, but may act as a carrier of electrons between isolated vanadium species that facilitate their reduction.



The concentration of V^{5+}, V^{4+} and V^{3+} during oxygen cut-off experiments at 210 °C

These results demonstrate the power of transient experiments in combination with operando time-resolved element-specific XAS to uncover the complex redox mechanisms in heterogeneous catalysts and electrocatalysts.

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Influence of preparation method on Pt/Al_2O_3 catalysts activity in the hydrogenation of nitrobenzene to aniline

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Supported platinum (Pt) has a long history of application in catalysis, primarily owing to its high activity in a wide range of chemical reactions(1). The catalytic activity of Pt nanoparticles has been shown to strongly depend on the nanoparticle's size(2), shape, interfacial electronics, and other components. In this work, we have used different methods to synthesize the Pt/Al2O3 and study the performance of nitrobenzene hydrogenation.

The metal dispersion was characterized by TEM analysis. in a case of catalysts with lower platinum loading (1 wt.%), Pt particles are uniformly and separately dispersed on the catalyst surface. The particle size of commercial Pt/Al_2O_3 was 3.0 ± 0.7 nm. In the normal method, the particle size was 3.2 ± 0.8 nm, which is the same size as those in the commercial catalysts. In our new colloid method, the particle size was 2.5 ± 0.7 nm. In the incipient method, the particle aggregated as load increased (5%). The particle size in was 5.8 ± 1.6 nm, which was larger than 1% (2-3 nm). In the colloid method, the two different loading amounts have the same particle distribution. But in the 5% Pt/Al_2O_3 catalysts, a second layer of platinum appeared on the surface, which caused a decrease in accessibility for previously existing catalyst centres (2.0 ± 0.4 nm).

The catalysis performance of nitrobenzene hydrogenation was tested in autoclave. All the catalysts showed the same selectivity of above 95%. The different method showed different catalysis performance at lower (1%) loading amounts. The nitrobenzene conversion of the commercial catalyst was 47.3%. The conversion was 33.7% for the deposition precipitation method. With the incipient wetness impregnation method by H_2 reducing catalyst, the activation was 58.6%, which was higher than in the commercial catalyst. With the methanol colloid method catalyst had an activation of 70.0%, which was the best performance in the nitrobenzene hydrogenation.

When the loading amount increase, the catalyst activation decreased for all methods. The commercial catalyst with 5% shows the lowest activation (3.2%). The catalyst (normal method) activation was 21.2%, which was not much less than that of the lower loading amount. The H_2 reducing method catalyst activation was 19.2%. The colloid method catalyst activation was 35.5%, which was half that of the lower loading amount catalyst, but the highest activation among the higher loading amount catalysts.

We used three different methods (colloid, deposition precipitation, and the incipient wetness impregnation) to prepare the ten Pt/Al_2O_3 catalysts. Each method mainly influenced the catalysts' nanoparticles structural properties, rather than their electronic properties. We found that the colloid method is more suitable to synthesize the high metal loading.

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Ultra-Thin Coordination Polymer Derivatives Towards Efficient Oxygen Generation

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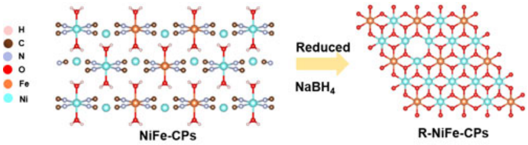
Coordination polymers (CPs) are prominent candidates for multifarious applications (e.g., drug delivery,[1] gas storage/separation,[2] and battery[3]), owing to their unique structural properties. However, the confined metal centers and poor conductivity need to be addressed when employing CPs as electrocatalysts towards water splitting. Recent studies demonstrated that the construction of discorded structures is a more appropriate approach to achieve high catalytic performance in CPs.[4] Herein, we employed a conventional strategy to prepare a series of NiFe-based ultra-thin coordination polymer derivatives with rich structural deficiencies (denoted as R-NiFe-CPs) for efficient oxygen evolution reaction (OER).[5] Transmission electron microscopy (TEM) and atomic force microscopy (AFM) characterizations indicate the as-prepared low crystalline R-NiFe-CPs display an ultra-thin nanosheet morphology with a layered thickness of sub-2 nm. The obtained ultra-thin morphologies could shorter the ion's diffusion length and thus endow the faster electron transfer properties. Moreover, combined with the X-ray absorption spectroscopy (XAS) and density functional theory (DFT), the results reveal that the existence of structural deficiencies plays a pivotal role in the intrinsic OER activity. As a result, the as-prepared R-NiFe-CPs shows excellent OER performance with a very low overpotential of 225 mV at 10 mA/cm^2 and robust electrochemical stability for over 120 h.



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Synthesis and catalytic activity of SOMC-derived Co nanoparticles

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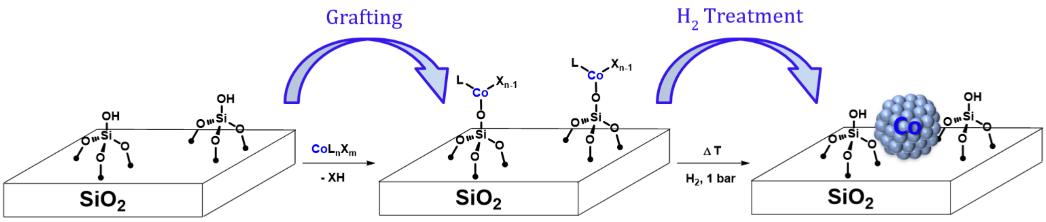
Cobalt is commonly used in heterogeneous catalysis. Typically, cobalt-based catalysts are made from the cobalt nitrate which are deposited on various oxide supports, calcined to the respective Co oxides and eventually treated under H_2 to yield supported Co nanoparticles. The synthesis of cobalt metal particles with high dispersion and narrow size distribution remains challenging due to a multitude of factors. Strong support interaction typically leads to the use of higher reduction temperatures that in turn facilitate nanoparticle growth, while weakly interacting supports are usually not able to stabilize very small nanoparticles. [1] Additionally, conventional heterogeneous catalysts often yield ill-defined systems where part of the Co can be integrated into the support, in part, due to the synthetic protocol used, hence they are inherently difficult to study.



In order to synthesize small and narrowly distributed supported Co nanoparticles, we turned to surface organometallic chemistry (SOMC, scheme 1), which has been shown to be an unique tool to generate isolated metal sites but also for generation of highly disperse metal nanoparticles with controlled interfaces and composition. [2] This approach has been shown to be particularly suited to understand the molecular origin of the effects related to dopants, ligands, and supports, and promising to provide guiding principles for the rational design of cobalt-based catalysts. Here, we report that SOMC enables to generate supported Co(0) nanoparticles with an average particle size of 1.5 nm with homogeneous size distribution by selecting appropriate molecular precursors. The materials are found to be highly active in selective hydrogenation reactions.

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A unified understanding of indium oxide promotion by transition metals at the atomic scale

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Promotion of heterogeneous catalysts by transition metals is a ubiquitous strategy to boost performance of catalytic systems. Several metal promoters such as palladium[1], platinum[2], and nickel[3] have recently been shown to enhance the activity of In_2O_3, a highly selective and stable catalyst for CO_2 hydrogenation to methanol, by improving its H_2 activation ability. A direct and rational comparison of these metal promoters is however lacking since they exhibit distinct active architectures, *i.e.*, single atoms, low-nuclearity clusters, nanoparticles, films, or a mixture of these, descending from different metal loadings and synthesis methods. Here, we employ flame spray pyrolysis (FSP) as a unified procedure to synthesize highly dispersed metal-promoted In_2O_3 catalysts at low loadings (*ca.* 0.5 wt.%), to decouple nuclearity effects from the intrinsic electronic impact of the promoters on the active ensemble (**Fig. 1**). All catalysts display increased methanol productivity compared to unpromoted In_2O_3 and selectivity falling into distinct families. Current activities center on the in-depth characterization of the nanostructure of the metals and the surface vacancy chemistry on In_2O_3. This information will be combined with kinetic studies supported by mechanistic insights from density functional theory (DFT) calculations, to derive structure-performance-mechanism relationships across the spectrum of promoters. This study offers new insights into atomic-level promotion of In_2O_3 based on a common platform of materials with potential for extrapolation to other catalyst families for CO_2 valorization.

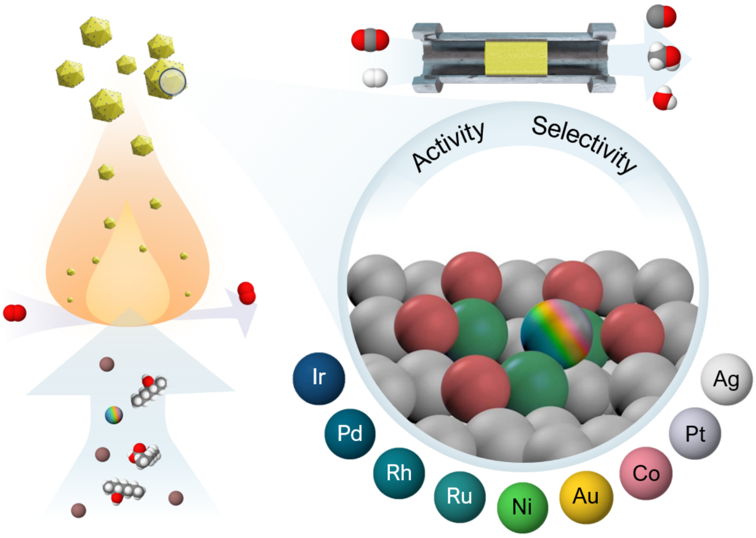

Fig. 1. Conceptual illustrations of metal-promoted catalyst synthesis using flame spray pyrolysis (left) and investigation of the effect of the promoters on the CO_2-to-methanol performance (right).

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