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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.

A mechanistic study of carbon dioxide hydrogenation to methanol by *operando* XAS, XRD and SSITKA-FTIR techniques

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Due to an increased demand for renewable energy, direct catalytic valorization of CO_2 into methanol (liquid fuel additive and precursor to other value added chemicals) has been receiving increasing attention over the past decade [1]. Among a variety of catalyst formulations that can produce methanol from the mixture of carbon dioxide and hydrogen - copper-zinc-alumina catalyst (CZA), industrially designed for methanol synthesis from syngas, shows the most promising results. In spite of extensive efforts, the activity and selectivity threshold for this well investigated material is still far from commercial utilization and further catalyst improvement is still required. Numerous studies, investigating mechanistic aspects of methanol synthesis over CZA material, are based on experiments usually made under conditions (low temperature, vacuum) that are far away from the real catalytic experiment (>15 bar; 220-280 ºC). Hence, even the structure of active sites and especially the role of copper-zinc alloys in this catalytic system, are subject of intense debate [2-3]. This situation has motivated us, to investigate the mechanistic role of copper-zinc alloy in carbon dioxide hydrogenation to methanol by using *operando* time-resolved XAS (at both Cu and Zn K-edges), SSITKA-FTIR and XRD under relevant catalytic conditions (15 bar; 260 ºC), supported by theoretical modelling and TEM [4].

Applying different *in situ* activation protocols by varying of reduction temperature and partial pressures of hydrogen and carbon dioxide during pretreatment steps, we were able to tune content of copper-zinc alloy in CZA catalyst. We found that CZA materials, containing significantly different amount of reduced zinc (49 and 16 mol. %), possess almost identical catalyst activity (0.38 and 0.44 mmol g^{-1} min^{-1}, respectively), pointing out that no correlation exists between the observed methanol productivity and the amount of CuZn brass present in the system. To provide a more unambiguous understanding of the role of copper-zinc alloy in this reaction, *operando* XAS (time resolution 10 s) and XRD measurements during transient switches from hydrogen to CO_2/H_2 reaction mixture and back were performed. It was revealed that CuZn alloy, which was considered as an active site in this reaction, upon relevant catalytic conditions (CO_2/H_2 reaction mixture, 260 ºC, 15 bar) undergoes oxidation with the formation of wurtzite ZnO, which can activate CO_2 and form surface zinc formate species, which according to SSITKA-FTIR and qXAS is the reactive intermediate. We found that formation of the copper-zinc alloy followed by oxidation under reaction conditions forms a well-developed Cu/ZnO interface, which is where the reaction takes place. Metallic copper facilitates hydrogen splitting, while the zinc phase is responsible for CO_2 activation, which subsequently forms methanol.

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Palladium-Gallium Alloyed Nanoparticles on Silica: Metal Synergy Yields Highly Active Catalyst for Selective CO_2-to-Methanol Hydrogenation

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The conversion of CO_2 to liquid fuels has garnered significant attention in recent years, as a strategy to mitigate anthropogenic CO_2 emissions and as an alternative feedstock to fossil fuels.[1] In particular, the direct conversion of CO_2 to CH_3OH has been highlighted as an appealing target.[2] For this purpose, metallic nanoparticles supported on oxide supports, modified with various promoters, have been extensively studied. For the most part, efforts have focused on copper particles promoted by zinc oxide/alumina ($Cu/ZnO/Al_2O_3$) or related copper/zirconia (Cu/ZrO_2) systems.[3] However, Cu-based catalysts show low activity and relatively rapid deactivation by water.[4] To combat this, alternative transition metals, oxide promoters and supports have been proposed and investigated.[3] In particular, Pd-containing systems (Pd/MO_x, M = In, Ga, Zn) show superior activities with respect to Cu-based systems. [5,6]

Here, we report that small, narrowly distributed alloyed PdGa nanoparticles supported on Ga-doped silica ($PdGa@SiO_2$), prepared through a Surface Organometallic Chemistry (SOMC) approach, selectively catalyze the conversion of CO_2 to CH_3OH. The bimetallic material $PdGa@SiO_2$ material is 40 times more active than the monometallic material ($Pd@SiO_2$), and an order of magnitude more active than benchmark Cu-based systems in the hydrogenation of CO_2 to CH_3OH. In contrast to most Cu-based systems, methanol selectivity appears to be largely independent of conversion. Through the use of rationally designed molecular precursors, amenable to an SOMC approach, we show that the presence of a PdGa alloy in the precatalyst is critical for the selectivity of CO_2-to-methanol in Pd-based systems doped with Ga. Furthermore, the presence of an alloyed phase in reaction conditions was confirmed by *in situ* X-ray Absorption Spectroscopy (XAS), and the partial re-oxidation of metallic gallium in reaction conditions was tracked using XAS.

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Unveiling the promotional effect of nickel in indium-catalyzed CO_2 hydrogenation to methanol

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The thermocatalytic hydrogenation of CO_2 with renewable hydrogen stands as a sustainable route to produce the commodity and potential fuel methanol. In_2O_3 emerged as a promising catalyst for this reaction owing to superior selectivity and stability[1] and can be effectively promoted by anchoring tiny palladium clusters to its surface *via* a coprecipitation synthesis.[2] Herein, here we gather comprehensive molecular-level understanding on nickel as an alternative activity booster, which could better fulfil economic requirements of a practical process. Following the more easily scalable impregnation method, no methane formation was detected even at 10 wt.% nickel loading, despite the high stand-alone CO_2 methanation activity of nickel nanoparticles. Altering the amount of indium in In-Al mixed oxide supports (0-100 mol% In) while keeping the nickel content constant corroborated that only very small indium quantities are sufficient to produce the unexpected selectivity switch on nickel. In-depth characterization revealed a highly dispersed two-dimensional nickel phase onto In_2O_3 in low-loading samples, which is accompanied by nanoparticles at high promoter contents. Upon reaction, nickel alloyed with indium atoms from the oxide surface forming indium- or nickel-rich intermetallic compounds depending on the promoter loading (**Fig. 1**). DFT simulations elucidated that indium-modulated nickel species are intrinsically active in the reverse water-gas shift reaction rather than in methanation, while simultaneously providing activated hydrogen to In_2O_3 that enhances the methanol formation rate. This explains why 5 wt.% nickel on the oxide offers an optimal balance between metals' alloying and In_2O_3 surface coverage and hence, between suppression of methanation and fostering of CO_2-to-methanol. Overall, this study identified key structural and electronic phenomena controlling the behavior of the classical hydrogenation metal nickel in contact with indium oxide, relevant to attain a stable promoted system for an emerging application.

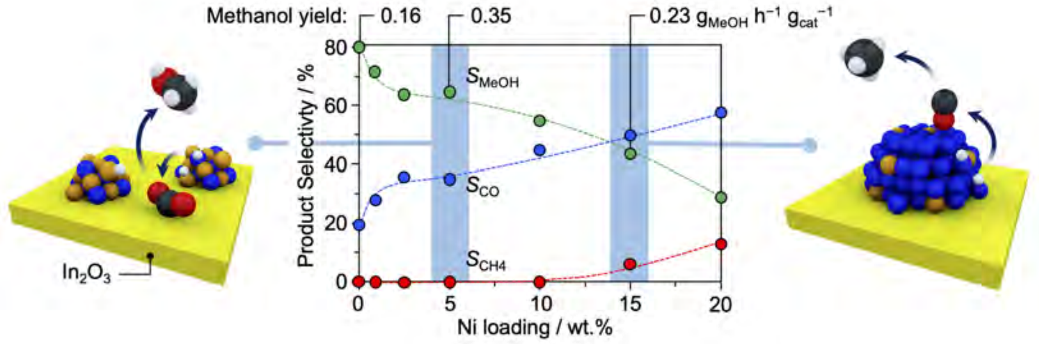

Fig. 1. Catalyst selectivity in CO_2 hydrogenation as a function of nickel loading in Ni/In_2O_3 catalysts. Relevant structures formed under reaction conditions and the dominant hydrogenation mechanisms are depicted for indium- (orange atoms) and nickel- (blue atoms) rich systems to the left and right, respectively.

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Operando Spectroelectrochemical Observation of Surface States and Active Sites in Chalcopyrite Photocathodes for Solar Water Reduction

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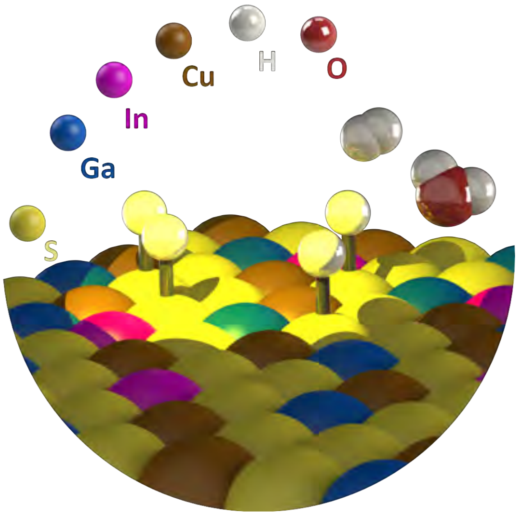
Photoelectrochemical (PEC) water splitting is emerging as a solid platform that could potentially sustain a carbon-free hydrogen community.[1] Among the different photoactive materials that could integrate a PEC device for overall water splitting, the group of I-III-VI semiconductors composed of $CuIn_{0.3}Ga_{0.7}S_2$ (CIGS) is drawing increasing attention as photocathode materials owing to their outstanding optoelectronic properties and tunable band gap. However, serious bottlenecks for the implementation of this class of materials arise from first, the costly fabrication of PV-grade thin-films normally relying on non-scalable vacuum techniques, and second, the need for overlayers/catalyst to perform the hydrogen evolution reaction.[2,3]

Recently, we reported a novel all-solution-processed CIGS photocathode that demonstrates an unprecedented photoelectrocatalytic performance, even in the absence overlayers or co-catalyst.[4] Although the photocurrent onset is still delayed with respect to the flat-band potential, this breakthrough offers an elegant solution for cost-effective solar fuel production. Motivated by its splendid intrinsic catalytic properties and unsatisfactory photovoltage, we deployed three complementary operando spectroelectrochemical techniques viz. photoelectrochemical impedance spectroscopy (PEIS), intensity-modulated photocurrent spectroscopy (IMPS) and operando Raman spectroscopy to find out the reason for the limited photovoltage of this material. The new insights gained into the characteristics of the semiconductor-liquid junction (SCLJ) offer unprecedented information on the interfacial carrier dynamics (e.g. surface states, charge transfer/recombination kinetics and catalytic active sites) on this type of materials. Our results provide a closer look at the SCLJ and build the fundamental understanding for not only shift the onset potential but also further increase the PEC performance.



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Surface over-layer formation and dynamics in the strong metal-support interaction state on supported metal catalysts

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In the early days of catalysis research, oxide carriers were considered to be mere inert carriers for highly dispersed metal nanoparticles. Forty years ago, experiments with noble metal-TiO_2 catalysts demonstrated that oxide supports are far from inert in such catalytic systems and can strongly effect the adsorption behavior of catalysts and the phenomenon was named the strong metal-support interaction (SMSI). SMSI was observed in noble metal (NM) catalysts supported on reducible oxides such as TiO_2. This phenomenon is of paramount importance, since the adsorption behavior of molecules on catalysts is a key factor in determining the catalytic activity. The SMSI phenomenon has, for the most part, been characterized ex situ or by means of model systems.

Here, complementary in situ TEM, ambient pressure X-ray Photoemission Spectroscopy (APXPS) and in situ synchrotron X-ray diffraction (XRD), supported by theoretical density functional theory (DFT) modelling, are used derive a holistic view of the SMSI formation mechanism. The results of this study identify the dual role of hydrogen in the formation of the SMSI state and elucidated the role of oxygen, which had not been recognized before. The migration of reduced titanium oxide, limited in thickness, and the formation of an alloy occur as competing mechanisms during reduction (Fig. 1 A–D). Subsequent exposure to oxygen segregates the titanium from the alloy, and a thicker TiO_X overlayer forms (Fig. 1 E–H). If exposed again to hydrogen the alloy formation and partial surface layer reduction state is re-stabilized. This new understanding of the formation and dynamics of oxide layers on actual powder catalysts, is an important aid to resolve disagreement about the formation mechanism of the SMSI state.

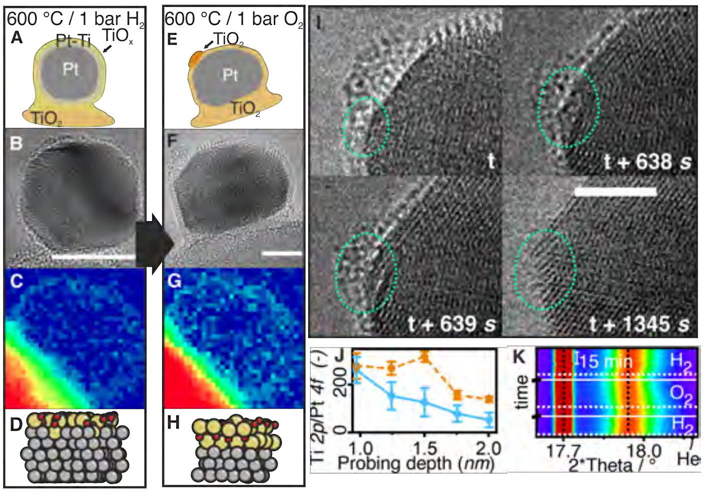

Figure 1: Schematic of the evolution of the SMSI state (A, E); in situ TEM (B, F); EELS mapping of the Ti $L_{2,3}$-edge (C, G), most stable DFT surface model 1 monolayer (ML) TiO + 1 ML Pt_8Ti on Pt (D) in H2 and 2 ML TiO_2 on Pt (H) in O2; dynamics observed with in situ TEM when switching from O_2 to H_2 at 600 °C (I). Depth profiling derived from APXPS and in situ XRD (K) at 17.5 keV revealing the reflection shift of Pt at 17.9° upon gas switches.

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Revealing the structural secrets of random catalyst packings

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Spheres, tablets, rings, double alphas, three-holed trilobes or flower shapes, extruded or tablet pressed – the list of readily available catalyst shapes is long and diverse. More precisely, catalyst geometries became uniquely prevalent for certain reactions as each shape promotes different aspects in fluid dynamics, heat and mass transfer. Still, catalyst shape development has long been a matter of instinct and experience while being significantly constrained by the limits of catalyst manufacturing techniques and experimental characterization capabilities.

But with on and on raising computing capabilities including numerical packing generation tools and computational fluid dynamics, an in-depth and highly resolved virtual representation of catalytic reactors is facilitated. Using these reactor models in virtual screenings, reaction systems can be optimized at highly reduced cost, time and manpower while simultaneously allowing a detailed understanding of specific phenomena.

Numerical Screening Methodology

The catalyst shapes are numerically packed into tubes using an automated python script in Blender™ (procedure adopted from [1]) or the Discrete Element Method tool DigiDEM™ (procedure as of [2]). Subsequently, the random packings are meshed and steady state flow simulations are performed using OpenFOAM®. If desired, dynamic flow simulations (e.g. for residence time distribution evaluation) can be added. The existing script is currently enlarged to allow heat and mass transfer evaluations. In a final step, extensive post-processing is performed allowing an in-depth evaluation of the flow profiles including the discrimination of bulk flow and flow through the holes of holed particles.

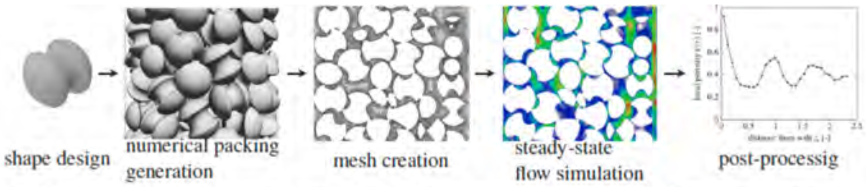

Fig. 1: Simulation procedure, exemplarily shown for the yo-yo shape (taken from [3]).

Validation strategy

The numerical packing procedure is validated with highly resolved x-ray tomography scans, both for simple spheres [4] and more complex shapes (see fig. 2). Pressure drop experiments have been performed [5] to confirm the fluid dynamic simulations.

Results

Several studies have been performed all targeting the evaluation of catalyst shape effects on packing geometry especially porosity (distribution), pressure drop, flow profiles and residence time distribution. These comprise the evaluation of the influence of the tube-to-particle diameter ratio, especially in terms of spheres [4], the influence of shape aspect ratios, e.g. in terms of cylinders [5], or the development of (novel) promising catalyst geometries such as the yo-yo shape (fig. 1) [3]. Currently, the transfer from ideality (in terms of catalyst shape and material) to reality is the main focus of our research.

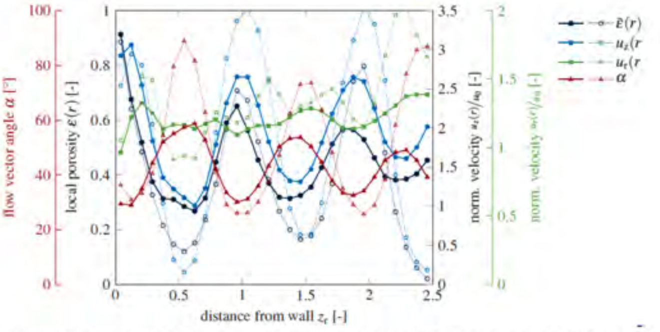

Fig. 2: Radial distribution of porosity, axial flow, radial flow and flow vector angle for the yo-yo shape (fig. 1; sphere with circumferential duct; solid line) and a reference sphere (dotted lines), taken from [3].

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Time-resolved spectroscopy of vanadia-based SCR catalysts under transient conditions

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Understanding the mechanisms behind chemical transformations is key to developing improved catalytic systems. Here we show the application of complementary spectroscopic techniques (Fig. 1a) to elucidate the mechanism of a reaction that has always occupied a central role in emission control research – the selective catalytic reduction (SCR) of NO_x over vanadia-based catalysts [1]. IR spectroscopy revealed that NH_3 could adsorb on Lewis and Brønsted-Lowry acid sites as NH_3 and NH_4^+, respectively. Upon NO addition, the SCR reaction started and adsorbed NH_3 on Lewis sites were consumed preferentially over NH_4^+ species (Fig. 1b), thereby suggesting that the Lewis sites are the active sites for SCR [2, 3]. The catalyst also reduced simultaneously as indicated by UV-Vis spectroscopy (Fig. 1c). Under reaction conditions, vanadyl species (VO_x) adopt various states of coordination, as reflected in the width of the VO_x peak in the time-resolved Raman spectra (Fig. 1d). However, only the coordinatively unsaturated species (i.e., Lewis sites) were found to be responsible for the SCR activity as their response to repeated NH_3 pulses caused their characteristic signal to appear in the phase-resolved spectra (Fig. 1e) [4]. These molecular insights go beyond what can be achieved with spectroscopic experiments under steady-state conditions. Therefore, the synergy between complementary operando techniques, demonstrated here in the particular case of SCR, opens up new possibilities in deciphering the structure-performance relationship of catalysts and other functional materials.

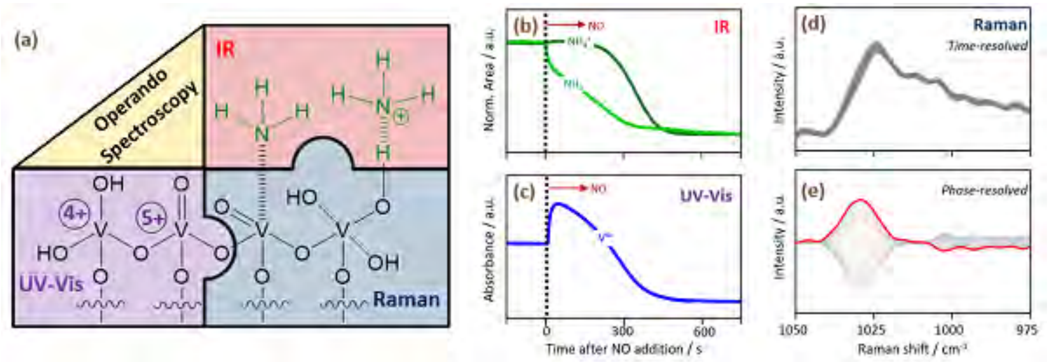

Fig.1 (a) Complementarity between IR, UV-Vis, and Raman spectroscopies. (b) IR signal of adsorbed NH_3 (Lewis) and NH_4^+ (Brønsted-Lowry) species after NO addition. (c) UV-Vis signal of V^{4+} species after NO addition. (d) Time-resolved and (e) phase-resolved Raman signal of the V=O stretch.

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Atom-by-atom active site synthesis by liquid-phase atomic layer deposition

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Understanding and engineering the active sites of heterogeneous catalysts is often elusive due to the high structural complexity of the surfaces involved and the co-existence of different sites. However, a better understanding and control of active sites' atomic configuration could facilitate the optimization and even rational design of heterogeneous catalysts down at the atomic level. The study of single-atom catalysts represents a promising way to assess individual properties of elements. However, the activity of a given site is often controlled as much by the active atom than by its surroundings, and the latter is still challenging to control [1].

Here, we will present a heterogeneous catalyst preparation method that goes beyond single-atom catalyst synthesis by providing additional control over the composition and the structure of the surrounding catalytic site [2]. Our approach based on liquid-phase atomic layer deposition [3], provides an atomic control over the atomic cluster surrounding the active atom by building coordination spheres shell by shell. As a proof of concept, a series of multi-nuclear catalytic clusters were prepared using aluminum, zinc, silicon and magnesium precursors on a high surface area dehydroxylated silica. Catalytic non-oxidative propane dehydrogenation was used as model reaction to probe the influence of the atomic composition and structure surrounding a single site zinc catalyst. Extensive spectroscopy (X-ray absorption, solid state NMR, XPS, STEM-EDX) analysis were performed in order to confirm the targeted structures and better understand the role atomic surroundings on the properties of the single site.

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Metal-organic frameworks as kinetic modulators for branched selectivity in hydroformylation

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Metal-organic frameworks (MOFs) find applications in gas capture and storage, catalysis and various other fields[1]. Their application in catalysis is strongly related to how MOFs can deliver results that are very challenging to obtain with other materials.

Hydroformylation is the reaction of an olefin with syngas to form aldehydes. Since the addition of CO happens at both carbons of the olefinic bond, the product is a mixture of a linear and a branched aldehyde. The selectivity towards the linear aldehyde has been the major focus of the chemical industry. The branched products can be used in the fine chemical industry, but are not easy to obtain selectively unless olefins with directing groups and complex rhodium catalysts are employed[2].

We found by Monte Carlo and DFT simulations that microporous MOFs with UMCM-1 and MOF-74 topologies increase the density of linear liquid olefins beyond neat conditions[3]. At the same time, they reduce the local concentration of H_2 and CO. Exactly these conditions favor the selective formation of the branched aldehydes in cobalt-catalyzed hydroformylation[4]. The experimental procedure consists of simply adding the MOF to the reaction mixture prior to the insertion in the autoclave. Our experiments showed that the branched aldehyde is produced with up to 90 % selectivity in unmodified Co-catalyzed hydroformylation using 1-hexene to 1-nonene as starting material. This selectivity is unreached by homogeneous catalysis making MOFs an interesting kinetic modulator in the fine chemical industry. The experimental results are supported by computational simulations, which show that the active complex has a high affinity for the MOF such that a small amount drastically changes the ratio between linear and branched product

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Operando X-Ray Absorption Spectroscopy Identifies Monoclinic ZrO_2:In Solid Solution as the Active Phase for the Hydrogenation of CO_2 to Methanol

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The direct hydrogenation of CO_2 to methanol is a valuable yet underdeveloped reaction.[1] Recent studies have shown that In_2O_3-based catalysts are promising for this process.[2,3] The active phase of such catalysts is In_2O_{3-x}, i.e. partially reduced india with In–Vo–In active sites.[4] Using *operando* XAS-XRD studies on In_2O_3 nanocrystals (In K-edge), we have shown that these sites deactivate with time-on-stream (TOS) by over-reduction, forming metallic In.[5] ZrO_2 support increases the activity and stability of In_2O_3 during CO_2 hydrogenation, and monoclinic zirconia is superior to tetragonal zirconia phase.[3] However, it remains elusive how the phase of the ZrO_2 support affects the oxidation state and the local structure of the In sites with TOS. Here, In_2O_3 nanocrystals with an average size of 7 nm were studied on amorphous, tetragonal and monoclinic zirconia (In_2O_3/m-ZrO_2, In_2O_3/t-ZrO_2, and In_2O_3/am-ZrO_2 catalysts, respectively). Using a capillary flow reactor interfaced with a gas chromatograph (GC) (Figure 1), combined *operando* XAS (In K-edge)-XRD data were recorded under CO_2 hydrogenation conditions (300 °C, 20 bar, H_2:CO_2:N_2 = 3:1:1).

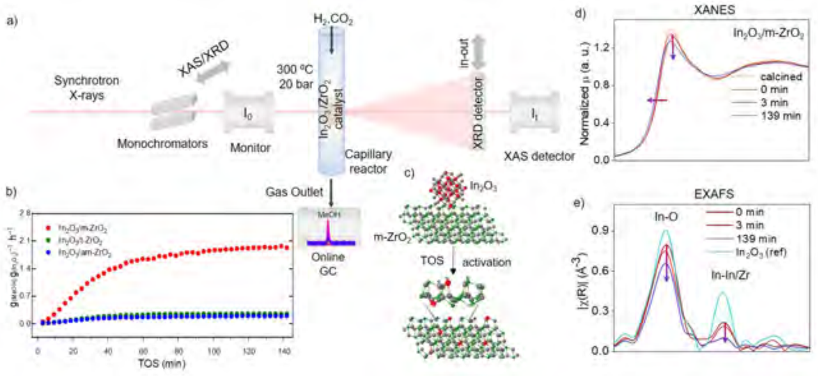

Figure 1. a) Schematic of the *operando* setup for CO_2 hydrogenation to methanol (BM31, ESRF, Grenoble, France), b) catalytic activity (gMeOH $gIn_2O_3^{-1}h^{-1}$) of In_2O_3 on m-ZrO_2, t-ZrO_2 and am-ZrO_2, c) structural evolution of In_2O_3/m-ZrO_2 during CO_2 hydrogenation with selected d) XANES and e) EXAFS data.

The catalytic activity directly correlates to the extent of In_2O_3 reduction and the evolution of the local structure of In sites with TOS, affected strongly by the phase of the ZrO_2 support. Am-ZrO_2 promotes the rapid reduction of In_2O_3 to metallic In leading to an almost inactive amorphous catalyst. The tetragonal ZrO_2 avoids the complete reduction of In_2O_3 to In^0, but gives an average oxidation state of In below +2, which is associated with poor catalytic activity. In_2O_3 on m-ZrO_2 evolves into In^{2+}/In^{3+} sites atomically dispersed in the lattice of m-ZrO_2, which leads to the activation of the catalyst with TOS. The formed ZrO_2:In solid solution functions via active In–V_o–Zr sites (in contrast to less active In–V_o–In sites) that are stabilized by the m-ZrO_2 lattice against deactivation by over-reduction to In^0.

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Development of a Microfluidics-based Assay for the Directed Evolution of Artificial Metalloenzymes using a Cell Surface-Display Strategy

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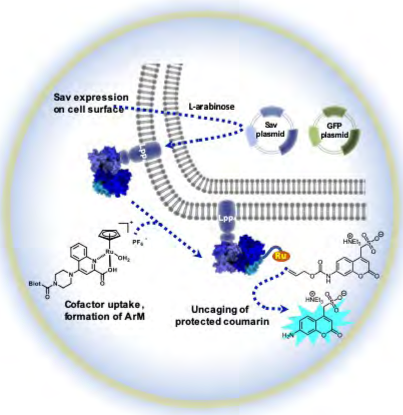
Herein, we present a project combining microfluidics-based single cell encapsulation and artificial metalloenzymes (ArMs) for the high throughput directed evolution of the latter. The catalytic activity and selectivity of ArMs can be optimized by either chemical optimization of the metal cofactor or genetic evolution of the host protein. Single *E. coli* cells with surface-displayed Sav are encapsulated in double emulsion droplets together with a caged coumarin substrate and a biotinylated cofactor. The artificial deallylase catalyzes the uncaging of the protected coumarin yielding a fluorescent product, and the catalytically active mutants can be sorted by fluorescence activated cell sorting (FACS). The identified hits can be subjected to further rounds of optimization. This method can be applied to evolve various ArMs *in vivo* and enables the screening of large libraries in an iterative and straightforward manner.



We present a high-throughput screening assay to perform directed evolution on single *E. coli* encapsulated in double emulsion droplets. The compartmentalization in droplets allowed us to screen a library of over 5’000 mutants within a week, significantly reducing the work load of six months necessary for traditional screening approaches in 96-well plates.

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Copper-Gallium Alloy Structure Determines Promotional Effect of Gallium in the CO_2 Hydrogenation to Methanol

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The hydrogenation of CO_2 to Methanol is a highly promising reaction to mitigate the impact of anthropogenic CO_2 emission[1]. Recent reports show that Cu-based catalysts prepared via Surface Organometallic Chemistry (SOMC) from silica-supported supported Ga(III) single-sites display exceptionally high methanol selectivity.[2] Detailed characterization show that the as-prepared material catalyst corresponds to supported $CuGa_x$ alloyed nanoparticles along with residual Ga^{III} sites that evolves under reaction conditions to generate an intimate mixture of Cu nanoparticles and gallium oxides. These observations contrast with the low activity of the corresponding systems prepared by incipient wetness impregnation with the same Ga and Cu loading, raising the question of what are the structural difference(s) between these two apparently similar and yet different systems.

Here we show by XANES that the promotional effect of gallium is highly dependent on the structure of the alloy formed in the precatalyst. The highly active and selective SOMC derived Cu-Ga@SiO_2 precatalyst was observed to adopt a fcc $CuGa_x$($x<0.2$) structure. In the inactive Cu-Ga_2O_3/SiO_2, it was shown that Ga is substantially more reducible, resulting in the adoption of an hcp $CuGa_x$($0.2<x<0.3$) structure. Consequently, lowering the Ga weight loading in the incipient wetness impregnation system, which was predicted to again result in the favorable fcc $CuGa_x$ structure, lead to restoration of the promotional effect of Ga in Cu-based CO_2 hydrogenation catalysts.

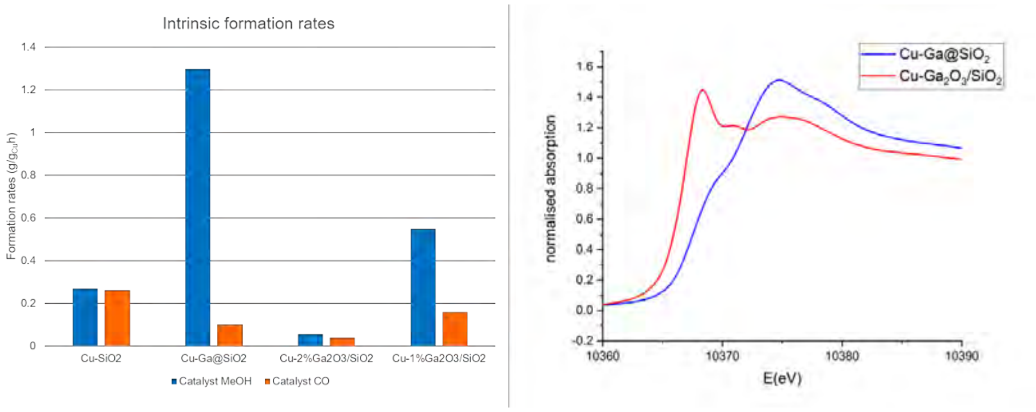

Figure 1: Intrinsic CO and MeOH formation rates of the described catalysts (left), and Ga K-edge XANES of Cu-Ga@SiO_2 and Cu-Ga_2O_3/SiO_2 after reduction at 500°C

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Formation and dynamics of copper-oxo species in zeolites evaluated using oxygen-18 isotope exchange and oxidation kinetics

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Copper-containing zeolites are promising materials for selective catalytic reduction of nitrogen oxides [1] and direct methane conversion to methanol via chemical looping [2]. These materials contain a mixture of copper-oxo species possessing different intrinsic activity. Several structures for active sites were suggested comprising one, two, three or even more copper atoms [2]. In all of them extra-lattice oxygen associated to copper plays a key role in redox transformations [1,2]. Therefore, studying copper reducibility can help in establishing the structure-performance relationship aiding a rational design of better-performing materials.

We employed two complimentary methods to study the formation and dynamics of copper-oxo species in zeolites of MOR, MFI, BEA and FAU topology, with different Si/Al ratios and copper loadings. The first method implies the analysis of kinetics of re-oxidation of the pre-reduced copper-exchanged zeolites yielding the rate constants and activation energies. For copper-exchanged MOR, at least two parallel first-order oxidation reactions were observed. The corresponding apparent activation energies are 20 and 10 kJ/mol. This indicates the presence of several parallel processes taking place during the interaction of oxygen with pre-reduced copper-exchanged mordenite, which in turn indicates the existence of different families of sites. Moreover, variation of Si/Al ratio and copper loading has a significant influence on the relative contributions of these two processes in the overall kinetic behavior.

The second method implies oxygen isotope exchange, which is a powerful tool for determination of lability and concentration for both framework and non-framework oxygen atoms in transition metal-exchanged zeolites [3]. We studied oxygen-18 isotope exchange in the temperature-programmed (TPIE) and isothermal regimes. TPIE shows that copper zeolites with different topology have a different isotope exchange onset temperature. For CuMFI and CuMOR onset temperature is around 700 K, while exchange in CuBEA and CuFAU starts only above 900 K. This indicates that MOR and MFI zeolites contain more reactive copper-oxo species than FAU and BEA. Notably, at temperatures above 770 K, the presence of copper induces isotope exchange of oxygen atoms of the zeolite framework in concert with extra-framework ones. To quantitatively describe the mechanism of exchange and compute the corresponding exchange rates and activation energies, we developed a numerical model, which accounts for both framework and extra-framework oxygen atoms. This model indicates that copper-oxo species induce lability of about 30% of zeolite framework oxygen atoms. At the same time, exchange of extra-framework oxygen occurs several orders of magnitude faster than those in the framework.

In summary, copper-containing zeolites with different framework type, Si/Al ratio and copper content demonstrate different dynamics of framework and extra-framework oxygen atoms, apparently, due to presence of copper-oxo species with various structures. The amount of reacting non-framework oxygen together with the known copper content enable to determine the elemental composition of copper-oxo clusters (Cu/O ratio), and, therefore, can help establishing of the structure of the active sites.

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Thermal degradation of UiO-66: Glass formation

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UiO-66 is a zirconium based MOF, which is well known due to its extraordinary thermal stability up to 500°C. However, in situ PXRD of UiO-66 containing missing linker defects showed that it loses its crystallinity at 250°C indicating the absence of a crystalline framework. TG-MS shows that some amount of water is lost at 230°C which is paralleled by loss of crystallinity and formation of a glassy MOF. In this state, the MOF is stabilized by short range bond forces between the inorganic cationic units and organic anionic ligands. This is further supported by the fact that no further mass loss occurs over the wide temperature range up to 450°C. At this temperature, the MOF decomposes into highly ordered monoclinic and tetragonal phases of zirconia nanoparticles supported over the porous carbon matrix with the evolution of carbon dioxide, water and some traces of benzene. Formation of glassy state for UiO-66 has not yet been reported to our knowledge. This study will help better understand the degradation mechanism of the MOF as well as generation of new MOF composites having unique properties.

Etched Nickel Foam as promising Catalyst for Overall Water Splitting

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Water splitting into hydrogen and oxygen is one of the most important challenges in the field of sustainable energy research, and it is becoming an essential strategy for renewable and green energy generation.[1] Electrocatalytic hydrogen production can potentially solve the rising energy demand of global society. Currently, the most active materials for electrocatalytic water splitting are iridium and platinum-based catalysts for the oxygen evolution reaction (OER) and hydrogen evolution reactions (HER), respectively.[2] As these rare and precious noble metals are less convenient for scaling up in industrial purposes, intense efforts have been put forward to design efficient and stable water-splitting catalysts based on transition-metal elements, which are earth-abundant and offer an alternative to precious metal catalysts. Nickel foam, a low cost, and commercially available material has been widely applied as an electrode for overall water splitting, because of its enhanced electronic conductivity, large surface area, porous structure, and high activity.[3] Therefore, its optimization is a sustainable way to design efficient catalysts for electrochemical hydrogen generation. In this work, an etched nickel foam catalyst was synthesized and characterized by powder XRD, XPS, FT-IR, Raman, SEM, and HRTEM. Besides, the activity of this catalyst during OER and HER was studied with cyclic voltammetry (CV), linear sweep voltammetry (LSV), and electrochemical impedance spectroscopy (EIS). The optimized catalyst showed promising overpotential of 220 mV for OER at a current density of 60 mA $cm^{-2,}$ which is competitive with the noble metal-based catalyst such as iridium oxide. Results showed that the etching process has a significant effect on the electrochemical OER and HER activity of nickel foam.

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Introducing Lewis acidity in zeolites by Ion-Exchanging Extra-Framework Cations

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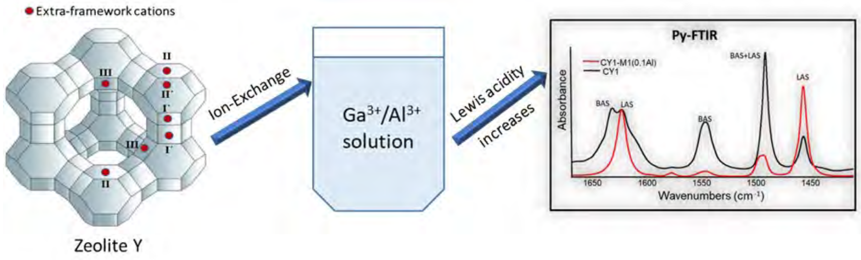
In this work, a simple ion-exchange route to introduce Lewis acidity in zeolite Y is developed. Extraframework gallium and aluminum cations are established as the Lewis acid sits. ^{27}Al-MAS NMR spectroscopy and pyridine probed by Fourier Transform Infrared (Py-FTIR) spectroscopy enabled quantification of the Lewis acid sites in the cation-exchanged materials. The exchanged samples were further investigated by XRD, N_2-physisorption, SEM, HRTEM and ICP analysis. The X-ray diffraction results show successful incorporation of ions at extraframework positions without destroying the zeolitic framework. No significant change in framework aluminum coordination was observed for the gallium and aluminum-exchanged samples; The Lewis acid sites in the latter samples adopt an octahedral coordination during the NMR measurement. A noticeable increase in total LAS content as evident from Al-NMR, Py-FTIR spectra and their quantitative data is observed in all cation-exchanged zeolite Y materials. Different cations' concentration as well as different number of ion-exchanges were tested in order to study in detail the effect of EF cations on subsequent LAS concentration. The zeolite with low Si/Al ratio reached a maximum amount of LAS of 0.62 mmolesg^{-1} which is a promising candidate for Lewis acid-catalyzed reactions.



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Low-Temperature Activity and Initiation of Reduced Supported Mo and W Olefin Metathesis Catalysts

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Olefin metathesis is an atom-efficient reaction that can produce olefins of diverse structures and functionalities, with applications ranging from petrochemicals to pharmaceuticals. Heterogeneous catalysts (based on Mo or W), are used industrially for light olefin conversion at high temperatures (>400 °C), though the routes by which high-oxidation-state metal oxo sites form catalytically-active species remain largely unknown. This is due in part to the low quantities and complicated distributions of metal species (isolated sites, oxo oligomers, and/or oxide particles), which yield different reaction properties and spectroscopic signatures that are challenging to interpret. Correspondingly, the applications of heterogeneous metathesis catalysts have been limited outside of light olefins. To determine the site-specific reactivities of supported olefin metathesis catalysts, well-dispersed supported W or Mo oxo sites are synthesized via surface organometallic chemistry (SOMC) techniques. The resulting catalysts are active for low-temperature (1,2 However, the initiation mechanisms of such supported metal oxo sites are still largely unknown, as are the relations between catalyst synthesis protocol, active site structure, and reactivity.

Here, the initiation and deactivation properties of heterogeneous metathesis catalysts are shown to depend strongly on the architecture of the olefin substrate, as well as the surface composition of the catalysts that depend on the conditions of synthesis and activation. Mo- and W-based metathesis catalysts, synthesized either by SOMC using different molecular precursors or by conventional incipient wetness impregnation (IWI) approaches, exhibit markedly different reaction properties upon activation. Specifically, the supported Mo oxo catalysts are found to exhibit substantially improved activity for metathesis of diverse terminal olefins compared to their W analogues, in keeping with past studies on well-defined molecular and supported metal alkylidene catalysts.[3] The initiation and reaction kinetics are additionally found to depend on the architecture of the molecular metal oxo precursor, the choice of reducing agent (high temperature reducing conditions or molecular organosilicon reductants), and the substrate structure (chain length, branch positions). The experimental analyses provide new design criteria for metal oxo-based metathesis catalysts that are expected to be generalizable to industrial systems, enabling new applications for heterogeneous olefin metathesis catalysts.

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Hydride Catalysis

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A detailed understanding of hydrogen species at catalyst surfaces is of crucial importance to understand catalytic hydrogenation processes. Accordingly, the number and activity of hydrogen on the catalytic surface has been in the focus of surface scientists for a long time. With the advent of synthetic energy carriers as renewable alternatives to fossil fuels, new processes such as membrane reactions are explored to increase the energy efficiency of the conversion reactions. In these cases, the number and activity of hydrogen in the subsurface and possibly in the bulk are additional, usually neglected parameters. In particular in metal hydrides, these parameters are subject to external parameters, i.e., pressure and temperature, and compete with the surface parameters. We explored the use of the archetypal intermetallic hydride $LaNi_5$ to catalyze the hydrogenation of CO_2 and of ethylene. At room temperature in a CO_2/H_2 mixture, $LaNi_5$ dissociates hydrogen as evidenced by the hydride formation to $LaNi_5H_6$, but does not catalyze CO_2 reduction. At higher temperature, the latter reaction may proceed, but the material rapidly oxidizes. The hydrogenation of ethylene on $LaNi_5$ proceeds at room temperature and the dissociation of hydrogen was found to be limiting. We show using an experimental operando approach that the amount of hydrogen in the bulk is the relevant parameter for the hydrogenation reaction being a compelling example of "hydride catalysis".

Silica-supported cobalt for the heterogeneous aerobic oxidation of methane to a methyl-derivative

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A scale-flexible process for the direct selective oxidation of methane to primary oxygenates is of high interest academically and industrially, yet a commercially feasible approach has yet to be realized due to a number of challenges. Most notably, the facile over-oxidation of methanol in heterogeneous catalytic systems leads to a selectivity-conversion limit that greatly restricts achievable yields [1-3], and therefore necessitates a strategy to protect methanol from further oxidation in order to surpass this limit [3, 4]. One such strategy for product protection is the esterification of the methanol product to a more stable methyl ester less prone to over-oxidation, which has been demonstrated previously in various homogeneous catalytic systems [5]. However, the commercial potential of many current methane-to-methyl ester processes is hindered by their use of homogeneous catalysts [5], reliance on economically infeasible oxidants, and operation under harsh corrosive operating conditions, all factors that pose difficulties for industrial process development [6].

In this study, we demonstrate an approach for the direct partial oxidation of methane to a methyl ester using solely a molecular oxygen oxidant under milder reaction conditions than those typical of similar esterification approaches. Using a reaction medium of trifluoroacetic acid diluted in an inert perfluoroalkane co-solvent, methane oxidation to methyl trifluoroacetate occurs under conditions more conducive for heterogeneous catalysis, and the product can be subsequently recovered through a simple liquid-liquid extraction with a polar solvent. We find that silica-supported cobalt catalysts are highly active in this system and can heterogeneously catalyze the reaction in methane- and oxygen-based yields of 22% and 15%, respectively, with turnovers that are higher than those typically observed in homogeneous systems using a molecular oxygen oxidant. The promising performance and advantages characterizing this novel system therefore signify a substantial advancement of direct methane partial oxidation technologies.

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Carrier induced modification of palladium nanoparticles on porous boron nitride for selective alkyne hydrogenation

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Tailoring the properties of active sites in precious metal catalysts, a crucial feature to ensure their efficient utilization, often heavily relies on the use of chemical modifiers to overcome intrinsic constraints. The introduction of these additives can increase the synthetic complexity and environmental footprint of technical catalysts.[1,2] Carriers are an integral component of many catalytic systems and can have distinct effects on the reactivity of supported metals, that are mainly of interfacial or structural nature.[3] In contrast, little is known about potential of carriers to introduce chemical modifiers into supported metals. Here, we show that a porous boron nitride carrier can directly modify supported palladium nanoparticles (Pd/PBN), originating unparalleled performance in the continuous semi-hydrogenation of alkynes (**Fig. 1**). Analysis of the impact of various structural parameters reveals that using a defective high surface area boron nitride and ensuring a palladium particle size of 4-5 nm is critical to maximizing the rate per metal atom. Simulations show that boron can diffuse from defects (e.g. Stone Wales, Schottky, or B defects) in the carrier to the palladium subsurface. These dopants induce an electronic modification, creating slightly electron deficient regions on the surface of palladium that confine ensembles which retain their metallic character. This arrangement of active sites suppresses side reactions and hence originates high selectivity that is preserved even at almost full conversion. The practical approach highlights an unexplored potential of using tailored carriers for catalyst design.

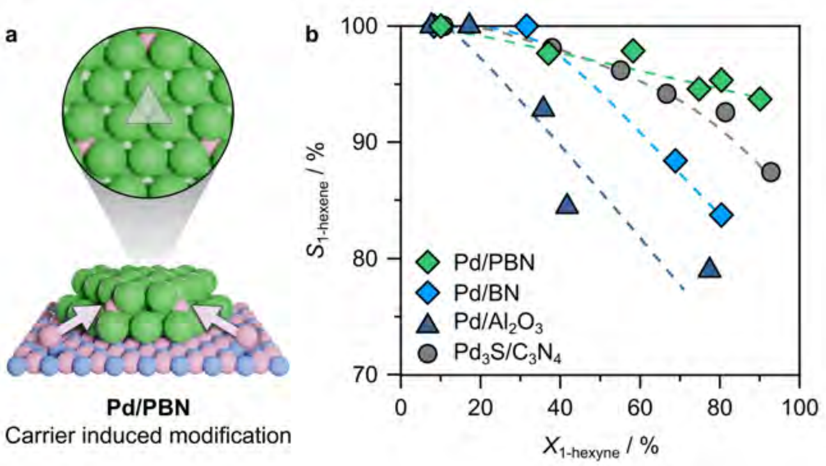

Fig. 1. a Scheme of the carrier-induced modification of Pd/PBN identified in this work. The diffusion of boron (pink atoms) into the subsurface of the palladium nanoparticles (green atoms) creates spatially isolated surface ensembles with metallic character (grey triangle). **b** Conversion vs. selectivity plot demonstrating the superior performance of Pd/PBN compared to state-of-the-art catalysts in the semi-hydrogenation of 1-hexyne.

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Defective UiO-66 and its interaction with solvents, acids and bases

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UiO-66 is an extremely robust metal organic framework (MOF) based on $[Zr_6(OH)_4O_4]^{12+}$ nodes[1]. Because of its high thermal[2], mechanical[3] and chemical[4] stability it is an appealing material for catalysis, gas capture and material science. Defects in the framework structure increase its porosity[5], but the reduced connectivity of the framework decreases its thermal stability[6]. Here, we elucidate the role of defects on the chemical stability of UiO-66. Post-synthetic modification procedures and the use of this material in catalysis cause the exposition of the framework to acids and bases in solution of organic solvents, making understanding the interaction of defective UiO-66 with such chemicals essential.

We synthesized a highly defective UiO-66, with a surface area of 2000 m^2/g, and systematically studied its reactivity upon treatment with solvents, acids and bases. We used standardized reaction conditions and characterized the spent material by nitrogen physisorption and powder X-ray diffraction. In this way we could quantitatively and qualitatively compare the effect of these treatment on the porosity and the crystallinity of the framework.

We studied the effect of different acids and bases in aqueous solution, and showed how the pH of the solution is not the only parameter to play a role. Potassium carbonate caused a loss of more than 70% of the surface area while 1,1,3,3-tetramethylguanidine and triethylamine reduced it by only 50%, despite guanidine being the stronger base. We observed how the interaction with solvents with basic sites, such as water and tetrahydrofuran significantly affects the crystallinity and the surface area of the material, while inert solvents, such as dichloromethane do not. This might be caused by the reduced connectivity of the metal nodes to the framework. We studied the effect of acids and bases in organic solvents as well, observing how the solvent capacity to selectively solvate species, or to modulate acid-base interactions, cause completely different textural properties from the ones obtained in water. Sulfuric acids caused the complete destruction of the framework when it was not modulated by water, while solutions of triethylamine in organic solvents decreased the surface area by less than 15%.

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Assessment of the impact of mesopore geometry in hierarchical MFI zeolites on the performance in methanol to olefins by hysteresis scanning

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Elucidation of the complex role of hierarchical pore networks is crucial to design zeolites with enhanced functionality.[1,2] Differential hysteresis scanning (DHS) by gas sorption has been introduced as a powerful tool to map the geometry of mesopores within hierarchical faujasite-type zeolites, yielding an unprecedented picture of the impact of common demetallation treatments on porosity development.[3] Here, the scope and versatility of DHS is extended through the investigation of the effect of multilayer adsorption on mesopores of distinct geometry in materials prepared via bottom-up or top-down synthetic approaches (**Fig. 1**). Furthermore, the use of oxygen as sorbate is shown to extend the resolution of this technique, permitting determination of the geometry of smaller mesopores that are non-hysteretic when argon is used. This knowledge is applied to assess the impact of the pore architecture on the performance in the conversion of methanol to olefins, where coke formation is the primary cause of catalyst deactivation. The findings contribute key information for the design of hierarchical zeolite catalysts.

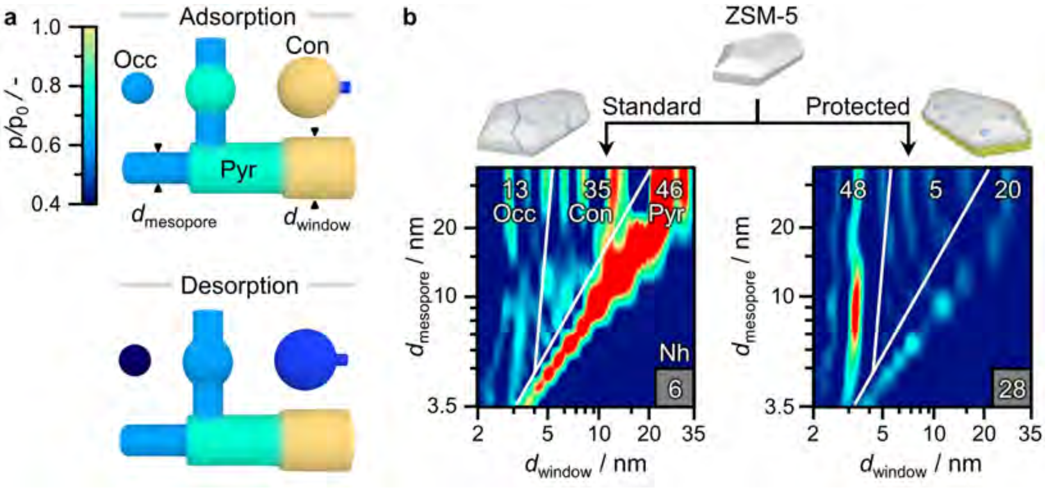

Fig. 1. **a** Schematic representation of the influence of the mesopore geometry on the adsorption and desorption behavior with increasing relative pressure and definitions. **b** Contour plot derived from Argon isotherm at 87 K of two hierarchical ZSM-5 zeolite prepared with different synthesis conditions indicating the percentage of pyramidal (Pyr), constricted (Con), occluded (Occ), and non-hysteretic (Nh, grey box) mesopores.

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Time-resolved XAS study of the formation of cobalt hydride intermediates of cobaloxime catalyst during photoinduced pH jump

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The storage of solar energy in H_2, derived from the photo-catalytic splitting of water, has attracted renewed interest as a possible source of renewable energy. For this process to ever become sustainable, it is important that the photo-catalyst is based on earth abundant metals. The understanding of the detailed catalytic mechanism is the basis to design and develop those systems. The difluoroboryl-bridged Co(II)-diglyoxime complex is one of the most active earth-abundant photocatalytic H_2 evolving catalysts reported to date.[1]

In this work, we study a cobaloxime catalyst $Co(dmgBF_2)_2$ (dmg^{2-} = dimethylglyoximato dianion) combined with photoinduced pH jump experiments to observe reaction intermediates. As shown in Figure 1(a), the reaction is proposed to proceed as a catalytic cycle through 4 main states: initial Co(II), intermediate Co(I) and hydride intermediates Co(III)H and Co(II)H. The hydrides are essential steps to produce H_2. Electrons can be transferred from the photosensitizer to the catalyst, which reduces Co(II) to Co(I). At catalytic conditions and continuous light illumination a Co(III)H intermediate is present in very low quantities and therefore has not been observed up to date. We suggest forming it transiently using photoinduced pH jumps caused by pulsed laser light absorption by a photoacid which exhibits pK_a shift on excitation and produces proton donors. We also expect to see Co(II)H at longer time scales as a result of Co(III)H reduction by Co(I). Time-resolved XAS can be used to characterize the structure of these intermediates.[2,3,4] Optical pump-probe experiments with a photoinduced pH jump have been reported in the literature[5] with reaction rate constants determined from the decay of the Co(I) signal. Based on these results we expect a maximal concentration of Co(III)H at ~2 µs after pH jump and significant signal from Co(II)H at ~1 ms for our conditions.

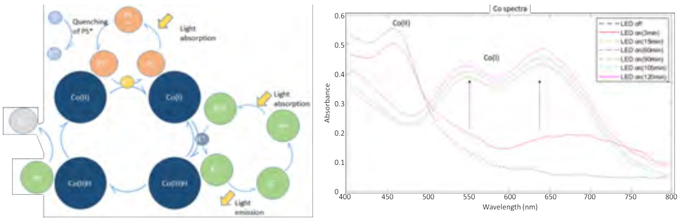

Figure 1. (a) Scheme of reaction mechanism catalyzed by cobaloxime. PS is the photosensitizer, D is the electron donor, and AH is the photoacid. (b) UV-vis spectra recorded before and after of visible light irradiation on anhydrous CH_3CN solutions of Co(II), $[Ir(ppy)_2(bpy)](PF_6)$ (photosensitizer) and ^{Br}NaphOH (photoacid) in the presence of TEOA (5%, electron donor).

In a flowing jet system integrated within a chamber filled with N_2, Co(II) can be converted into Co(I) quickly in the presence of the photoacid ^{Br}NaphOH when illuminated with a blue LED to excite the photosensitizer. The UV-vis spectra for Co(I) and Co(II) are shown in Figure 1(b). Under the LED illumination, the formation of Co(I) is clear from its two-band spectrum while the ~450 nm band of Co(II) decreases. Time-resolved XAS experiments are planned for June this year (delayed due to the COVID induced lockdown).

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Design and Evolution of Chimeric Streptavidin for protein-directed Dual Gold Catalysis

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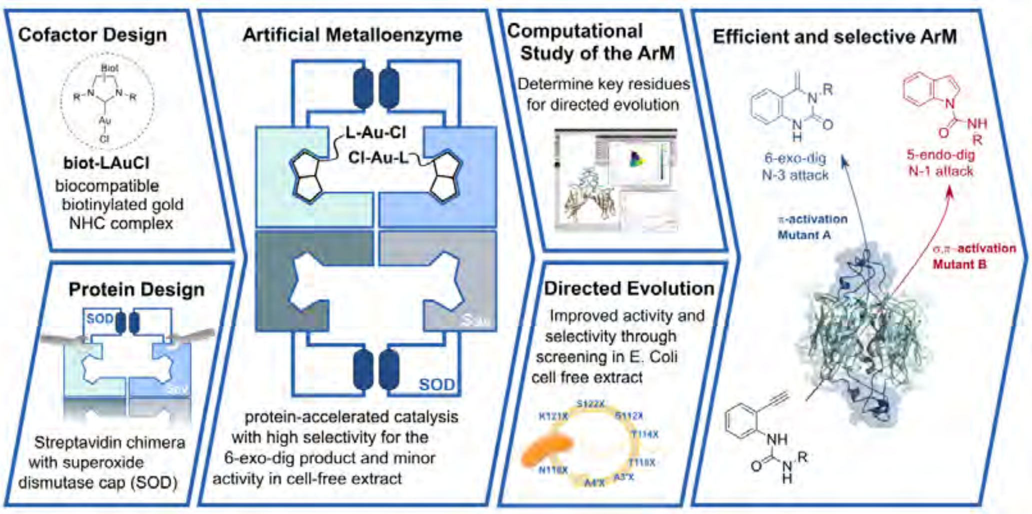
Artificial metalloenzymes (ArMs) provide a unique means to pre-organise metal complexes within a well-defined environment. Thanks to its unique topology, streptavidin (Sav), which presents two biotin moieties facing each other within a hydrophobic vestibule, may allow to develop ArMs for dual catalysis. To validate this hypothesis, we present the first dual gold-based ArM for regioselective hydroamination that proceeds via a σ,π-activation of a terminal alkyne. To shield the active site of the ArM, Sav was fused with a 34 aminoacid loop from superoxide dismutase c (Sav_SOD). The activity of the resulting chimeric ArM was subsequently fine-tuned by directed evolution to give access to both the 5-endo dig- (anti-Markovnikov) and 6-exo dig (Markovnikov) regioisomers, depending on the Sav_SOD mutant. QM-MM calculations help rationalize the remarkable effect of single point mutations on regioselectivity. Importantly, the free biotinylated cofactor displayed no activity in the absence of Sav_SOD and was not irreversibly inhibited in *E. coli* cell-free extracts, thus opening fascinating perspectives towards *in vivo* catalysis.



In-situ investigations of spillover over molybdenum-based catalysts

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In catalysis, the phenomena of spillover plays an important role and describes the transport of species that are adsorbed or formed on one surface onto another surface, which does not adsorb or form this species under the same conditions.[1] As Teichner suggested, “there is a very high probability that spillover exists in the mechanism of most catalytic reactions or may be introduced by a new design of the catalysts”[2]. Therefore, creation of catalitically active sites for NH_3 synthesis and decomposition; methanol synthesis, hydroisomerization, alkenes and aromatics hydrogenation are processes that can benefit from mechanistic insights of the hydrogen spillover phenomenon. Because of its importance in catalysis, interest in spillover has grown significantly over the years. This study is focusing on molybdenum oxides that find widespread application in catalysis and the semiconductor industry. One of the most striking features of molybdenum oxides is the versatility of their catalytic properties. Molybdenum oxide-based catalysts are active and selective in many reactions belonging to both redox and acid-base processes, such as hydrogenation, oxidation, isomerization, and addition and decomposition reactions. Solid-acid catalysts based molybdenum(VI) oxide have been explored widely due to stability, regenerative properties and high activity at a wide range of reaction temperatures. The synergistic effect between an activator and a support is relevant when cosidering techological applications. Bifunctional catalysts consisting of acidic oxides and noble metals showed high efficiency in the acid-catalyzed reactions, such as alkylation, reforming, and cracking. It is known that hydrogen bronze materials (H_xMoO_3) have great application potential as hydrogenation/dehydration catalysts, fuel cell electrodes, and electrochromic devices. The question that remains unanswered is how hydrogen migrates over the surface under catalyticall-relevant conditions [3]. Both theoretical studies and indirect observations via surface sensitive techniques are unable to resolve the laterally and temporally aspects of this phenomenon for mechanistic insight.The aim of observing spillover is acheivable by the use of a novel method for real-time observation of gas-phase induced surface dynamics: variable pressure- or environmental-SEM (ESEM). Although traditionally mostly used for the study of biological, non-conducting samples, its applicability in the field of catalysis and corrosion science has already been demonstrated [4]. Surface-sensitive imaging and real-time observation of collective dynamics under controlled atmosphere at pressures between 10^{-5} to 10^{+2} Pa is ideally suited to complement laterally integrating spectroscopic methods, such as in situ XPS and XPEEM. Compared to surface-science methods, the ESEM is relatively flexible in terms of sample geometry and size and can thus be used to bridge the “materials-gap” between model systems and complex real-world catalysts. The high sensitivity of the gaseous detection device in the ESEM enables the detection of changes in the work-function due to surface coverage of adsorbates. Thus, the goal of resolving spatially and temporally the role of the surface structure, the relation between hydrogen difussion and reducibility of the substrate and the structural response of the surface will shed light on the spillover effect in relevant catalytic systems.

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Molecular-Level Insight in Supported Olefin Metathesis Catalysts by Combining Surface Organometallic Chemistry, High Throughput Experimentation, and Data Analysis

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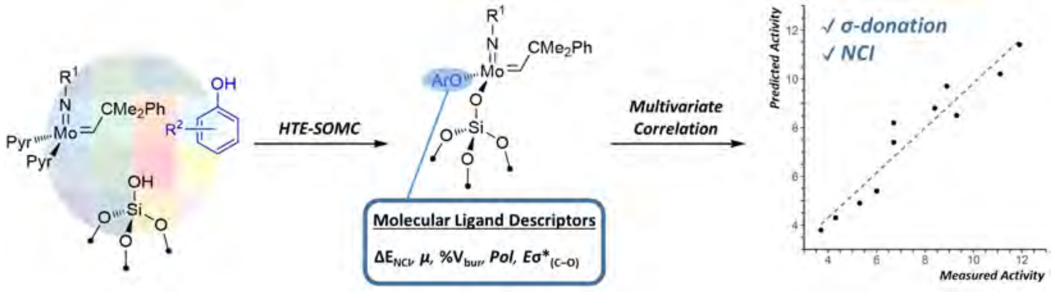
Metathesis is a very active field of research ranging from petrochemical production to the synthesis of polymers and fine chemicals.[1] While improvement of molecular metathesis catalysts over the last three decades was driven by a rational approach based on structure-activity studies, research for the corresponding heterogeneous catalysts is still mostly empirical. Here, we disclose a high-throughput experimentation (HTE) approach combined with a multivariate modelling study based on robotized experimentations to prepare and test libraries of heterogeneous olefin metathesis catalysts, derived from Surface Organometallic Chemistry (SOMC).[2] Namely, a library of heterogeneous catalysts generated in situ from 35 phenolic ligands, two Mo precursor complexes and dehydroxylated silica support, was obtained and evaluated by automated catalyst testing; activity trends were rationalized by multivariate analysis providing molecular-level structure-activity relationship.[3]



Combined Surface Organometallic Chemistry and high-throughput experimental approach for identification of active catalysts in homodimerization of 1-nonene.

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Structure and reactivity of low-nuclearity iron-based catalysts on carbon nitride for alkyne semi-hydrogenation

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To reduce the environmental footprint of selective hydrogenations, there is a need for decreased reliance on precious metal catalysts. Earth-abundant iron would be an attractive alternative, but, although molecular iron complexes are known to catalyze alkyne semi-hydrogenation, the use of this element in heterogeneous catalysts has been scarcely studied likely due to the poor hydrogen splitting ability of the bulk metal.[1] Nanostructuring approaches to reduce the size of metal ensembles can drastically alter reactivity patterns.[2,3] By supporting iron carbonyl or pentadienyl complexes with defined nuclearity on mesoporous carbon nitride, we here demonstrate that iron single atoms attain superior performance compared to larger ensembles. The single atom catalyst shows higher metal-specific rates and stable performance in the continuous, liquid-phase hydrogenation of a range of substituted alkynes (**Fig. 1**). The exclusive presence of atomically-dispersed species is confirmed by a combination of microscopy and spectroscopic techniques. Analysis of the electronic properties identifies a correlation between performance and a more oxidized nature of iron with decreasing nuclearity of the metal precursor. Molecular-level simulations uncover the respective structure, stability, and reactivity of the iron species of distinct nuclearity. This contribution accentuates the potential of nanostructuring for greening up hydrogenation catalysts.

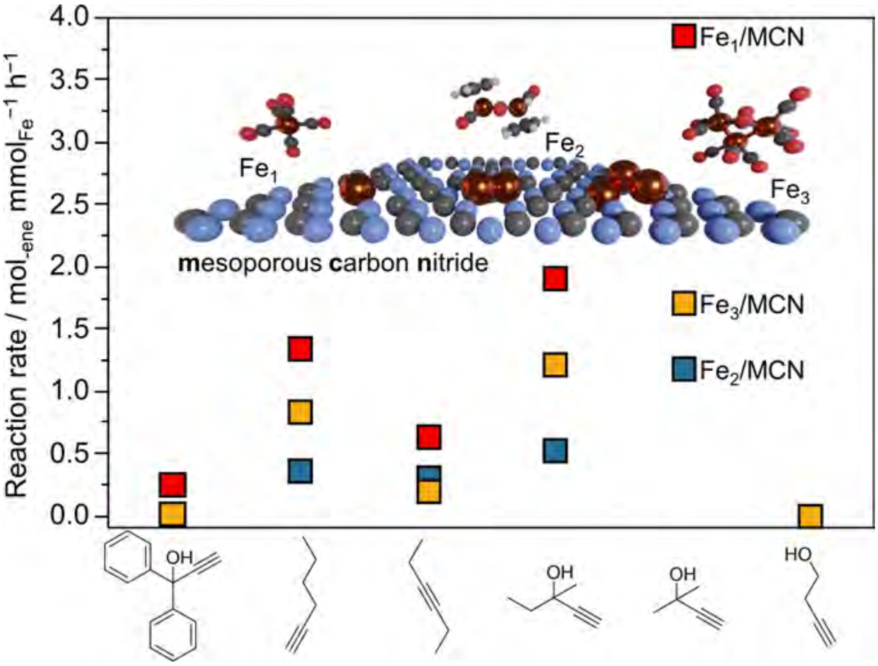

Fig. 1. Performance of low-nuclearity iron catalysts based on carbon nitride in the semi-hydrogenation of various substituted alkynes.

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Windowless *in situ* imaging at increased pressure: Perforated MEMS chips in an ETEM

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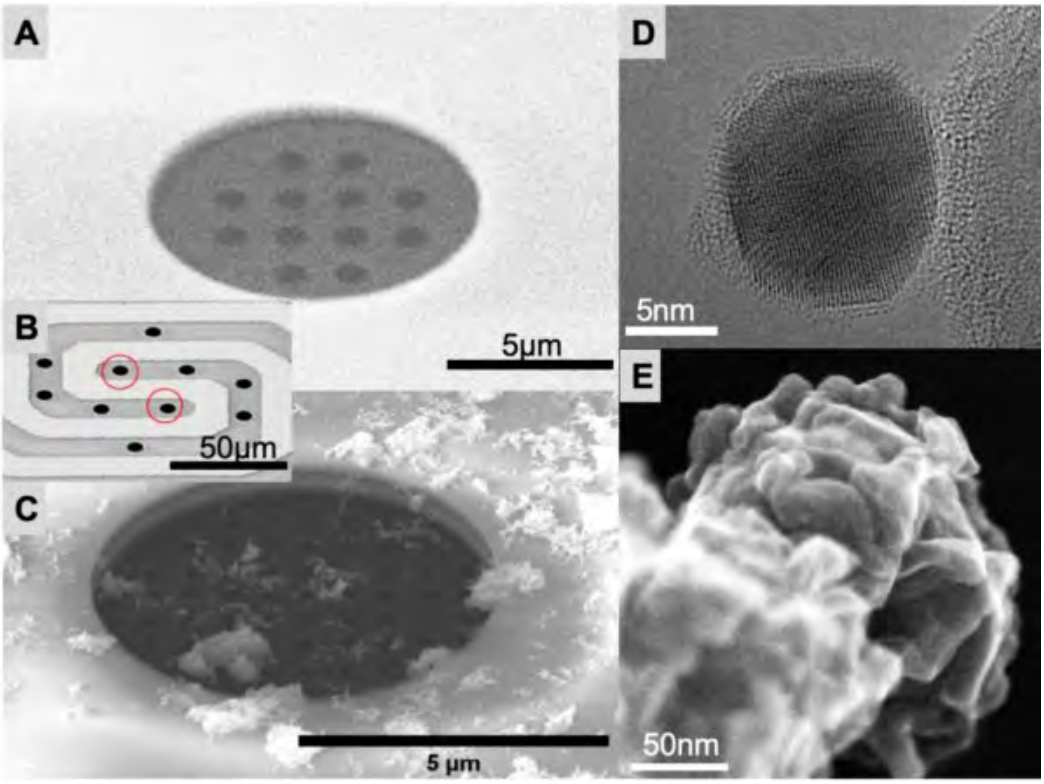
For our understanding of processes that are induced by the interaction of a material with its surrounding, observation of isolated systems in vacuum, such as in conventional transmission electron microcopy, are not sufficient. E.g. core-shell nanoparticles used in catalysis might reconstruct to form an alloy at relevant gas conditions that cannot be observed in vacuum[1]. I*n situ* observation of processes related to catalysis are either performed using environmental TEM´s, i.e., a TEM equipped with a differentially pumped objective lens[2], or with the use of membrane-type gas cell holders[3]. Experiments in environmental TEM´s are generally pressure limited, with a significant pressure gap compared to catalytic conditions. Detection of catalytic conversion is difficult. In case of membrane-type gas cell holders, experiments at pressures up to a few bars and, due to a better confinement of the gas-phase and reduced dead-volume, detection of catalytic conversion is possible. One drawback of the micro-reactors is associated to the use of electron transparent windows that shield the vacuum in the TEM column against the gas volume of the micro-reactor. Although electron beam transparent, the two 30 and 50 nm thick SiN_x windows add significant background to the recorded images and reduce the obtainable resolution. The ability to detect nm-sized particles and light elements is reduced. In order to combine the advantages of both approaches, we performed *in situ* experiments in a TEM, which can be operated in an environmental mode, using micro-reactors with perforated SiN_x windows (Figure 1A-C). This way, we can obtain high image quality while simultaneously preserving relatively high pressures inside the reactor cell. Windows were cut into the top and bottom membrane using focused ion beam milling. This approach makes it possible to perform window-free observation (Figure 1D, SMSI induced coverage of a metal nanoparticle), record secondary electron images (Figure 1E, copper oxide) and to measure conversion.



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Structure - adsorption relationship in metal-organic frameworks revealed by molar surface area and molar adsorption capacity

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Metal-organic frameworks (MOFs) are a class of porous, crystalline materials that feature high surface area and gas uptake properties. The principle of reticular chemistry allows synthesizing MOFs with the same topology but employing different linkers and metal nodes. So far, the impact of changing the linker and metal in MOFs on the surface and sorption properties has been mostly assessed by gravimetric methods. However, using gravimetric measurements on a molar problem does not allow to understand the underlying principles and design better materials.

Molar properties were already employed to compare the performance of different MOFs [1-3]. Using the approach to compare uptake per unit cell, the assessment of different MOFs was limited to isoreticular ones. Here, we propose a novel concept, which allows to compare MOFs with different topologies for the first time by including several structural parameters. We were able to identify MOF topologies that are more efficient in creating surface area per linker length and to describe the influence of linker substituents. This concept yields correlations between performance and molecular properties giving additional insights and widens the designing possibilities.

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Platinum single-atom catalysts for sustainable vinyl chloride production

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A worldwide replacement of the toxic mercuric chloride catalyst applied in vinyl chloride manufacture *via* acetylene hydrochlorination[1] is slowed down by the limited durability of alternative catalytic systems, including gold single-atom catalysts[2,3] and graphene-confined ruthenium nanoparticles[4] at high space velocities. Here, we demonstrate that platinum single atoms on carbon carriers are substantially more stable (up to 1073 K) than their gold counterparts (up to 473 K), enabling facile and scalable preparation and precise tuning of their coordination environment by simple temperature control. By combining kinetic analysis, advanced characterization, and density functional theory, we assess how the platinum species determines the catalytic performance and thereby identify Pt(II)−Cl as the active site, being three-times more active than platinum nanoparticles (**Fig. 1a**). Remarkably, we show that platinum single atoms exhibit outstanding stability in acetylene hydrochlorination and surpass the space-time-yields of their gold-based analogs after 25 hours time-on-stream, qualifying as candidate for sustainable vinyl chloride production (**Fig. 1b**).[5] Going beyond hydrochlorination, our approach to control the reactivity of platinum atoms is generally applicable to other areas and gives perspectives for the tunability of metal species for a wide range of catalytic applications.

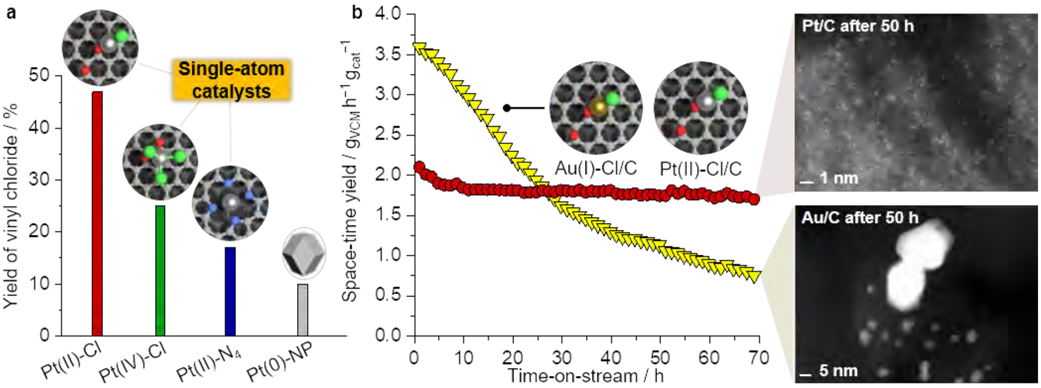

Fig. 1. a Initial catalytic activity of distinct Pt SACs and nanoparticle-based catalysts in acetylene hydrochlorination. **b** Time-on-stream performance of Pt and Au-SACs, accompanied by their respective STEM images after use in acetylene hydrochlorination for 50 h, visualizing preserved atomic dispersion of Pt and Au particle agglomeration.[5]

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Na K-edge XANES combined with ^{23}Na-NMR unravel structure-property relationships in Na_2CO_3-promoted CaO-based sorbents for CO_2 capture

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Calcium oxide-based solid sorbents have emerged as a promising material for high temperature (600-700 °C) CO_2 capture from flue gas due to a high theoretical CO_2 uptake of 0.78 g/g and high cost-efficiency[1]. However, these sorbents are prone to deactivation during cyclic operation due to severe sintering at elevated temperatures[1]. Significant improvements in the cyclic CO_2 uptake of CaO have been reported for a variety of stabilizers and promoters including alkali carbonates such as Na_2CO_3[2]. Yet, the mechanisms behind the effect of alkali carbonates on the CO_2-capture performance of CaO remain poorly understood[1,2]. Here, we investigate the correlation between the structure and the CO_2 uptake performance of CaO-based sorbents prepared via amorphous-Na_2CO_3-$CaCO_3$ precursors, with varying Na_2CO_3 content. To this end, we use ^{23}Na-ssNMR, TEM-EDX and XANES (assisted by theoretical simulations) to correlate the structural properties of the sorbent with the CO_2 capture performance determined by thermogravimetric analysis.

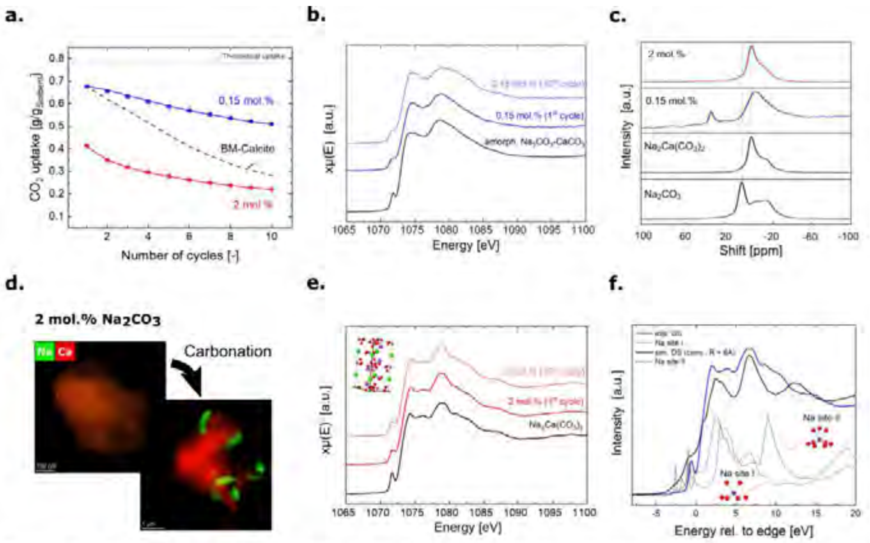

Figure 1: a) Cyclic CO_2 uptake of the sorbents b) Na K-edge XANES of: 0.15 mol.% Na_2CO_3-CaO sorbent after 1 and 10 cycles; and amorphous Na_2CO_3-$CaCO_3$ reference c) ^{23}Na-NMR spectra of 0.15 mol.% and 2 mol.% Na_2CO_3-CaO sorbents after 10 carbonation-calcination cycles (carbonated state) and references (γ-Na_2CO_3 and $Na_2Ca(CO_3)_2$) d) TEM-EDX maps for Na and Ca for the 2 mol.% Na_2CO_3-CaO sorbent before and after carbonation e) Na K-edge XANES of the 2 mol.% Na_2CO_3-CaO sorbent (enhanced deactivation) as a function of cycling number and $Na_2Ca(CO_3)_2$ reference e) Simulated and experimental spectra of $Na_2Ca(CO_3)_2$

CO_2 uptake experiments reveal a promotional effect on the CO_2 cyclic uptake for low Na_2CO_3 concentrations (i.e., 0.1 – 0.2 mol.%), while for higher Na_2CO_3 contents ≥ 2 mol.% a drastic decrease of the CO_2 uptake is observed. Using ^{23}Na-NMR, XAS and TEM-EDX, we show that in the poorly performing material (CaO with ≥ 2 mol.% Na_2CO_3) a crystalline double salt phase, i.e., $Na_2Ca(CO_3)_2$, forms during carbonation which segregates as micron-sized particles on the surface of CaO. For concentrations of 0.1 – 0.2 mol.% Na_2CO_3, we found an amorphous Na_2CO_3-$CaCO_3$ phase homogeneously distributed within the CaO particles. This phase has two leading benefits. Firstly, our morphology analysis shows that the pore network is being stabilized. Secondly, our kinetic analysis reveals an improvement in the effective diffusion of CO_2, ultimately enhancing the CO_2 uptake during carbonation.

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Role of Water on the Structure of Palladium for Complete Oxidation of Methane

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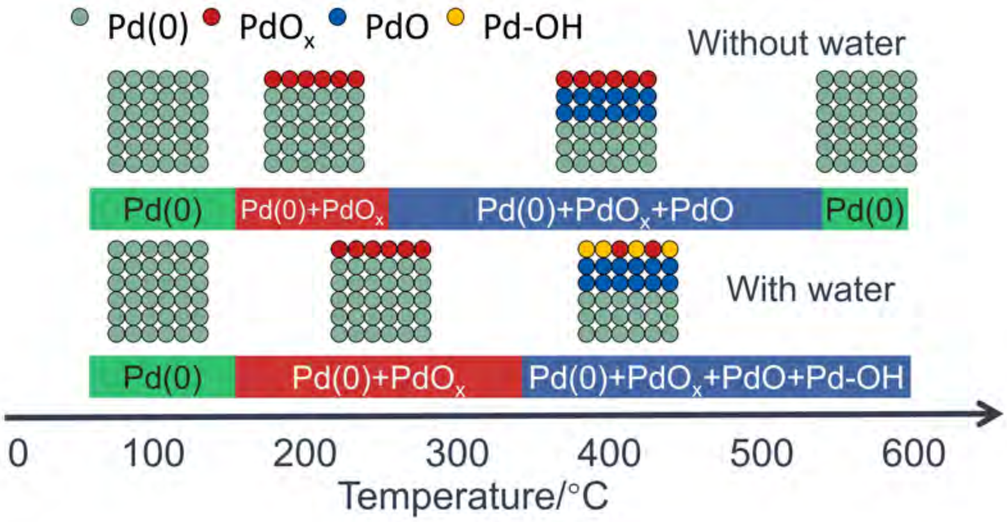
Palladium-based catalysts are attractive for methane combustion on natural gas vehicles at low temperatures. By means of ambient pressure X-ray photoelectron spectroscopy, we investigated the reaction on a palladium foil exposed to different mixtures at increasing temperature. Water affects the long-term catalyst stability and blocks the active sites, ascribed to the hydroxyl inhibition effect. We investigated such an effect both under steady-state and transient reaction conditions to understand the mechanism of inhibition. The hydroxyl formation on the surface of palladium blocks the sites for methane activation, postponing the formation of the active palladium oxide phase in the bulk.



Xiansheng Li, Xing Wang, Kanak Roy, Jeroen A. van Bokhoven, and Luca Artiglia, *ACS Catal.* 2020, 10, 10, 5783–5792

Dynamic semiconductor-electrolyte interfaces during photoelectrochemical water oxidation

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Understanding the interfacial phenomenon between semiconductor surface and liquid electrolyte is essential for designing efficient photoelectrochemical devices.[1] The boundary property is very sensitive to those operation conditions that are applied.[2] In this work, we studied the kinetics of the oxygen evolution reaction (OER) at the hematite photoanode-electrolyte interface under regulated experimental conditions, namely applied bias, photon flux and electrolyte pH. With the help of pseudo-steady state cyclic voltammetry (CV) measurements, transient photocurrent spectra and (photo)electrochemical impedance spectroscopy,[3] three descriptors (electron transfer coefficient, proton reaction order, reaction order of surface holes) which are capable of probing the change of the underlying reaction kinetics were derived independently. The evolution of every descriptor is specifying the change of the reaction pathway depending on the modulation of corresponding experimental parameter. In this way, it is now possible to identify or predict the detailed OER kinetics for a given set of reaction conditions. Meanwhile, our analyses here highlight the complexity of the reaction kinetics during experimental conditions, and point to a dynamic behavior of the reaction mechanisms depending on the interplay of multiple reaction conditions. To the best of our knowledge, this is the first attempt to probe the kinetics of water oxidation reaction at hematite photoanode surfaces while covering a very wide range of reaction conditions.

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Operando Spectroelectrochemical Observation of Surface States and Active Sites in Chalcopyrite Photocathodes for Solar Water Reduction

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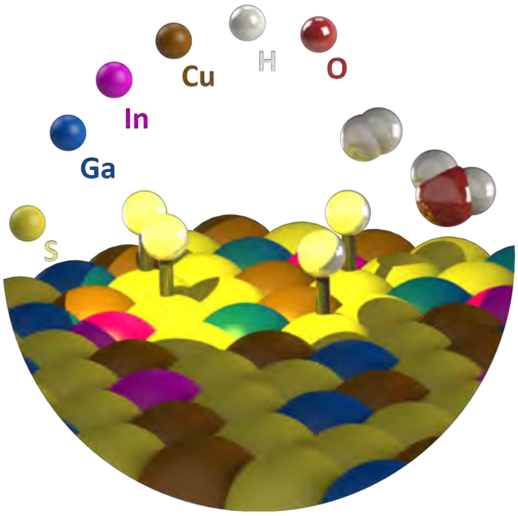
Photoelectrochemical (PEC) water splitting is emerging as a solid platform that could potentially sustain a carbon-free hydrogen community.[1] Among the different photoactive materials that could integrate a PEC device for overall water splitting, the group of I-III-VI semiconductors composed of $CuIn_{0.3}Ga_{0.7}S_2$ (CIGS) is drawing increasing attention as photocathode materials owing to their outstanding optoelectronic properties and tunable band gap. However, serious bottlenecks for the implementation of this class of materials arise from first, the costly fabrication of PV-grade thin-films normally relying on non-scalable vacuum techniques, and second, the need for overlayers/catalyst to perform the hydrogen evolution reaction.[2,3]

Recently, we reported a novel all-solution-processed CIGS photocathode that demonstrates an unprecedented photoelectrocatalytic performance, even in the absence overlayers or co-catalyst.[4] Although the photocurrent onset is still delayed with respect to the flat-band potential, this breakthrough offers an elegant solution for cost-effective solar fuel production. Motivated by its splendid intrinsic catalytic properties and unsatisfactory photovoltage, we deployed three complementary operando spectroelectrochemical techniques viz. photoelectrochemical impedance spectroscopy (PEIS), intensity-modulated photocurrent spectroscopy (IMPS) and operando Raman spectroscopy to find out the reason for the limited photovoltage of this material. The new insights gained into the characteristics of the semiconductor-liquid junction (SCLJ) offer unprecedented information on the interfacial carrier dynamics (e.g. surface states, charge transfer/recombination kinetics and catalytic active sites) on this type of materials. Our results provide a closer look at the SCLJ and build the fundamental understanding for not only shift the onset potential but also further increase the PEC performance.



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Hybridization of Fossil and CO_2-Based Routes for Ethylene Production using Renewable Energy

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Carbon capture and utilization (CCU) has recently gained broad interest as an effective strategy to curb carbon emissions while creating economic value. At present, direct electro and thermo catalytic technologies are the focus of intense research.[1,2] The former employs electric potential in the presence of water to reduce the CO_2 molecule, while the latter comprises hydrogenation of CO_2 in tandem with electrocatalytic water splitting. Focusing on ethylene, the most demanded organic compound by tonnage, we here compare the two main CCU routes with the established fossil-based process (naphtha cracking). From an economic perspective, the CCU routes are economically unattractive even when considering externalities (indirect cost of environmental impacts), i.e., 1.7 to 3.9-fold higher cost compared to fossil-based ethylene. This poor economic performance of the CCU routes is mainly due to the high energy costs at current electricity prices. Nonetheless, we find that the CCU routes significantly improve the carbon footprint (236%) and impacts on human health, ecosystem quality, and resources compared to fossil-based ethylene (64, 140 and 80%, respectively). Acknowledging the current limitations of CCU, we explore CCU-fossil hybridization schemes to smooth the transition towards more sustainable chemicals. Remarkably, we find that hybridization allows carbon-neutral (cradle-to-gate) ethylene at a premium of only 30% over current price levels. Among the CCU routes, the thermocatalytic is to date economically and environmentally superior due to the higher energy efficiency of electrocatalytic water splitting. However, CO_2 electroreduction shows a larger potential.

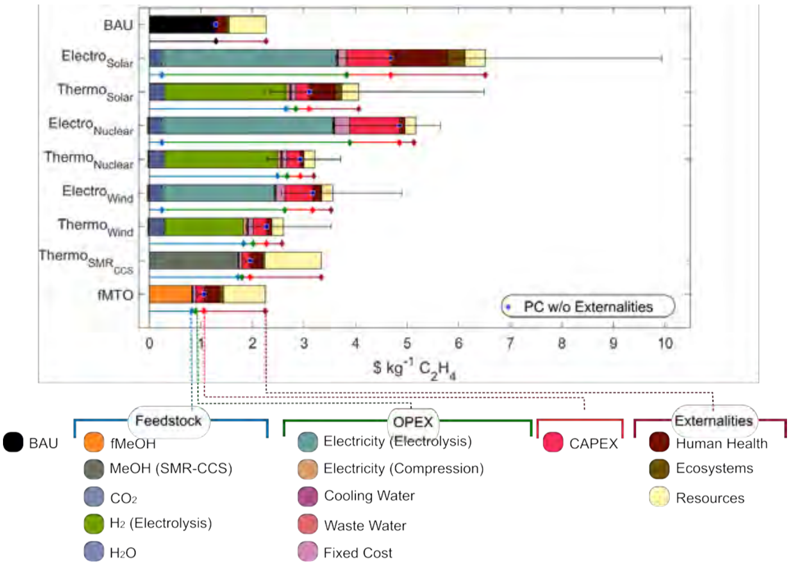

Figure 1 Breakdown of the total annualized cost for the electro- and thermo-route with externalities, comparing with steam cracking of naphtha (fossil-based ethylene, BAU). The thermo CCU (MTO) uses MeOH produced from either electrolytic H_2 or SMR H_2 with CCS, while the fossil MTO (fMTO) uses fossil MeOH from syngas from natural gas. The electrocatalytic step is powered by wind, nuclear, or solar energy and the CO_2 is captured in natural gas power plants. The uncertainty bars denote 5th and 95th percentiles for the electricity cost, excluding externalities, and the CO_2 purchase cost (worst and best estimate).

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Revealing the dynamics of Sabatier reaction by IR thermography

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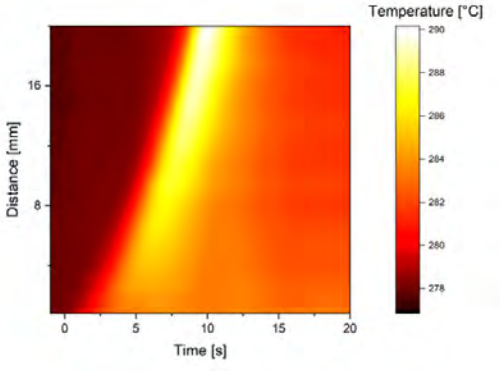
The exploitation of the Sabatier reaction in energy applications has to face important variations in the gas load, as well as in the gas quality and composition, due to the intermittent H2 source. An important challenge in the operation of the reactor is thus to keep the necessary quality of the product gas in a large range of inlet conditions[1]. In order to evaluate the effect of these variations in the reactor operation conditions, we performed a series of dynamic CO2 methanation experiments changing gas composition and space velocity. These experiments were analyzed by means of IR thermography to obtain a temperature profile with high time and space resolution. Furthermore, a fast MS spectroscopy analysis method was developed, to integrate the large spectrum of temperature data available with highly time resolved information on composition. We manufactured a special reaction cell, with a ZnSe window above the catalyst bed. The material of the window is selected to allow transmission of the signal in the reaction conditions. The thermal images were recorded with an InfraTec VarioCAM® hr camera with 50 Hz acquisition rate and a resolution of 640x480 pixels. A 2 wt.% Ru catalyst supported on Al_2O3 was used in all of the experiments. The temperature profile in time and space at the activation of the Sabatier reaction, under stoichiometric CO_2:H_2 ratio, is shown in figure 1. When the catalyst is pre-heated at 280 °C, the reaction starts immediately at the reactor inlet and the reaction front propagates through the cell. As the reaction front advances, the extent of the hotspot increases, reaching the maximum at the reactor outlet. This is due to the heat transport related to gas convection, that generates a larger heat production, as the reaction rate is increased with temperature. This first reaction hotspot is generated by the initial surface reduction state of the catalyst, which allows for a fast reaction rate. As the first reaction front has moved through the reactor, the reaction rate is decreased and the reactor reaches the steady state operation, with a hotspot of moderate extent. In order to investigate the reaction activation in different conditions, the CO_2/H_2 mixture is fed to a catalyst exposed first to a CO_2 or H_2 rich environment. When the cell is filled with H_2, the Sabatier reaction is activated in a similar way as over the fresh catalyst, with a first activation front that moves regularly through the reactor. When the cell is filled with CO_2, the reaction is strongly inhibited, due to the formation of carbon species on the catalyst surface. In this case, the activation front is not observed and the whole catalyst bed activates at the same time, when an appropriate degree of surface reduction is reached. In our presentation, we will report the results of the dynamic investigations in a wide range of conditions, including the modification of the space velocity or when using diluted gases.



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Efficient membrane-based solutions for increasing sustainability of processes in fine chemical and pharmaceuticals industry

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The global increasing attention towards sustainability and resource efficiency, within Chemical industry is often translated making processes more compact, safer, more energy-efficient, and environmentally friendly. Process and discovery chemists are then challenged to develop and optimize complex chemical syntheses, focusing on the less efficient unit operations often separation, purification and isolation.

Two aspects having a major impact on all process are management of process side streams and catalyst recycling.

In this study we present the outcomes of

1.) A research project, initiated by the pharmaceutical companies Janssen and Ajinomoto Bio-pharma services (former Omnichem) and the OEM company InOpsys, on the development of innovative membrane-based solutions for the sustainable and economic treatment of the typical solvent-rich, and often very alkaline waste waters, that are currently incinerated externally.

2.) The integration of a in line membrane separation protocol with the gold-catalyzed hydration of alkynes. Several gold catalysts were screened in the hydration of diphenylacetylene, and catalyst recycling was achieved up to 4 times using [Au(OTf)(IPr)] (3). In addition, the retained catalyst in the last catalytic cycle was analyzed and readily converted into its synthetic precursor, using a straightforward treatment.

Defect-induced activity enhancement in Ce-substituted lanthanum strontium manganites for solar thermochemical CO_2 splitting

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Solar thermochemical CO_2/H_2O splitting has the potential to generate industrial-scale quantities of synthetic liquid fuels while simultaneously limiting greenhouse gas emissions. Thermochemical pathways utilize concentrated 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. The two-step thermochemical temperature-swing cycle involves an endothermic reduction step of a redox metal oxide at high temperatures (1573–1773 K), generating oxygen vacancies, followed by an exothermic re-oxidation step with CO_2 and H_2O at low temperatures (1073–1273 K).[1] Particularly, non-stoichiometric ceria ($CeO_{2-\delta}$), is considered as the state of the art redox material because of its structural stability, variable Ce^{3+}/Ce^{4+} valence, and rapid kinetics. However, ceria suffers from low reducibility and demands high temperatures (≥1773 K) to achieve even moderate oxygen non-stoichiometry ($\Delta\delta$).[2,3] Perovskite oxide ($ABO_{3-\delta}$) materials are currently emerging as an alternative class of redox materials, mainly because of their thermodynamic and structural tuning options through engineered composition, which, however comes at the expense of slow re-oxidation kinetics. Here, we have identified a novel class of Ce substituted (at A- and B-sites) lanthanum strontium manganite (LSM) perovskite oxide redox materials, which can overcome the individual limitations of pure ceria and perovskites. Amongst them, 25% Ce-substituted LSM displayed 2 times faster CO_2 splitting ability than pure LSM and 1.2 times higher CO yield than commercial ceria, when tested using thermogravimetric analysis (TGA) and IR furnace reactor experiments. In addition, long-term redox cycling stability experiments showed a steady and gradual increase in CO production rate over 100 thermochemical cycles, mainly due to inter diffusion of Ce in a two-phase material. Furthermore, detailed structural characterization using in-situ high temperature neutron, synchrotron X-ray and electron diffraction experiments elucidated the role of structural distortions and induced oxygen vacancy defects in enhancing the thermochemical CO_2 splitting ability of these redox materials.

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Revealing the Reaction Mechanism of Benzenediols in Catalytic Pyrolysis Using HZSM-5

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Lignin, as one of the three main components of biomass, can be converted to bio-oil, rich in value-added chemicals, such as benzene, toluene, xylenes (BTX) and phenols by catalytic pyrolysis.[1, 2] Lignin is a three-dimensional amorphous polymer yielding a complex product distribution after pyrolysis. Performing catalytic pyrolysis is done with the aim to control the product selectivity. Understanding the catalytic pyrolysis reaction mechanism by detection of highly reactive and elusive intermediates, such as radicals and ketenes, would help to tackle this challenge. Imaging Photoelectron Photoion Coincidence Spectroscopy (iPEPICO) as developed at the Vacuum Ultraviolet Beamline of the Swiss Light Source at Paul Scherrer Institute is a versatile tool to analyze complex reaction mixtures ranging from combustion to catalysis, to identify reactive intermediates and an advanced understanding of reaction mechanisms. [3, 4, 5]

Benzenediols, especially catechol, are common structural units in the lignin network and were investigated by py-iPEPICO. The results indicate that depending on the position of the OH group, different reaction mechanisms are responsible for the conversion of catechol, resorcinol, and hydroquinone. Catechol showed the highest conversion and produced fulvenone, an elusive ketene species, which evades detection using conventional py-GC/MS techniques. Fulvenone is formed by dehydration of catechol, which is made possible by the interaction between two adjacent hydroxyl groups. We also observed the isomerization between the three isomers as a minor process. Overall mechanistic pictures of the reaction mechanisms were obtained and will be discussed in this contribution, which will guide the development of predictive models to make lignin catalytic pyrolysis more selective.

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Bifunctional catalysts for coke hydrogenolysis in methanol-to-hydrocarbons processes

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ZSM-5- and SAPO-34-based catalysts that are employed in commercial methanol-to-hydrocarbons (MTH) processes face the challenge of inevitable activity loss caused by the formation of coke deposits [1-3]. This necessitates their periodic regeneration via coke combustion that wastefully converts the entrapped carbon equivalents into CO_2 and promotes the degradation of the catalyst structure due to evolution of steam under high oxidation temperatures (>823 K). Herein, we present a novel class of bifunctional MTH catalysts, M/ZSM-5, entailing ZSM-5 zeolite promoted with metal nanoparticles that can reduce the rate of coke formation while preserving the product distribution patterns of the conventional zeolites (**Fig. 1a,b**). Moreover, in contrast to the bare zeolites, the activity of the coked bifunctional materials can be regenerated via coke decomposition with H_2 at moderate temperatures (**Fig. 1a**). The hydrogenolysis of coke is generally enhanced by bringing the metal nanoparticles in close vicinity to Brønsted acid sites (e.g., via ion-exchange and/or the introduction of mesoporosity) and by increasing the H_2 pressure. In our ongoing research, we are investigating the impact of the catalyst structure and reaction conditions on the nature of the hydrogenolysis products, as well as the reactivity of different coke species towards H_2. Our preliminary results suggest the preferential evolution of C_1-C_2 hydrocarbons and substantial variations in the susceptibility of various coke components towards hydrogenolysis. The latter allows to decompose selected fractions of coke. Coupled with subsequent activity assessment of the partially regenerated MTH catalysts, this enables to uncover the deactivation potential of various coke components, which remains unexplored until today.

Fig 1. The MTH a) activity and b) product distribution over ZSM-5 and metal-promoted ZSM-5 catalysts in their fresh form and after hydrogenolysis subsequent to their deactivation.

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Multiscale First-Principles Calculations of Propane Dehydrogenation on PtGa Nanoparticles Supported on Ga-Doped Silica

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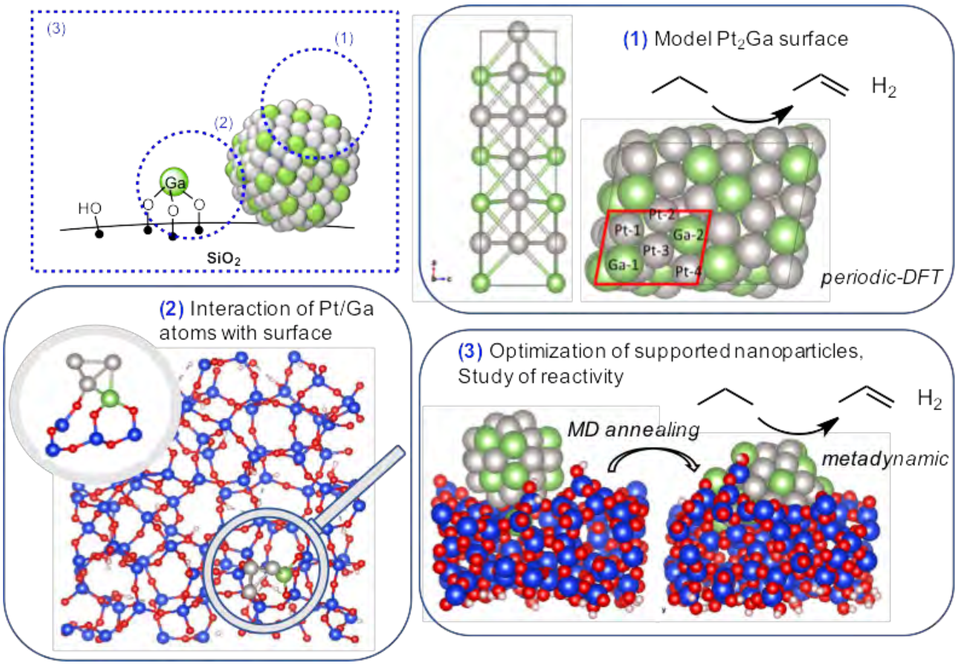
The reaction of dehydrogenation of light alkanes has seen a renewed interest in the recent years due to the increasing propene demand and the exploitation of Shale gas.**[1]** PtGa systems are attractive catalysts for propane dehydrogenation (PDH) and have been recently implemented in production plants.**[2]** However, the nature of the active site in PtGa-based catalyst is still under debate.**[3]** We recently reported the synthesis and characterization of a silica-supported PtGa-catalyst for PDH, using Surface OrganoMetallic Chemistry (SOMC).**[4]** This methodology allowed us to obtain highly active, selective and stable PDH catalysts, while also providing detailed information about the catalyst structure. Here, we use *ab initio* modeling to interrogate what determines the structure of PtGa alloy and what is the role of Ga in driving the activity of PtGa systems compared to pure Pt and Ga isolated sites. The structure and activity of PtGa alloy was first evaluated by investigating crystalline PtGa bulks and their associated surfaces by periodic-DFT approach. However, this simple periodic model cannot help to state the role of the supporting oxide as well as the cluster/nanoparticle size effects that experimentally proved to impact strongly the reactivity of these systems. We thus investigated the role of the interface on the structure and the reactivity of supported 1 nm Pt and PtGa nanoparticles on model silica and Ga-doped silica surfaces by using *ab initio* molecular dynamic and metadynamic to allow efficient exploration of the relevant configurational space.



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Catalyst design for direct CO_2 hydrogenation to transportation fuels

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Sustainable production of liquid hydrocarbon transportation fuels is imperative to effectively combat global warming and fulfil the rising demand for fuels. In this regard, technologies able to efficiently utilize carbon dioxide (CO_2) as a feedstock offer a powerful approach to tackle both pressing issues. At present, the direct thermocatalytic hydrogenation of CO_2 into transportation fuels using renewable hydrogen comprises the emerging technology with the most promising prospects. Besides for cheaper renewable H_2,[1] catalysts showing higher selectivity and durability shall be attained to meet economic requirements of a large-scale implementation. The transformation of CO_2 to long chain hydrocarbons (HC) is based on the reverse water-gas shift reaction (RWGS), where CO_2 is converted to CO, and subsequent Fischer-Tropsch synthesis (FTS). About 20 catalysts have been reported, based on the FTS elements iron and cobalt. The more studied Fe-based catalysts were applied both in bulk and supported forms, and were typically promoted by K, Na, Cu, Mn, and Zn, reaching a selectivity to C_{5+} hydrocarbons of 65%. Co-based systems showed inferior performance due to the low partial pressures of CO set by the RWGS equilibrium, limiting chain growth and increasing methane selectivity. Herein, we study novel Fe-based catalysts, exploring the effects of the synthesis route, of the presence of alkali or transition metals as promoters, of carriers acting as co-catalysts for the RWGS reaction, and of catalyst pretreatment conditions on fostering the demanding chain elongation step. Structure-performance relationships established through advanced characterization will guide synthesis and testing via high-throughput methods to accelerate the identification of catalysts displaying superior long-chain HC yield and stability for green gasoline, diesel, and kerosene production.

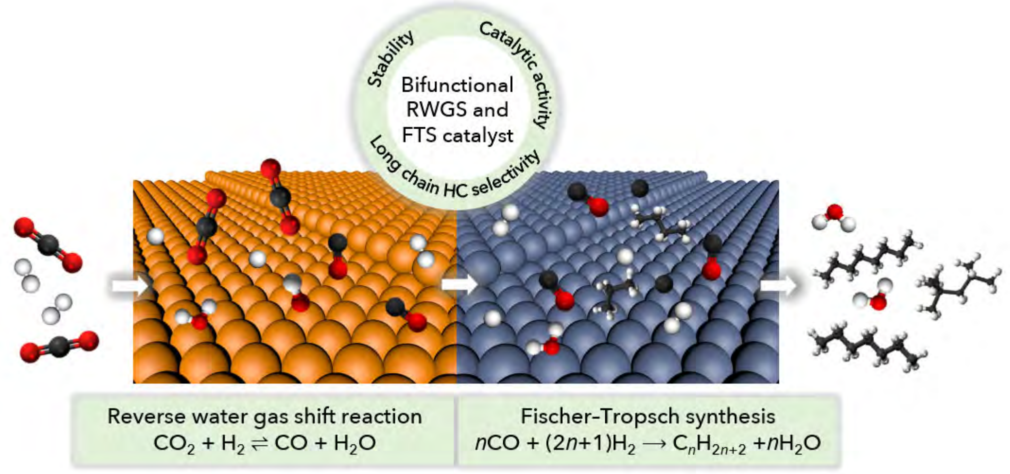

Figure 1. Schematic illustration of CO_2 hydrogenation to transportation fuels on a bifunctional catalyst that combines RWGS and FTS active sites.

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Impact of mixed CO_2-CO feeds on methanol synthesis over In_2O_3-based catalysts

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[1]ETH Zürich, [2]Total Research and Technology, Feluy

A recent analysis at the planetary level revealed that the thermocatalytic production of methanol using CO_2 and renewable hydrogen is sustainable in absolute terms.[1] At present, indium oxide (In_2O_3) represents a breakthrough catalyst for this reaction, showing unrivaled selectivity and stability when supported on monoclinic zirconia (m-ZrO_2).[2,3] Remarkably, its catalytic activity can be significantly improved by promoting it with low-nuclearity clusters of palladium aiding hydrogen splitting.[2-4] Looking towards industrial implementation, however, the assessment of catalytic performance has to go beyond the analysis of single-pass conversion using pure CO_2 and H_2, and include feeds that also contain recycled CO byproduct (**Fig. 1a**). Herein, In_2O_3 catalysts in bulk form, supported on m-ZrO_2 and other carriers as a reference, and promoted by Pd are comprehensively evaluated in CO-CO_2 cycle experiments, in which CO_2 in the hydrogenation feed is replaced by CO stepwise. While methanol productivity increases for In_2O_3/m-ZrO_2, both In_2O_3 and Pd-In_2O_3 catalysts exhibit some drop in their activity upon gradually increasing the CO concentration in a CO_2/H_2 feed (**Fig. 1b**). Variations in the concentration of oxygen vacancies on In_2O_3 and in the electronic properties and speciation of the promoter as well as the evolution of surface species upon exposure to distinct feed compositions are elucidated, providing sound evidence on the origin of beneficial and detrimental effects. Overall, the identified structure-performance relations offer practical insights to drive the development of industrially viable promoted and supported catalysts for CO_2-based methanol synthesis.

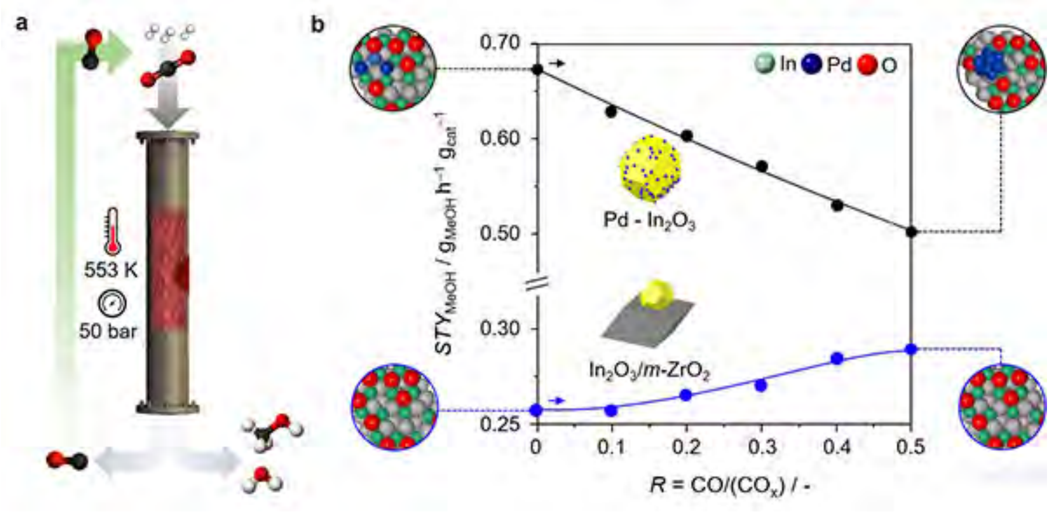

Fig. 1. a Representation of CO recycling in CO_2-based methanol synthesis. **b** Structural features and catalytic performance of Pd-In_2O_3 and In_2O_3/m-ZrO_2 in methanol synthesis upon the step-wise replacement of CO_2 by CO in the CO_2+H_2 feed. Reaction conditions: 553 K, 50 bar, and *WGSV* = 24,000 $cm^3\ h^{-1}\ g_{cat}^{-1}$.

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On the mechanism of methane conversion in non-oxidative conditions

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Methane is the simplest hydrocarbon and the main component of natural fuel resources such as natural gas, coal-bed gas, and methane hydrates deposited in the Earth [1]. It can be converted into valuable fuels and chemicals under non-oxidative conditions [2]. However, the advance in this field has been hindered by thermodynamic limitations of methane conversion, catalyst selectivity, and catalyst deactivation by coke formation [3]. Such efforts have been focused mainly in the analysis of final products and there is a lack of comprehensive mechanistic insight. A better understanding of the mechanisms involved is vital to improve the performance of the process. To provide mechanistic understanding, the conversion of methane under non-oxidative conditions in the presence of silica and iron-modified silica was studied by detection of elusive and reactive radicals as well as products. Experiments using packed bed reactors with selective analysis downstream under collision-reduced high vacuum environment by means of iPEPICO (VUV beamline, Swiss Light Source) provided access to reactive intermediates and products. Such information allowed proposing reaction mechanisms for the formation of C_2, C_3, and C_4 species, as well as C_6 species and higher molecular weight products. We have found compelling evidence that upon methane activation on iron-modified silica, propargyl (C_3H_3) radicals are formed, which are the precursors for the formation of fulvene and benzene (C_6H_6).

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The Impact of Preparative History and Driving Force on the Water Oxidation Activity of Spinel-Type Cobalt Oxide

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Artificial photosynthesis is a promising approach for harvesting sustainable energy through sunlight-driven water splitting into oxygen and hydrogen, which can be stored or converted into more suitable compounds. However, the four-electron transfer process of the water oxidation half-reaction remains the key challenge for water splitting. Therefore, the development of stable, efficient, and economic water oxidation catalysts (WOCs) is of great interest to the current renewable energy research. Spinel-type Co_3O_4 was chosen as an attractive model WOC offering low cost access and robust performance.[1] Herein, cobalt oxide is systematically investigated by a three-step approach to study (1) the effect of the preparative history on the material properties and (2) their interdependence with the activity as (3) a function of the driving force. To this end, cobalt oxide was synthesized via nine different synthetic routes. The emerging cobalt oxide samples were characterized with a wide range of analytical methods, including XAS, XPS, PXRD, Raman, BET, and TEM to reveal the key material properties for high catalytic activity. The performance was assessed with the three most widely applied protocols, namely, electrocatalytic, photocatalytic, and chemical oxidation. The applied test method was found to clearly influence the activity measured for the Co_3O_4 samples. High surface area, increasing disorder and a decrease in oxidation states were found to be key parameters for high chemical oxidation activity, which were accessed with low synthetic temperatures. While these property-activity relationships were not as sharply defined for photocatalytic water oxidation, samples obtained at lower temperatures were generally more active. In contrast, no such trends were observed for electrocatalysis, where all samples showed similar activity towards water oxidation. Our study demonstrates that the control of the synthesis parameters and comprehensive understanding of the preparative history and the applied driving force are crucial for the design of high-performance WOCs.[2,3]

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Crystallographic and morphological optimization of catalytic copper foil for hydrogen-sieving single-layer graphene membranes

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Gas separation membranes based on single-layer-graphene are highly attractive because the size of graphene nanopores can be tuned to separate gases by the size-sieving mechanism.[1] A prerequisite for this is the synthesis of high-quality polycrystalline single-layer graphene film by chemical vapor deposition (CVD).[2] The quality of graphene in the context of membranes is reflected by the size and the density of the intrinsic vacancy defects, and is affected by the catalytic metal substrate and the CVD environment. Generally, high-purity and smooth Cu foil is used to obtain gas-sieving performance from single-layer graphene.[3,4] Herein, we conduct a systematic high-temperature annealing study on two separate, commercial, low-cost Cu foils leading to their transformation to Cu(111).[5] We learned that all Cu foil variations could be converted to smooth Cu(111) substrate to improve the quality of subsequent graphene that was synthesized on top of the treated Cu foils, thus paving the way for eventual scale-up of graphene membranes.

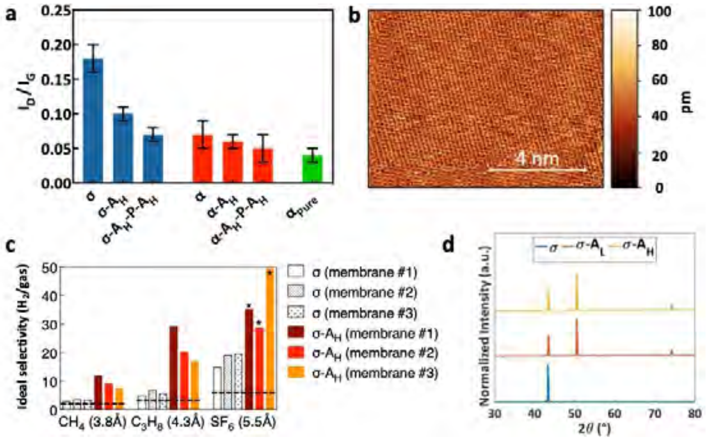

Figure 1. a) I_D/I_G ratio in the Raman spectra of graphene synthesized on as-received and annealed Cu foils; b) Atomic resolution STM images of the annealed ultra-flat TS Cu foil; c) ideal selectivities of membranes synthesized on as-received and annealed Cu foils ; d) XRD patterns of as-received Cu (blue trace), Cu annealed at 1000 °C during LPCVD (red trace), and high-temperature annealed Cu (orange trace).

The annealing process smoothened the Cu surface, RMS surface roughness from 206 to 99 nm. The RMS roughness on the individual Cu step was only 0.23 nm. The oriented Cu grains yielded single-layer graphene with a significantly lower defect density with I_D/I_G ratio decreasing from 0.18 ± 0.02 to 0.04 ± 0.01. Finally, single-layer graphene films, synthesized on the annealed low-purity Cu foil, yielded H_2-selective membranes with H_2 permeance reaching 1000 gas permeation units (GPU) in combination with attractive H_2/CH_4 and H_2/C_3H_8selectivities of 13 and 26, respectively. We attribute the improved membrane performance to (i) smoothened surface of Cu foil post-annealing (avoiding cracks during transfer process), and (ii) crystallographic re-orientation of Cu foils to Cu(111) (reducing the grain boundary defects due to the smallmismatch (3–4 %) between the lattice constants of the (111) facet of Cu and that of graphene.[6]

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Heterogeneous, Bimetallic Pt based Catalysts for Propane Dehydrogenation via Surface Organometallic Chemistry

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A shift from oil-based naphtha cracking to shale-based ethane cracking has created an imbalance in the production and demand of propylene.[1,2] This has resulted in an increased demand for alternative light olefin production routes. While on-demand propane dehydrogenation is practiced industrially, the current industrial catalysts suffer from fast deactivation requiring constant regeneration.[1,3] In attempts to deconvolve specific factors which effect catalyst stability to ultimately design more effective catalytic systems, we prepared several well-defined Pt based catalyst in combination with 3d transition metals using Surface Organometallic Chemistry.[4,5] This involves a two-step approach where a molecular 3d transition metal precursor was first grafted to the surface of a SiO_2 support followed by a thermolysis step. In a second grafting step a Pt precursor was grafted to the 3d transition metal doped SiO_2 support followed by a reduction treatment using H_2. The resulting materials were tested in the propane dehydrogenation reaction partially revealing superior performance compared to similar materials reported in the literature. This contribution will present the catalytic investigation along with a profound structural characterization of these heterogeneous systems providing insight in the factors leading to increased catalyst performance.

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Beneficial effect of steam reforming of CH_4 on NO removal on a three-way catalyst under transient conditions

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Natural gas vehicles (NGV) are an attractive solution for the reduction of greenhouse gas emissions arising from road transportation due to their intrinsic low CO_2 and NO_x emissions. However, due to the high global warming potential of CH_4 and to increasingly stringent legislations, post-combustion oxidation of unburnt CH_4 is essential. Besides CH_4, CO and NO_x are common pollutants in the exhaust gas of NGV, making three-way catalysts (TWC) the choice for this application.

In TWC, while CO oxidation is easily achievable, full removal of CH_4 and NO is more challenging. Together with the poor reactivity of CH_4, the strong inhibition of CH_4 oxidation by CO and NO results in the shift of the lambda factor (λ) from stoichiometry to net rich [1]. These observations allowed us to demonstrate that the use of repeated short reducing pulses (SRP) under stoichiometric (on TWC) and under lean operation (on Pd-zeolite) increase the activity and stability of the corresponding catalyst [1, 2]. We have shown by quick-XAS [2] that these reaction conditions involve the formation of Pd species with a large extent of oxygen vacancies (PdO_x) serving as the active species under SRP operation [2].

In this study, we demonstrate the beneficial effect of steam reforming of CH_4 (SR-CH_4) on pollutants removal on a $Pd/Al_2O_3/Ce_{1-x}Zr_xO_2$ TWC, and that SRP conditions promote this oxidation pathway compared to static operation mode. The catalytic results show that in the absence of water, complete removal of pollutants was only achieved under SRP conditions and coincided with the presence of SR-CH_4. In contrast, in the presence of water, in both static and SRP mode, slow removal of pollutants was observed at low temperature, where CH_4 was oxidized by O_2. Then, faster CH_4 oxidation took place with increasing temperature, during which CH_4 was oxidized likely by water to form H_2, in turn promoting complete NO removal. However, under SRP conditions, conversion levels were enhanced and SR-CH_4 was promoted. Identical experiments on Pd/Al_2O_3 aiming to investigate the role of the support encourage to consider the active role of Ce in SR-CH_4 through the regulation of H_2, which was detrimental to CH_4 conversion if it was not removed by the support.

Our results suggest that efficient removal of pollutants can be achieved if SR-CH_4 takes place and H_2 production is controlled. Because SRP operation promotes SR-CH_4 and efficient NO reduction, it could be exploited in dithering operation of TWC.

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Anomalous X-ray diffraction at the Al and Si K-edges

P. Rzepka[1], A. Pinar[2], T. Huthwelker[3], A. Knorpp[1], L. McCusker[4], C. Baerlocher[4], J. A. van Bokhoven[1,2]

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Zeolites are the materials of particular interest for refining industry, chemical production, and adsorption-driven processes or as environmental-friendly alternatives for mineral acids. Zeolites are crystalline aluminosilicates with micropores composed of tetrahedrally coordinated T-atoms (Si or Al) bridged by covalently bonded oxygen atoms. By replacing Si with Al a local negative charge is generated on zeolite framework which is compensated by a positively charged extra-framework cation. When the cations are exchanged with protons the zeolite becomes a solid acid catalytically active in Brønsted-acid catalyzed reactions. Determining the geometry and the accessibility of active sites in the zeolite structure is essential to fine tune catalytic properties. Proton is a poor scatterer, difficult to be observed directly, though its position is reflected by associating aluminum occupancy on T-site. However there is currently no method available that provides the information of Si and Al ordering in zeolite framework unambiguously and quantitatively. Although X-ray and neutron diffraction enable evaluating the T-sites distribution as part of the crystal structure determination, the aluminum and silicon cross sections are too similar to be distinguished.

Anomalous X-ray diffraction is a new method in zeolite science that exploits the dispersion of X-ray radiation of the energy near natural oscillation of an electron shell. Upon the vicinity of an absorption edge of the scattering atom the corresponding scattering factor undergoes a change and leads to relative intensity variation of respective Braggs’ reflections. Since the Al K absorption edge (1.56 keV) lays apart from the Si K-edge (1.84 keV), it allows on the differentiation of the elements and the allocation to specific T-sites. Performing diffraction on- and off-resonance enables an unambiguous assignment of the elemental composition of a crystal. Anomalous X-ray diffraction across the aluminum and silicon K edges was successfully exploited to pinpoint the locations of aluminum and silicon in several zeolite structures. We believe this method could become the technique of choice for zeolite scientists interested in locating the active catalytic sites in their materials.

Performance of metal-catalyzed hydrodebromination of dibromomethane analyzed by descriptors derived from statistical learning

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The catalyzed semihydrogenation of dibromomethane (CH_2Br_2) to methyl bromide (CH_3Br), a scarcely studied reaction, is a key step in the bromine-mediated upgrading of methane.[1-3] The search for new catalysts typically starts with high-throughput experimental screening, recently also guided by Statistical Learning (SL) approaches.[4] However, the main issues preventing the extensive application of current SL strategies are the lack of consistency between the databases and the fact that open literature mainly contains successful experiments. To overcome this, we have coupled a systematic catalytic preparation, testing, and characterization protocol of a wide range of metals (Fe, Co, Ni, Cu, Ru, Rh, Ag, Ir, and Pt) to mechanistic studies based on density functional theory (DFT) for employment as a complete database (**Fig. 1**).[5] The binding energies of the 272 intermediates retrieved by DFT were subjected to dimensionality reduction *via*principal component analysis (PCA), a robust mathematic construct. The two descriptors obtained from this unsupervised method were, together with the experimental data, employed in a random forest regressor, ultimately connecting the descriptor energy intervals with catalytic activity or selectivity for the identification of performance trends in terms of CH_3Br yield. In addition, a representative analytic model was found using Bayesian inference. This approach illustrates the exciting opportunities presented by integrated experimental/computational screening and sets a fundamental basis for the accelerated discovery of superior catalysts.

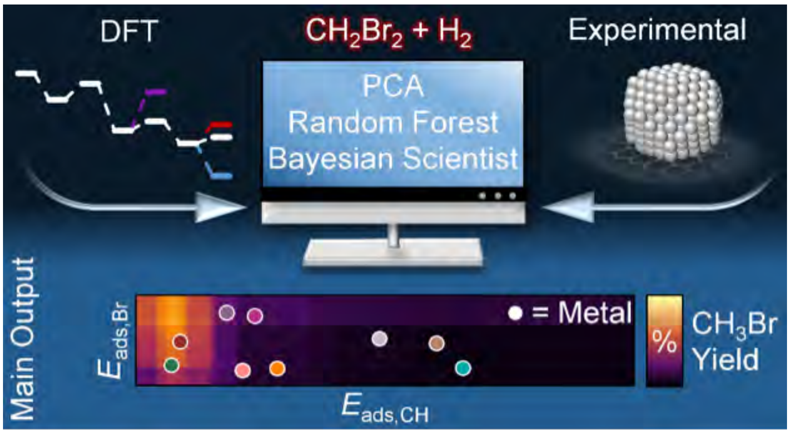

Fig. 1. Multi-technique strategy combining DFT calculations, experimentally obtained data, and statistical tools to analyze the activity and selectivity of metal-catalyzed CH_2Br_2 hydrodebromination.

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NHCAuOTf Catalyzed Alkyne Hydration Under Mild Reaction Conditions

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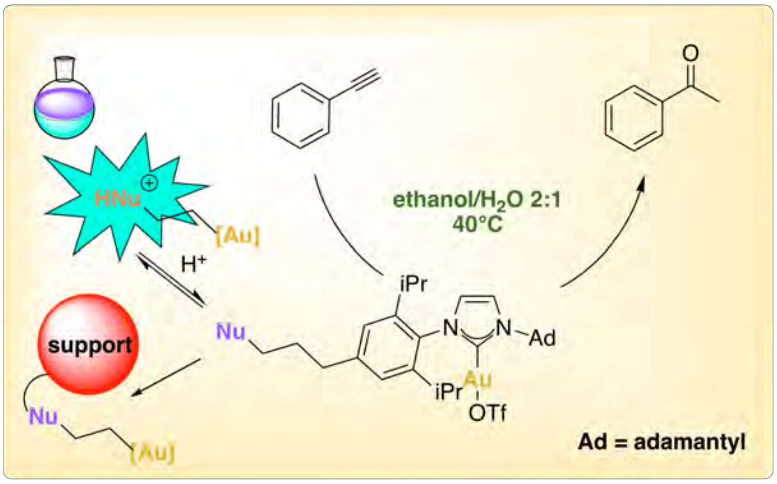
Gold(I) has become a powerful tool in the construction of carbon architectures in the past two decades. Hydration, hydroalkoxylation, hydroamination and enynes cycloisomerizations are just few of the useful transformations that gold(I) can catalyze. [1] Among these, the hydration of alkynes is a transformation of primary importance in organic chemistry [2] and is intrinsically green from an environmental standpoint with a 100% atom economy and 100% carbon efficiency. On the other hand many of the developed gold-catalysed hydration procedures suffer from several drawbacks, such as high catalyst loadings, high temperatures and use of silver additives. [3] In this sense the multiple recycling of expensive gold(I) catalysts is an impelling matter as well as their applicability to milder and greener procedures. Here we show a catalytic system for the hydration of terminal alkynes in mild reaction conditions with IPrAuOTf (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolylidene, OTf = trifluoromethanesulphonate) and the synthesis of its asymmetric derivative IAd(4-allyl)PrAuOTf (IAd(4-allyl)Pr = 1-adamantyl-3-(4-allyl-2,6-diisopropylphenyl)imidazolylidene). The installed allyl moiety enables functionalization to obtain a pH-responsive species or a nucleophile for conjugation to a support.



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Operando quick XAS of oxygen activation mechanism over supported bimetallic Pt-Fe catalysts

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Classical carbon monoxide oxidation over supported Pt in the low-temperature regime is limited by the oxygen activation step [1]. Iron oxide is one of the best promotors for Pt/γ-Al_2O_3 catalysts, as it substantially increases the catalytic activity [2], especially at low temperature. The origin of the promotor-effect and the structure of the active iron are unclear [3]. Furthermore, there is no experimental evidence that oxygen activation is linked to the Fe^{2+}↔Fe^{3+} redox couple, thus the mechanism of oxygen activation remains largely unknown.

We prepared a 2 wt. % Pt – 0.57 wt. % Fe / γ-Al_2O_3 catalyst by the incipient wetness impregnation method. This catalyst demonstrated a 16 times higher activity at 373 K than a 2 wt. % Pt / γ-Al_2O_3 catalyst with the dispersion of platinum particles. To probe the nature of active sites, we performed operando time-resolved quick X-ray absorption spectroscopy (XAS) in a dedicated plug flow reactor cell [4]. We collected time-resolved Fe K and Pt L_3 edges XAS spectra at the SuperXAS beamlime of the Swiss Light Source under steady-state (in the mixture of carbon monoxide and oxygen) and transient conditions (while cutting off carbon monoxide or oxygen flows) with one second time-resolution and simultaneously recorded carbon monoxide conversion using an on line mass spectrometer.

Linear combination fitting of the Fe K edge quick-XAS allowed us to determine the amounts of Fe^{3+} and Fe^{2+} in the catalyst and compare those with the amount of carbon dioxide released at every moment in time as monitored with an on line mass spectrometer. We used transient experiments with the periodic switching off of carbon monoxide or oxygen flow in the carbon monoxide and oxygen gas mixture to compare the amount of $Fe^{3+}$and Fe^{2+} formed with the amount of converted carbon monoxide. During the oxygen cut-off experiment we observed that the rate of Fe^{2+} oxidation during the carbon monoxide cut-off experiment was equal to the steady-state reaction rate in the mixture of carbon monoxide and oxygen. Coverage of platinum by carbon monoxide determined from Pt L_3 edge XAS spectra was independent on oxygen concentration. In conclusion, operando XAS quantitatively demonstrated that Fe^{2+}↔Fe^{3+} redox couple is involved in the catalytic cycle of carbon monoxide oxidation on the PtFe catalysts by activating oxygen. We observed that the resting state of active iron species during carbon monoxide oxidation is Fe^{2+}. While binding oxygen, active Fe^{2+} species oxidize into Fe^{3+} state and then react with carbon monoxide activated on the neighboring Pt atoms. Understanding the role of iron oxide promotors is crucial to create new catalysts with a higher oxygen activation rate and better performance.

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Magnetic field effect on the electrochemical hydrogen evolution reaction with ferromagnetic electrodes.

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External magnetic fields affect various electrochemical processes and can be used to enhance the efficiency of the electrochemical water splitting reaction. However, the overall impact of magnetic field on electrochemistry is poorly understood. One of the challenges lies in the incompatibility of the analytical requirements (e.g. bulk aqueous and extreme pH environment) with the available interface-sensitive techniques (e.g. XPS). Here, we present an experimental approach that overcomes such challenges and allows probing a ferromagnetic electrode in an applied magnetic field, while simultaneously monitoring the hydrogen evolution reaction.

The in situ magneto-optical response of Co-Pt multilayer, with Pt capping layer, hydrogen evolution electrode yields information on structural and chemical changes of the electrode-electrolyte interface. We report a magnetic field induced change of a few percent in the electrochemical current density below -0.8 V (vs RHE). Within the defined parameters, the electrode remains structurally and chemically stable, and the effect is assigned to the changes in the ratio of water to hydroxide ions within the electrochemical double layer. As indicated by the magneto-optical hysteresis, this change is induced by the alignment of the ferromagnetic domains in Co-Pt, which lead to the exceptionally strong local magnetic field gradients near to the electrode surface. We conclude that in an applied external magnetic field the chemical composition of the electrochemical double layer and the cell current density depend strongly on the magnetic properties of the electrode thin film.

Nanostructure Engineering for Heterogeneous Catalysis

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Greater control over catalytic surfaces will enable development of more efficient, stable, and selective catalysts. Atomic layer deposition (ALD) is an established technique used to build thin films with atomic accuracy. Typically, the technique is carried out in the vapor phase, at elevated temperatures, and with excess reactants that are purged between self-limited reactions with the substrate

We are studying the possibility of instead using acid and base catalysis in the liquid phase to facilitate the use of unreactive precursors such as trimethyl gallium. Another potential application of liquid-phase ALD is to bind together metal oxide nanoparticles. A proof of concept study shows that when silica is coated with a single layer of trimethyl aluminum, the exposed methyl groups will react with hydroxyl groups of a second metal oxide and form heterostructured nanodimers (Figure 1). The mixed-metal-oxide interfaces are likely to have unique catalytic activity with potential applications in tandem catalysis [3].

Liquid-phase ALD holds tremendous promise for expanding the horizons of how ALD has traditionally been used and developing new rationally-designed heterogeneous catalysts.

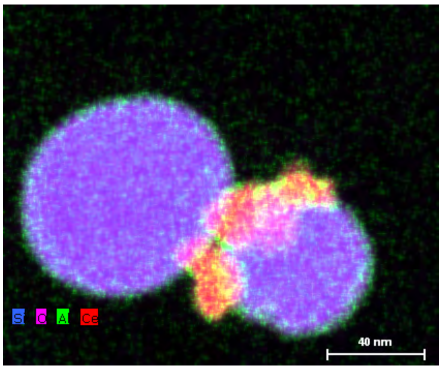

Figure 1: Scanning transmission electron microscopy energy-dispersive x-ray spectroscopy (STEM-EDX) of ceria nanoparticles (red) attached to silica spheres (purple) via trimethyl aluminum “nanoglue” (green).

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Formation of iron(II) single sites on the surface of silica and their role in the transformation of methane to higher hydrocarbons

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Upgrading of methane to higher hydrocarbons represents an interesting route with the potential to replace the conventional hydrocarbon feedstock for the chemical industry. Such a transformation is strongly limited by thermodynamics. For example, reaching methane conversion higher than 14 % requires a reaction temperature higher than 700 °C. In the last five years, several reports have shown that methane could be selectively converted to hydrocarbons even at 1000 °C. [1-4] Most of these systems are based on silicon dioxide with iron sites. However, the respective synthetic procedures lead to the formation of ill-defined materials, making mechanistic studies, determination of the active site, and establishment of any structure-activity relationship very challenging. To face this challenge, we combined surface organometallic chemistry and thermolytic molecular precursors to prepare a well-defined silica-supported material with iron(II) single sites that was characterized by multiple advanced spectroscopic techniques. The synthesized material promotes non-oxidative coupling of methane to higher hydrocarbons (C_2H_6, C_2H_4, C_2H_2, C_6H_6), reaching a selectivity of 20% at 3% conversion. This is accompanied by the deposition of coke, and the formation of defects. This contrasts with the reactivity of silica dehydroxylated at 1080 °C that favors, after an induction period, the formation of carbon deposits, rather than hydrocarbons. Such a result indicates that iron sites selectively suppress the surface reactivity and improve the selectivity.[5]

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Laser-microstructured copper reveals selectivity patterns in the electrocatalytic reduction of CO_2

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The strategy of engineering the local chemical environment to direct selectivity in the electroreduction of CO_2toward value-added products is only qualitatively understood.[1] The unfeasibility of measuring local concentrations and the limited applicability of simulations to systems with practical relevance hinder more precise guidelines. Here, we quantify the impact of the (electro)chemical environment on the selectivity pattern using microstructured Cu electrodes prepared by ultra-short pulsed laser ablation (**Fig. 1a**). We created regularly distributed micro-probes with controlled lengths and assessed their product distributions at distinct potentials (**Fig. 1b**). The regular geometry enabled the precise electrolyte modeling (**Fig. 1c**), which in turn enabled accurate simulation of the local pH and CO_2 concentration close to the catalytic surface (**Fig. 1d**). Selectivity maps emerged that are instrumental for mechanistic and applied studies (**Fig. 1e**). Combined, they reveal clear patterns for C1-C3 products (**Fig. 1f**), suggesting novel insights such as the presence of two reaction mechanisms for propanol. Additionally, combined selectivity maps offer profundity into the effect of operation parameters such as stirring and electrolyte composition on the product distribution. These findings can be directly translated to the design of practical devices like artificial leaves.[2]

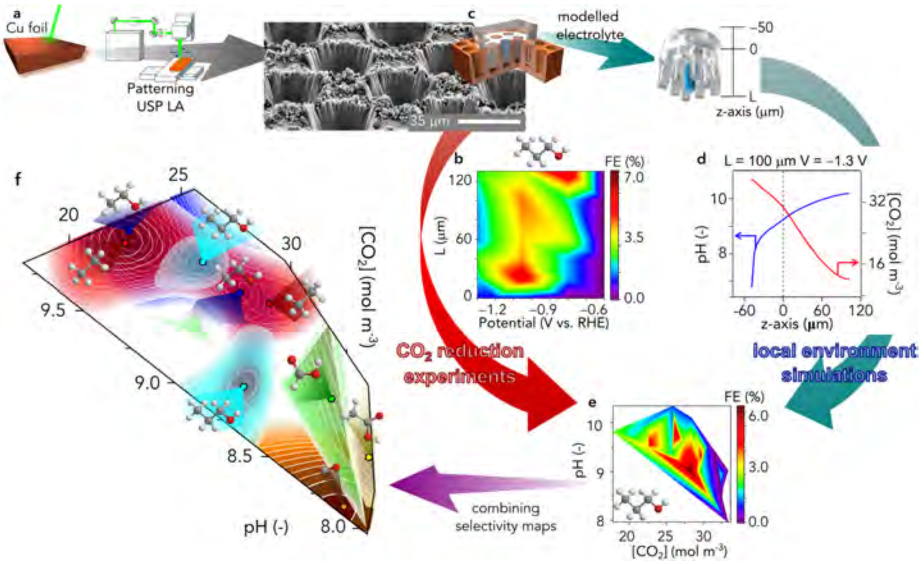

Fig. 1. a Ultra-short pulsed (USP) laser ablation (LA) created micro-probes on the surface of Cu foil, as observed in the SEM micrograph. **b** Representative experimental map (propanol is shown) displaying Faradaic efficiency (FE) vs. micro-probe length (L) and potential. **c** 3*D* model considered of the electrolyte volume next to the catalytic surface. The micro-probe under analysis is highlighted in blue with depth (L) along the *z*-axis. **d** Representative calculated evolution of the pH and CO_2 concentration along the z-axis (case: L = 100 µm, potential −1.3 V). **e** Selectivity map obtained by combining b) and simulations showing FE vs. local pH and CO_2 concentration. **f** Combined selectivity map for relevant products.

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Electron diffraction resolves the aluminium sites in a zeolite catalyst

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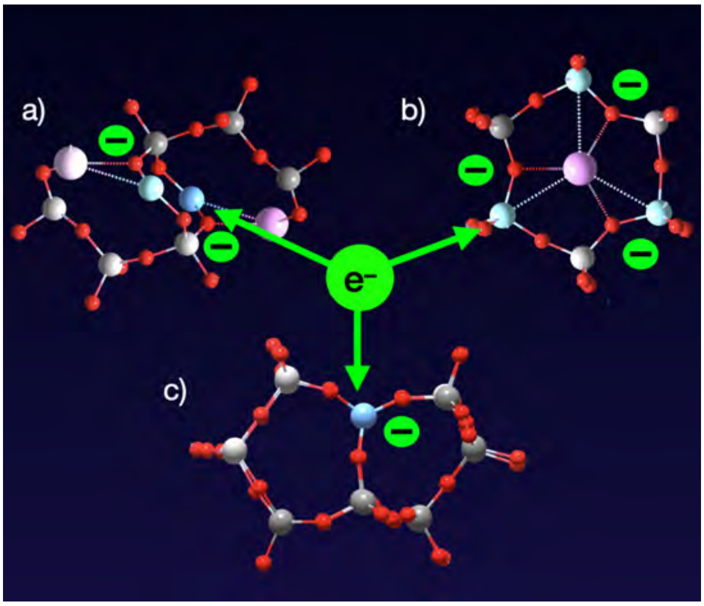
Zeolites are the most important industrial catalyst for hydrocarbon processing. It is the aluminium, that determines the chemical reactivity of these crucial aluminosilicates. Yet, the siting and chemical structure of aluminium in the zeolite framework remains elusive. Spectroscopic methods do not provide phase information and X-ray diffraction techniques are able to discern aluminium from silicon in the zeolite lattice for rare cases only [1]. Moreover, the aluminium content of industrially used zeolite catalysts is very low. We collected electron diffraction data that differentiate between aluminium and silicon in zeolite frameworks [2]. Electron diffraction enables complete atomic structure resolution of submicron-sized crystals and can carry delicate information about the chemistry of atoms [3]. We combined novel detector technology with a careful data collection protocol [4]. Our data differentiate between the high- and low-resolution shell of electron diffraction data to amplify its chemical sensitivity. This approach is scrutinised with the aluminosilicates albite (Fig.1, a)) and zeolite A (Fig.1, b)), where correct placement of aluminium atoms in the electron crystallographic structure improved modelled data. By restricting ED data to a specified resolution range, contrast between Si and Al atoms could be enhanced even. Intriguingly, we can show, that electrons also detect the charges associated with the aluminium, that present the active site of the catalyst. Former results might be used to elucidate preferred aluminium siting and the location of the „hidden“ active sites in the workhorse-of-industry-zeolite ZSM-5 (Fig.1, c)).Current results demonstrate the ability of electrons to sense and understand the chemistry of materials and will have a huge impact on the design of tailor-made zeolite catalysts for processing of fossil and alternative feedstocks. Our experiments tempt to conclude, that there is a meaning of ED beyond the mere elucidation of atomic structures.



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Dynamics of catalyst structure resolved on an atomic scale by in situ electron diffraction

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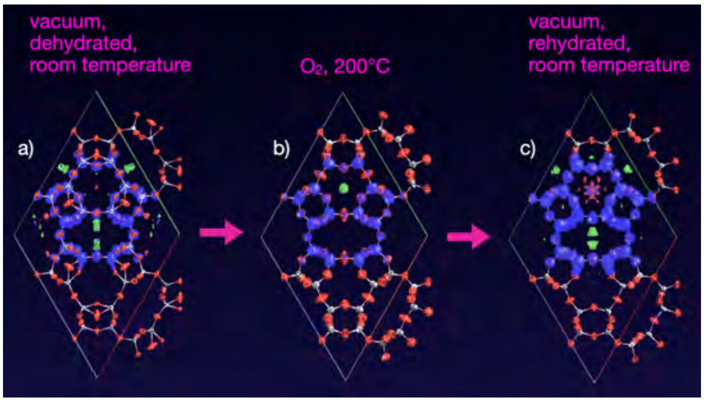
Many redox active systems, such as catalysts or battery materials, are present as nano- or microcrystalline powders. Elucidating the dynamics of their structural changes under reaction conditions helps in improving their performance. Three-dimensional electron diffraction (ED) has developed in a tool to yield the atomic structure of microcrystalline compounds in short time [1]. It is complementary to real-space high-resolution imaging and provides volume-integrated information about the atomic, and even electronic structure. Since ED data can be recorded at very low electron dose, the method is ideally suited for the study of extremely beam-sensitive materials that would suffer from severe beam-damage in conventional high-resolution TEM imaging. Furthermore, it helps to overcome issues related to the use of gas-flow *in situ* cells, where electron transparent SiN membranes disturb high-resolution imaging with undesired background. Additionally, ED is less sensitive to sample drift and vibrations and reduces beam-induced gas-phase chemistry. We investigated structural changes associated with the redox activity of a copper zeolite for the methane to methanol conversion [2]. The copper cation is observed to occupy different crystallographic positions (Fig.1a and b) in the framework of zeolite Omega depending on the gaseous environment. We aim to carry out diffraction experiments under reaction conditions in order to elucidate the dynamics of catalyst structure under operando conditions.



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Graphene conjugated single site catalysts for high performance electrocatalytic water oxidation

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As a unique platform for atomic-level studies of structure-performance relationships, single-atom catalysts (SACs) have attracted massive research interest in recent years.[1] However, the construction of well-defined active sites and understanding the influence of coordination environments on their activities are still challenging tasks.[2] In this work, we report a soft-landing strategy for tailored SACs by anchoring well-coordinated metal phthalocyanines (MPc, M = Ni, Co, Fe) on graphene oxide (GO) layers as models for mechanistic studies toward the oxygen evolution reaction (OER).[3] Our study revealed that electronic channels created through the π-π conjugation at the interface between molecules and GO enhance the performance of OER. The combination of operando X-ray absorption spectroscopy (XAS) and density-functional theory (DFT) calculations unraveled that the OER activities of the catalysts are linked to both thermodynamic and kinetic processes, via control at low and high potential ranges, respectively. The coordinating N and C atoms around the Ni and Co centers also participate in the OER, which provides more active sites for the reaction and result in higher OER performances compared to Fe center. Our selection of well-coordinated and highly defined molecular catalysts as the basis for SACs promotes the understanding of their coordination-activity relationships

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Self-Templating Strategies for Transition Metal Sulfide Nanoboxes as Robust Bifunctional Electrocatalysts

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Hollow nanostructures provide high surface areas and rich active sites, and construct a favorable interface to promote the electron transportation, regarding as a promising strategy to design efficient electrocatalysts for water splitting.[1] Meanwhile, transition metal sulfides (TMSs) have been explored as the efficient electrocatalysts for oxygen evolution reaction (OER) and hydrogen evolution reaction (HER).[2] Herein, we rationally prepared a series of metal sulfide nanoboxes (NBs) derived from metal based Prussian blue (PB) nanocubes as self-templates.[3] Analytical characterizations included XRD, EDX, ICP-AES, XPS, and XAS demonstrated that the Kirkendall effects of S^{2-} exchange reaction lead to the formation of TMSs NBs (referred as Co-S@PB, Co-Fe-S@PB, Ni-Fe-S@PB, and Co-Fe-Mo-S NBs). Furthermore, postcatalytic characterizations confirmed that the in situ formed transition metal oxides/(oxy)hydroxides were responsible for the real active species of TMSs during the OER process. This conclusion can give us a clear insight that TMSs are served as “pre-catalysts” for OER. Together with the advanced morphology, Co-Fe-S@PB NBs could afford excellent OER performance with a low overpotential of 286 mV at a current density of 10 mA/cm^2, a small Tafel slope value of 37.84 mV/dec, and high durability over 33 h with any activity decline. Moreover, the elegantly designed heterostructures of Co-Fe-Mo-S NBs are promising as hybrid electrodes for OER and HER throughout the pH range.

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Mechanistic insights into catalyzed propane oxychlorination by *operando* EPR spectroscopy

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The understanding of catalytic mechanisms governing alkane activation is pivotal to develop efficient technologies harvesting natural gas as a key energy vector in the transition towards renewables. This endeavor necessitates the application of *operando* techniques able to access materials properties under relevant reaction conditions. Herein, we show that *operando* electron paramagnetic resonance (EPR) spectroscopy can determine the oxidation state of benchmark chromium phosphate ($CrPO_4$) and europium oxychloride (EuOCl) systems during catalytic propane oxychlorination (POC), a very interesting route for the direct and selective production of propylene (C_3H_6).[1,2] These catalysts were chosen since Cr^{3+} and Eu^{3+}, the main oxidation states of these metals in these systems, are EPR active and silent, respectively. Accordingly, generation of reduced Cr^{2+} and Eu^{2+} ions (i.e. defects) during the reaction would result in the concomitant decrease and increase of the EPR response, respectively (**Fig. 1a**). This effect could indeed be observed by the strong difference in intensities of the EPR spectra of $CrPO_4$ and EuOCl obtained in POC as compared to those acquired under inert He at equivalent temperatures (**Fig. 1b**,**c**). Finally, additional tests conducted at different temperatures revealed that the yield of C_3H_6 correlates linearly with the intensity of the double integral of the EPR spectra (**Fig. 1d**), which is proportional to the amount of Cr^{2+} and Eu^{2+} ions generated in the catalysts upon the reaction. These results demonstrate *operando* EPR as a promising technique to monitor and quantify the oxidation state of redox active metal centers in selective oxidation catalysis, which can enable the design of effective catalysts for C−H activation.

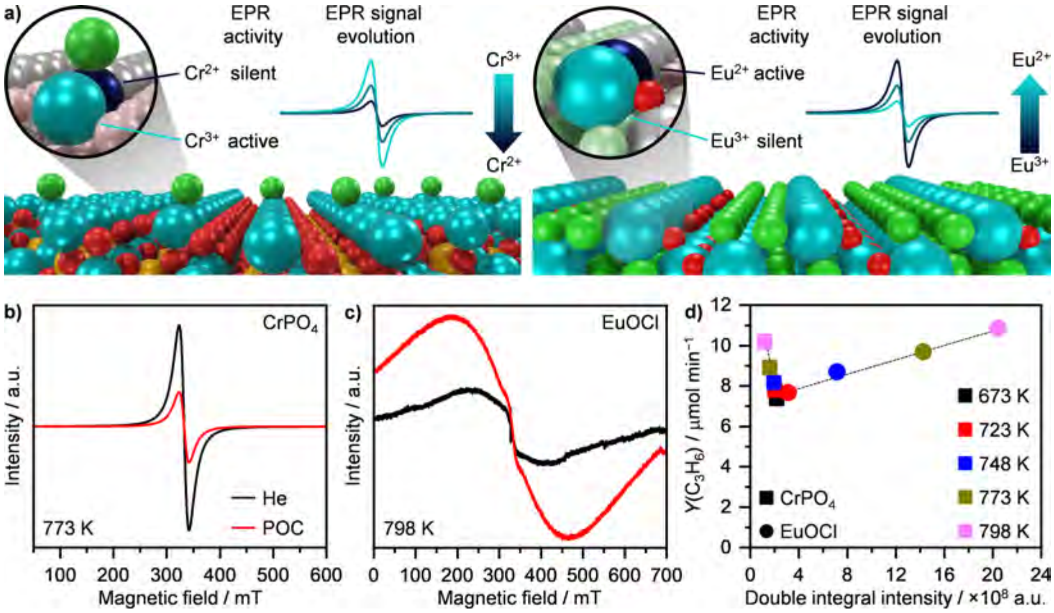

Fig. 1. a Schematic representation of the EPR response of $CrPO_4$ and EuOCl as pristine materials and upon formation of structural defects (e.g. halogen adsorption, oxygen vacancy) EPR spectra of **b** $CrPO_4$ and **c** EuOCl at fixed temperature during POC and under inert He. **d** Yield of C_3H_6 as a function of the double integral intensity of the EPR spectra during POC.

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