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Catalytic Methods for the Construction of Halogen-Functionalized Organic Compounds with Application to Late-Stage Functionalizations

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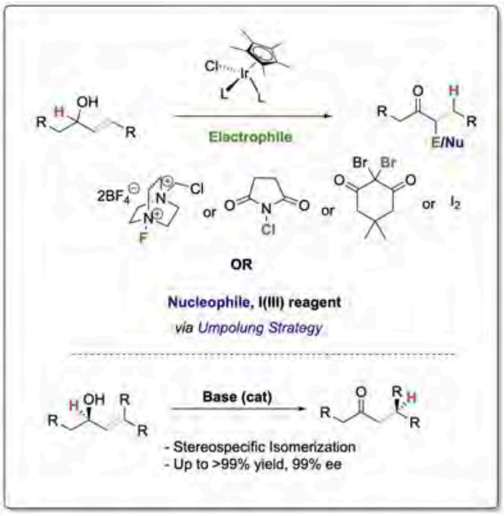
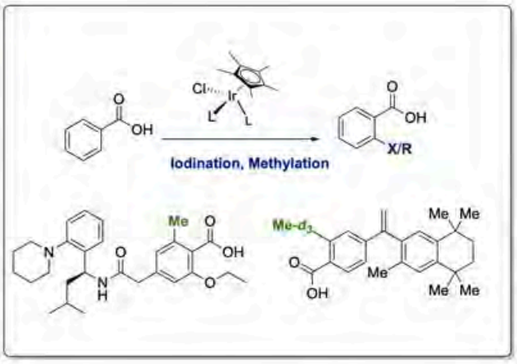
Our latest investigations on the development of catalytic methods for synthesizing heteroatom-functionalized building blocks and advanced drug-like molecules will be presented. The use of a family of simple P,N-ligandless complexes, with the general formula [Cp*Ir(III)] have been used for tandem 1,3-hydride shift / functionalization of allylic alcohols, as well as for the functionalization of C-H bonds in benzoic acids. Our attempts to develop asymmetric halogenation reactions resulted on the development of a novel organocatalytic stereospecific reaction mediated by a simple base, and which relies on the *in-situ* formation of ions pairs with induced non-covalent chirality. The scope as well as the mechanisms of these reactions will be presented.





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Catalytic Carbochlorocarbonylation of Unsaturated Hydrocarbons via C–COCl Bond Cleavage

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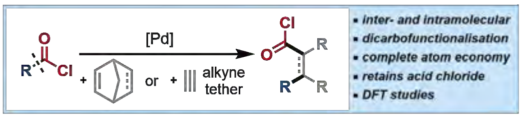
There is an urgent requirement to construct C–C bonds, essential to the production and discovery of materials and bioactive compounds, with a focus on sustainability. Reactions that can form multiple C–C bonds in a single step in a modular fashion are rare. This task is made more demanding if it is to be achieved with complete atom economy, one aspect of sustainable synthesis. Previous work using transition metal catalysis has made initial progress in this area, activating C–C bonds within functional groups (e.g. C–CN bonds) or with directing groups. This activation allows for a formal addition of the C–C bond across unsaturated hydrocarbons.

To further develop this area of catalysis whilst exploring fundamental reactivity, we considered using readily available acid chlorides for the formal addition of C–COCl bonds across unsaturated hydrocarbons.[1] The transformation was realized in both an inter- and an intramolecular setting, using strained alkenes and tethered alkynes, respectively. Notable features of the reaction include the high stereoselectivity, use of both aryl and alkenyl acid chlorides, good functional group tolerance, and the use of carboxylic acids as starting materials with *in situ* activation. Interestingly, the reaction also shows an example of temperature-dependent stereodivergence, which, together with plausible mechanistic pathways, was investigated by DFT calculations. Finally, the synthetic utility of the products was highlighted with the synthesis of tetrasubstituted cyclopentanes.



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Oxygen Atom Transfers Catalyzed by Cobalt Sulfide

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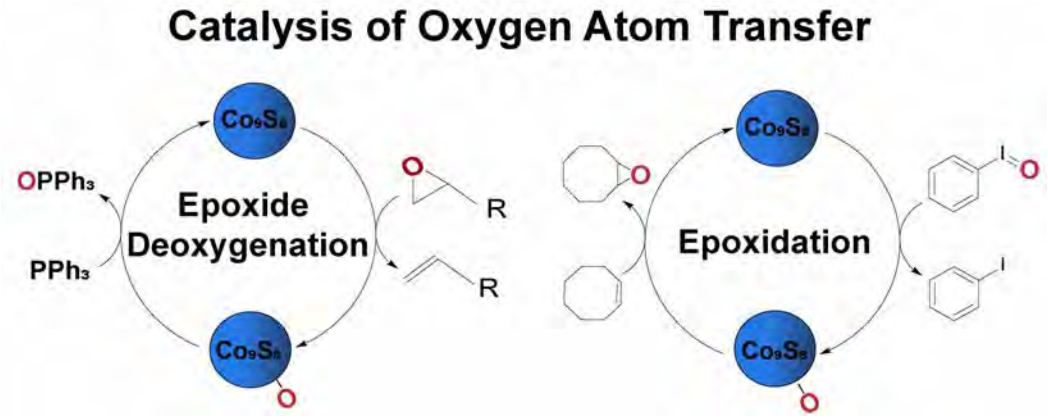
Transition metal sulfides have shown high activity for electrocatalytic oxygen evolution reaction (OER).[1,2] These materials form oxidized surfaces, under these conditions, which can catalyze OER more efficiently than the corresponding metal oxides.[2,3] The catalytic properties of transition metal sulfides for OER could indicate a general ability to catalyze oxygen atom transfer reactions. However, sulfide materials have not been much explored for thermal oxidative transformations so far. Application of the earth-abundant sulfides in thermal catalysis would be interesting for the development of more sustainable catalytic processes.

We demonstrate the catalytic activity of mesoscale cobalt sulfide (Co_9S_8) for thermal oxygen atom transfer reactivity including both epoxidations and epoxide deoxygenations. Similarly to what has been observed during OER, the Co_9S_8 surface can oxidize and transform in presence of the strong oxidizing agents of the epoxidation reactions. With use of mild oxygen donors, however, we can show that both pristine Co_9S_8 and surface-oxidized Co_9S_8 outperform cobalt oxide in the thermal catalysis of oxygen atom transfers. Our results show the high catalytic potential of pristine cobalt sulfide in thermal oxygen atom transfer reactions.



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Iridium complexes bearing O-functionalized PYE ligands for efficient formic acid dehydrogenation

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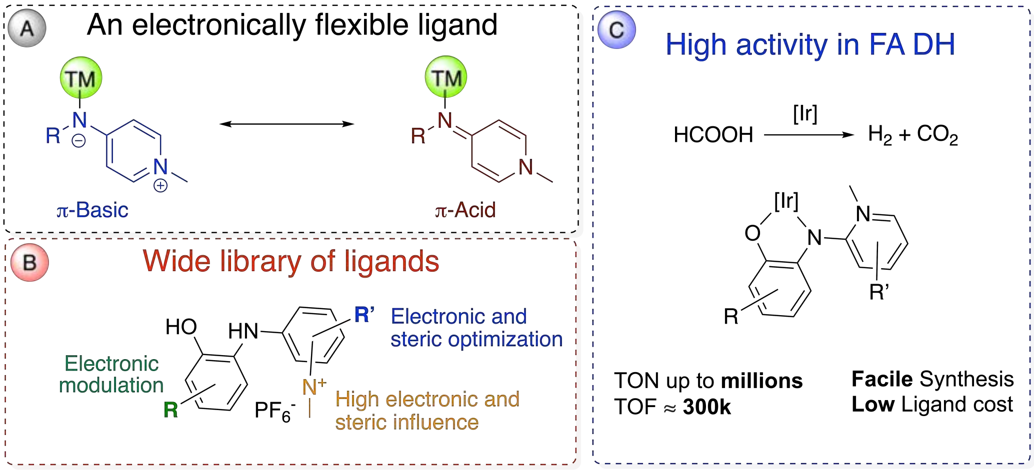
The long-term storage of renewable energies is a matter of urgency to accommodate seasonal variations. Hydrogen is a promising energy carrier for fuel, but its storage as a compressed gas is still problematic. Chemicals such as formic acid (FA) can act as liquid organic hydrogen carriers through hydrogenation and dehydrogenation cycles. The catalytic dehydrogenation of FA has found a growing interest during the past decade and several homogeneous complexes based on iridium, ruthenium and iron have been reported as catalysts for this reaction.[1-3]

We sought to propel FA dehydrogenation with complexes containing pyridylidene-amines (PYEs), that is, ligands which feature a unique electronic flexibility (Fig. 1a).[4] These ligands are known for their stabilization of various transition metals and for imparting high catalytic activity in, oxidation catalysis, *e.g*. in olefin and water oxidation.[4,5] We therefore developed a new bidentate ligand system comprised of synthetically simple and inexpensive O-functionalized PYE (Fig. 1b), and its corresponding iridium(III) complexes. Here we will present the extraordinary activity of these complexes in FA dehydrogenation catalysis with turnover numbers around 300,000 h^{-1} and turnover numbers in the millions (Fig. 1c). We will also discuss recent investigations into the homogeneity of the process, the electronic and steric versatility of the ligand to optimize catalytic activity, the effect of additives, and the cost-effectiveness of the catalytic system to envisage industrial applications.



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Tools for Predicting the Activity of Immobilized Frustrated Lewis Pair Catalysts

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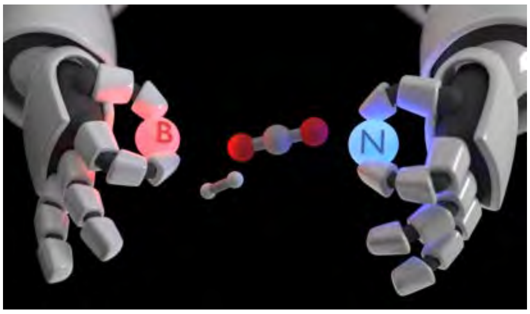
Developing and implementing tools for rapid estimation of catalyst performance can significantly expand the search space and accelerate discoveries. We present a computational framework for predicting the activity of a catalyst based on its minimal active site information. Our approach relies on establishing linear and nonlinear scaling relationships for mapping the chemistry/ geometry of the active site to their activity through intuitive electronic/structural descriptor variables. The resulting maps then guide us to recognize "sweet spots" in the respective descriptor spaces that fulfill the criteria for maximum activity. As such, these tools can be applied for extensive exploration of thousands of molecules and materials for the design of optimal catalytic environments to drive highly sought-after chemical transformations.

The ability of this framework is demonstrated with the challenging discovery of immobilized frustrated Lewis pairs (FLPs) [1,2] for the hydrogenation of CO_2. Since such catalysts feature a bifunctional active site with rigid donor and acceptor units, catalytic behavior is determined by their chemical as well as geometric composition. By constructing relevant activity maps and analyzing them, we show how to maximize performance by manipulating the chemistry of the Lewis pairs and controlling their spatial arrangements. [3,4] Utilizing the chemistry and the geometry-based tools together, we create a pipeline for rapid screening of curated databases of FLPs to not only identify promising combinations but also to formulate concrete design principles for building such hybrid active sites.



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Non-oxidative Coupling of Methane with Transition-Metal Carbides: Mechanistic Revelation of the Role of Carbidic Carbon

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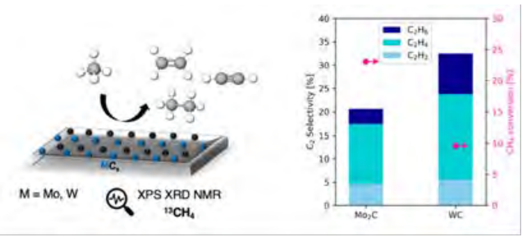
Non-oxidative methane coupling to higher hydrocarbons is gaining momentum.[1] In this study, the reactivity of molybdenum and tungsten carbides towards non-oxidative methane coupling is investigated. These transition-metal carbides display good selectivities towards C_2H_x (x=2,4,6). While methane coupling mechanisms are still debated, information regarding active site structure and initiation mechanism for C_2H_x formation are scarce, and metal carbides are often postulated as the *in-situ* formed active site.

In order to understand the role played by carbidic carbon, we monitor both the gas phase composition and the bulk carbide by comparing pristine and spent catalyst after reaction with ^{13}C-labelled methane at 1100 °C with various characterization techniques (XPS, solid-state NMR, pXRD). During this reaction, Mo_2C shows a stable selectivity over time on stream, while a loss of selectivity is observed for WC. XPS analyses indicate a partial reduction of WC to W(0) for the spent catalyst, pointing towards C depletion of the WC matrix over the course of the reaction, while no major changes are observed for Mo_2C. In parallel, carbon-exchange is observed between the gas phase and the metal carbide, as evidenced by the incorporation of carbidic carbon in the C_2H_x products. Carbon diffusion coefficients were calculated elucidating the different extent of C mobility for molybdenum and tungsten carbide. Furthermore, ^{13}C enrichment of spent Mo_2C and WC is evidenced by ^{13}C solid-state NMR with intense NMR signals at 274 and 307 ppm for Mo and W carbides, respectively. Overall, the presence of a significant amount of non-labelled isotopomer among C_2 products indicates a Mars-van-Krevelen-type mechanism with participation of the bulk carbon sites (in place of oxygen).



Left: Non-oxidative methane coupling to C_2H_x products over Mo_2C and WC. (x=2,4,6). Right: Selectivity distribution for C_2H_x species and CH_4 conversion at 1100 °C and 0.1 atm methane partial pressure over Mo_2C and WC.

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What is more important to enable efficient cyber-physical systems – digital twins or the degree of automation in R&D labs?

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Gamification, Internet of the Lab Tools, Digital Twins, Machine Learning / Artificial Intelligence combined with automation are pivotal tools to move research and its operations into the digital age.

Presented concepts and solutions highlight that digital twins are disruptive for every lab and enable the AI / ML pipelines in the future combined with ready-to-apply and quality assured catalysts, reagents, building blocks (SMOLE). The presentation shows Chemspeed’s top-down and bottom-up digitalization approach (ArkSuite Sofia) combined with its unique, proprietary protocolling that is shaping the R&D sphere.

Operando X-ray spectroscopy revealed the key role of the Pt-FeO$_x$ catalytic interface in preferential CO oxidation

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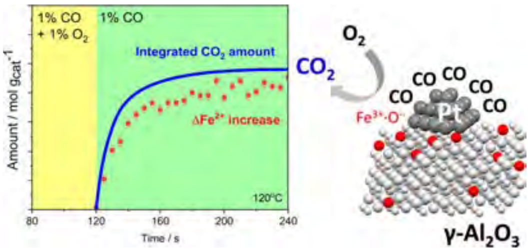
Preferential carbon monoxide oxidation (PROX) is of great importance for the implementation of hydrogen-based fuel cells and other modern hydrogen-based energy systems.[1] Catalysts required for this reaction must purify hydrogen fuel from traces of poisonous carbon monoxide, which is able to completely deactivate the fuel cell anode.[2] The main difficulty lies in a relatively low temperature of a fuel cell operation. PROX catalyst must oxidize carbon monoxide using molecular oxygen from air close to ambient temperature. Pt-FeO$_x$ catalysts show one of the highest PROX activities at ambient temperatures with 100% selectivity towards oxidation of carbon monoxide.[3] At the same time, commercial implementation of PROX Pt-FeO$_x$ catalysts is strongly limited due to their fast deactivation.[4] The reason for this deactivation process is unclear since no clear explanation for the reaction mechanism has been proposed.

To uncover the mechanism of preferential CO oxidation over Pt-FeO$_x$ catalysts, we used operando X-ray absorption spectroscopy that can quantitatively probe the redox activity of iron and platinum under in situ and operando conditions. Operando XAS at the Fe K and Pt L$_3$-edges identified that pretreatment conditions determine the structure of iron and platinum sites and their steady-state conversion. A quantitative comparison of operando structural change, obtained with time-resolved XAS spectroscopy, with catalytic rates revealed that the Fe^{2+}/Fe^{3+} redox pair is directly involved in the catalytic cycle of carbon monoxide oxidation as shown in figure below.[5] Two different reaction mechanisms of this reaction at 100^{o}C and at ambient temperatures were established. We have also determined the prerequisites for the Pt-FeO$_x$ catalyst deactivation and the role of Pt-FeO$_x$ interface in the preferential CO oxidation at ambient temperatures.



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OER Catalyst's Transport Layer Matters: Stability Comparison Between C-Based GDL and Ti-Based PTL

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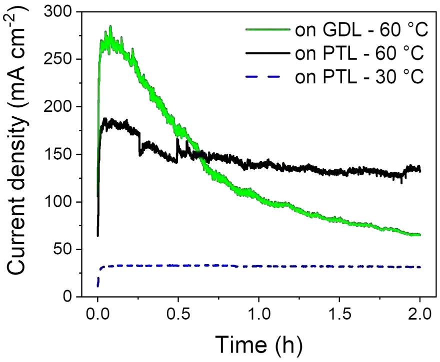
Currently, significant efforts are taken to find the most active and stable electrochemical oxygen evolution reaction (OER) catalyst diverting from critical raw material. However, one also needs to consider new catalyst screening methods, especially with respect to stability investigations where rotating disk electrode (RDE) studies are not suitable [1]. Recently, we introduced a gas diffusion electrode (GDE) setup as a new testing platform for OER catalysts [2]. This methodology stems from fuel cell approach using carbon gas diffusion layers (GDLs) as transport layer to bring the reactant to the catalyst. However, carbon is not stable under the harsh OER conditions, thus water electrolyser uses porous transport layers (PTLs) of titania instead. In the current work, we tested the influence of the transport layer on the stability of a highly active $Ir_{0.7}Ru_{0.3}O_x$ catalyst on homemade antimony doped tin oxide (ATO) support in a GDE setup. The test consisted in holding the potential at 1.6 V for 2 h. Firstly, the stability of the catalyst on a GDL or a PTL was compared at 60 °C. Rapid decline of the GDL-catalyst activity was observed, while the PTL-catalyst activity demonstrates a rather stable behavior (Fig. 1). We attribute this fast activity drop to the degradation of the GDL itself. Moreover, the activity at 30 °C of the PTL-catalyst was compared to literature data on RDE setup [1]. In the RDE setup, a breakdown is observed after only 30 min when applying a constant current density. In contrast, PTL-catalyst tested in the GDE setup exhibits no activity loss during 2 h under similar conditions.

Figure 1: Potentiostatic stability transients at 1.6 V of $Ir_{0.7}Ru_{0.3}O_x$/ATO deposited on C-based GDL (green full) and on Ti-based PTL at 60 °C (black full) and 30 °C (blue dashed).



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Bimetallic CoPt Nanoparticles for the Dry Reforming of Methane: Understanding Structure-Performance Relationships

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Bimetallic nanoparticles are an attractive alternative to the conventional monometallic systems, providing an elegant and versatile toolbox to modify the electronic and geometric structure[1] of the metals and in turn their catalytic activity.[2] Yet, structure-performance relationships which form the basis of a rationally guided design of effective bimetallic systems remain elusive. In this regard, the synthesis of well-defined bimetallic nanoparticles and their detailed characterization under reaction conditions will pave the way for more accurate structure-performance relationships. We use Co_xPt_y based catalysts as model catalysts for dry reforming of methane (DRM) – a reaction catalyzed by monometallic noble or transition metals including Ru, Rh, Pt, Ni, and Co (typically supported on metal oxides). The aim of the study is to understand how modifications in the structure of the bimetallic nanoparticles influence their DRM performance. Here, we synthesized small Co_xPt_y (and the monometallic references) supported onto SiO_2 through strong electrostatic adsorption.[3] X-ray absorption spectroscopy of CoPt/SiO_2 revealed differences in the XANES region (Fig. 1A, similar observations in the Pt L_3-edge) and in the extended X-ray absorption near-edge structure (EXAFS) in comparison to monometallic Co/SiO_2. This result indicates the formation of alloys and is explained by a charge transfer from Co to Pt.[4] By scanning transmission electron microscopy (STEM, Fig. 1A inset) and pair distribution function analysis of the X-ray total scattering data, we show that the nanoparticle size is ca. 1.2 nm after the reduction at 700 and 800 °C, respectively.

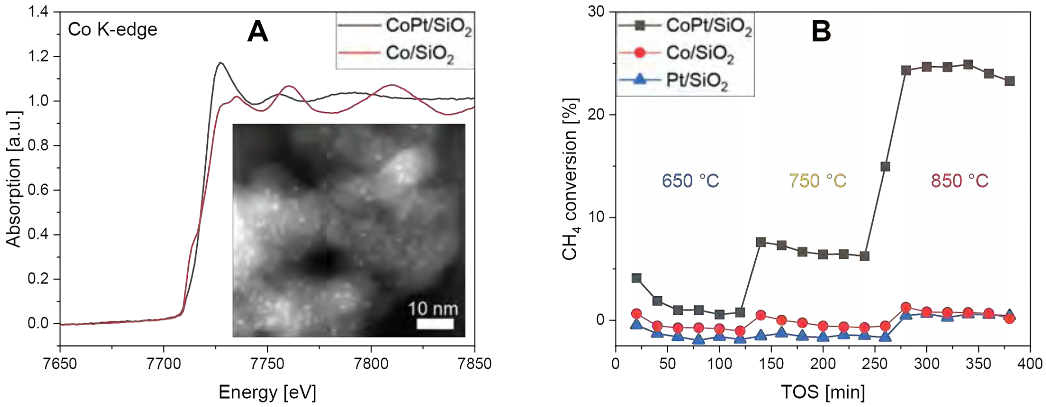

Figure 1: A) X-ray absorption near-edge structure (XANES) of Co/SiO_2 (red line) and CoPt/SiO_2 (black line) measured at 50 °C after reduction at 800 °C for 1 h. The increased white line intensity and edge energy shift in CoPt/SiO_2 with respect to Co/SiO_2 is attributed to the formation of a CoPt alloy. The inset shows an exemplary STEM image of the bimetallic nanoparticles after reduction at 700 °C in a 10 % H_2/N_2 gas mixture for 1 h ($d_{STEM} \approx 1.2$ nm). **B)** CH_4 conversion over Co/SiO_2, Pt/SiO_2, and CoPt/SiO_2 under DRM conditions (300 L/g/h, 650-850°C).

We observed a very high DRM activity for catalysts with x:y ~ 1:1 (i.e. CoPt/SiO_2) when compared to the monometallic counterparts (Fig. 1B). Surprisingly, monometallic Co and Pt show very low DRM activities at all temperatures tested, while the DRM activity of CoPt/SiO_2 is appreciably higher at 750 and 850 °C. These results suggest that the formation of a Co-Pt alloy, leading to a material with a modified electronic structure compared to the monometallic references, leads to a highly active DRM catalyst.

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Atomically precise design of bimetallic Au-Ru and Ru-Pt low-nuclearity catalysts via carbon host functionalization

V. Giulimondi[1], S. K. Kaiser[1], A. Ruiz-Ferrando[2], A. J. Martín[1], S. Büchele[1], F. Krumeich[1], A. H. Clark[3], N. López[2], J. Pérez-Ramírez[1]*

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Bimetallic low-nuclearity catalysts (**b-LNCs**) have recently gained prominence by virtue of the unique cooperative interactions they often exhibit. However, the lack of synthetic strategies with control over intermetallic bond formation and the intrinsic limitations of characterization techniques pose major hurdles to their development.[1] Furthermore, the study of catalytic synergies is still in its infancy, so far exclusively focusing on direct cooperativity mechanisms. Herein, we conduct the first comparative investigation between bimetallic dimers and isolated atoms. To this end, a holistic approach is developed combining (*i*) precision synthesis, (*ii*) advanced characterization, (*iii*) exploration of single-site proton adsorption properties *via* the hydrogen evolution reaction (**HER**), and (*iv*) density functional theory. Aiming to explore the impact of virtually inactive metal atoms for the HER (*e.g.*, Au) on moderately active ones (*e.g.*, Ru), Au-Ru LNCs are studied. Control over metal-bond formation is achieved by careful formulation of the carbon host, delivering Au-Ru dimers on O-functionalities and isolated atoms on N-functionalities (**Fig. 1a**).[2] Intriguingly, Au atoms enhance the HER kinetics of their Ru analogs already when isolated, magnifying the effect twofold in dimers. While the cooperativity action in the dimers is attributable to direct intermetallic charge redistribution, the nature of the synergy in the isolated architecture is unknown. Notably, by substituting Au atoms with Pt ones, exhibiting higher affinity for N-cavities and similar activity to Ru atoms, the synergy is amplified tenfold (**Fig. 1b**). Structural alterations induced by the integration of a second metal species are analyzed. Pt atoms are found to occupy the most energetically-favorable N-cavities, leading Ru atoms to adopt a distinct and more active configuration (**Fig. 1c**). These findings provide novel insights into complex metal-metal and metal-host interplays in b-LNCs.

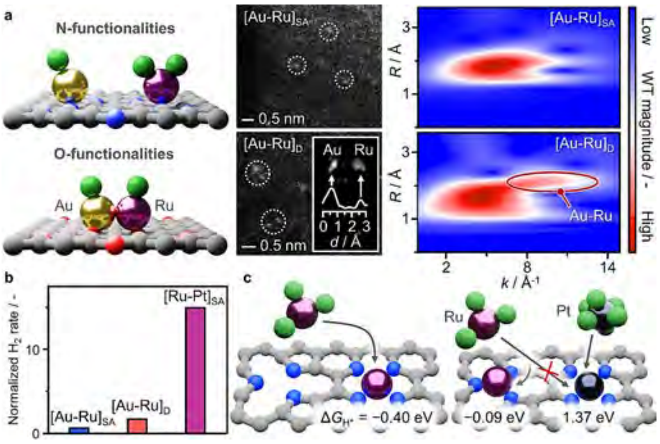

Fig. 1a Distinct architectures of Au-Ru LNCs and corresponding microscopy and spectroscopy analyses. **b** HER activity of b-LNCs normalized to Ru single atoms. **c** Cavity control exerted by Pt atoms, displacing Ru atoms to more active configurations, as reflected by their proton adsorption energy (ΔG_{H*}).

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Dynamics of nanoparticle motion and metal-oxide support in redox-reactive gases

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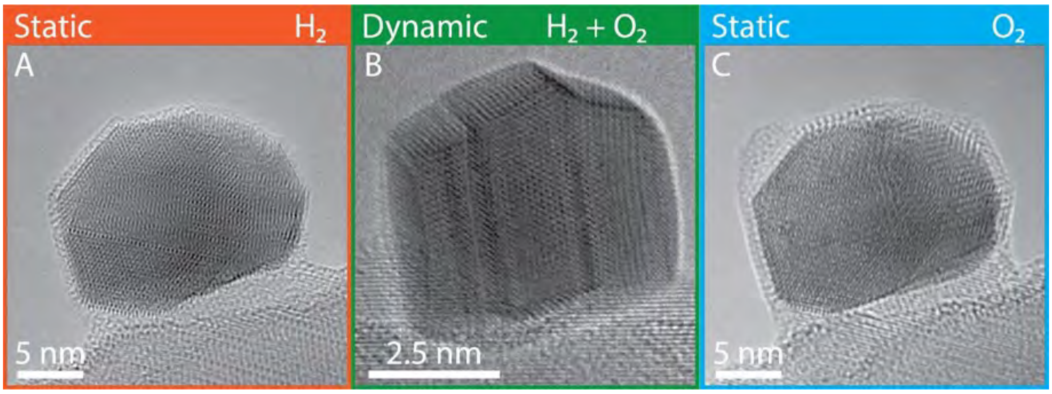
style="text-align: justify;">In the early days of catalysis research, oxide carriers were considered to be mere inert carriers for highly dispersed metal nanoparticles. Forty years ago, experiments with noble metal-TiO_2 catalysts demonstrated that oxide supports are far from inert in such catalytic systems and can strongly effect the adsorption behavior and structure of catalysts and the phenomenon was named the strong metal-support interaction (SMSI) [1]. SMSI was observed in noble metal catalysts supported on reducible oxides such as TiO_2. This phenomenon is of paramount importance, since it can determine the catalytic activity and stability. The SMSI phenomenon has, for the most part, been characterized *ex situ*. Such an approach is not able to capture the ongoing dynamics of a working system. The dynamic interactions between noble metal particles and reducible metal-oxide supports can depend on redox reactions with ambient gases. In our work [2,3], *operando* transmission electron microscopy revealed that the SMSI–induced encapsulation of platinum particles on TiO_2 observed under reducing conditions is lost once the system is exposed to a redox-reactive environment containing oxygen and hydrogen at a total pressure of ~1 bar. Destabilization of the metal–oxide interface and redox-mediated reconstructions of TiO_2 lead to particle dynamics and directed particle migration that depend on nanoparticle orientation (Figure 1). A static encapsulated SMSI state was reestablished when switching back to purely oxidizing conditions. This work highlights the difference between reactive and nonreactive states and demonstrates that manifestations of the metal-support interaction strongly depend on the chemical environment.



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Structure of selective and non-selective dicopper (II) sites in CuMFI for methane oxidation to methanol

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Direct methane oxidation to methanol via chemical looping over copper-containing zeolites is considered as a promising process for the effective valorization of natural gas [1]. Significant attention has been directed to the elucidation of the structure of the active sites, and various motifs, including mono- and bis-µ-oxo copper dimers, were proposed [1-5]. However, the selectivity of methane activation over copper active sites of different nature remains a subject of debates, creating obstacles in establishing the general structure-to-performance relationships for methane activation over copper-containing zeolites. Moreover, the factors controlling copper speciation in the materials are yet to be determined, being an essential step to develop methods for controlled synthesis of better-performing materials.

In the present contribution, we have studied the structure of the active sites hosted in well-defined copper-containing MFI (CuMFI) materials by means of *in situ* UV/vis and XAS spectroscopy and correlated the results with material's performance in methane selective oxidation. We have demonstrated that the copper speciation in CuMFI is governed by Cu/Al ratio in the material, providing a possibility to control materials' activity and selectivity. CuMFI materials with low Cu/Al ratio contain preferably mono-µ-oxo dimeric sites which selectively oxidize methane to methanol in a wide temperature range. An increase in Cu/Al ratio for CuMFI results in the formation of another type of mono-µ-oxo dimeric sites with longer Cu-Cu distance. The corresponding sites were generally believed to be capable of methane conversion of methanol [2,3]; however, we clearly showed that they are non-selective and overoxidize methane to formate species even under mild reaction conditions.

The obtained detailed information on the structure and spectroscopic features of both selective and non-selective mono-µ-oxo dicopper sites is essential for the characterization of state-of-the art materials applied in chemical looping. Moreover, it opens novel opportunities for the controlled synthesis of the defined copper sites in copper-containing materials beyond methane conversion to methanol.

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Insights into Lewis acidic nature of extra-framework aluminum centers incorporated in zeolites by ion-exchange

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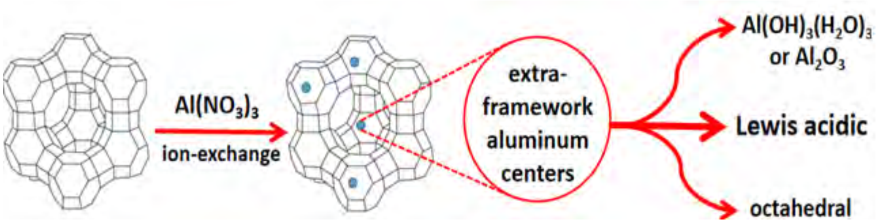
The catalytic activity of zeolites originates from Brønsted acid and Lewis acid sites. Brønsted acidity is well-defined as it stems from a hydroxyl group, which bridges the framework silicon and aluminum atoms of the zeolite **[1-2]**. However, due to their plural nature, the structure of Lewis acid sites remains much less defined **[2]**. In this work, we modulate the Lewis acidity of zeolites, with the aim to understand their structure by quantitatively determining their structure-activity relation. We introduce Lewis acidity into zeolite Y by a facile ion-exchange of aluminum species followed by calcination **[3]**. The zeolite framework remains preserved after incorporation of extra-framework aluminum species by ion-exchange, as suggested by X-ray diffraction and N_2 physisorption. An increase in the total extra-framework aluminum in the modified zeolites led to a marked increase in the number of Lewis acid sites, as illustrated by FTIR spectroscopy of adsorbed pyridine and carbon monoxide. However, no considerable change in the number of Brønsted acid sites was observed. After ion-exchange, there was a significant improvement in the catalytic conversion and rate of reaction for the MPV reduction of 4-*tert* butyl cyclohexanone over zeolite catalysts. The catalytic activity of modified zeolites quantitatively correlated with the concentration of the introduced extra-framework aluminum species and the total Lewis acid content from pyridine-FTIR. Therefore, it is inferred that the newly introduced extra-framework aluminum species are certainly Lewis acidic, with an octahedral coordination under the conditions of NMR measurement and are responsible for enhanced Lewis acid catalytic activity of the aluminum exchanged zeolites **[3]**. The preservation of Brønsted acid sites further identifies these extra-framework aluminum species as charge neutral, likely in the form of nano-sized $Al(OH)_3(H_2O)_3$ or Al_2O_3 clusters **[3-5]**. The strength and thermal stability of these Lewis acid sites is also capable of improving the activity of zeolites for catalytic dehydrogenation of light alkanes to light olefins.



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Air and Moisture Tolerant Hydroamination Reactions using Alkali-Metal Amides as Catalysts

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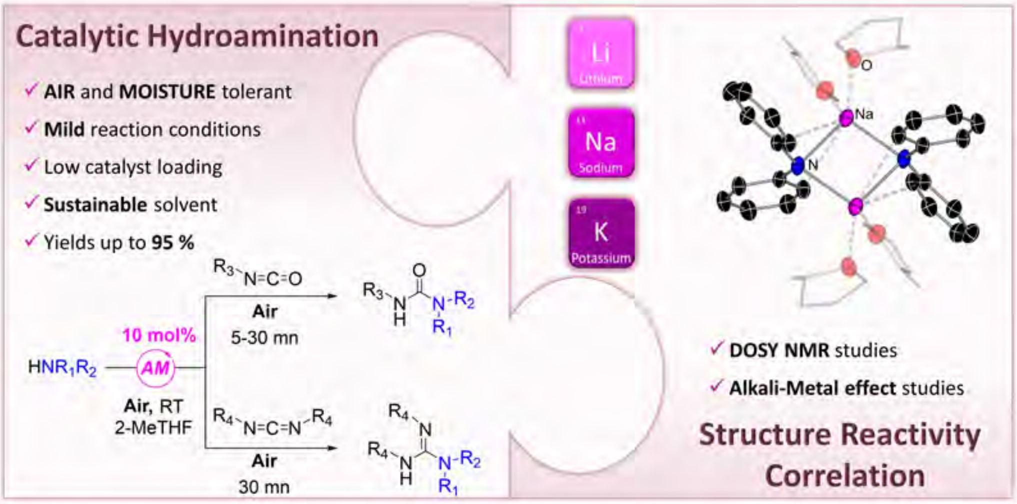
Alkali-metal amides are commodity reagents used on a daily basis in synthetic laboratories worldwide. This near ubiquitous utilization stems from the high reactivity of their highly polar Metal-N bonds. However, their reactivity also imposes severe drawbacks such as the need to perform reactions under inert conditions, in dry toxic organic solvents, and at low temperatures to control their selectivity.[1] Breaking down the barrier between organometallic and aerobic/aqueous chemistry, our group has recently reported the stoichiometric applications of lithium amides for ester amidation[2] and hydroamination of styrenes[3] in air, at room temperature using biorenewable 2-methyl THF as solvent.

Upgrading stoichiometric reactions to catalytic regimes, in this work we report the first examples of catalytic hydroamination of organic heterocumulenes such as carbodiimides and isocyanates mediated by lithium amides in the presence of air and moisture, conditions traditionally disallowed for this type of organometallic reagents. Reactions can be carried out using a one pot approach, employing *n*BuLi as a precatalyst. Key reaction intermediates have been isolated and characterised in 2-methyl THF, with the aid of X-ray diffraction and ^{1}H DOSY NMR, shedding light towards the special kinetic activation observed for these systems under the reaction conditions employed in this study. The role played by the alkali-metal has also been assessed by investigating a selected number of reactions using sodium and potassium amides as catalysts.



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Identifying and Advancing Strategies for High-Yield Methane Partial Oxidation

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A direct methane valorization process that achieves high product yields in a scale-flexible manner would provide numerous opportunities in the sustainable production of fuels and high-value chemicals; however, a commercial process has yet to emerge due to numerous challenges [1-3]. Despite the high volume of research on this reaction, the big picture for thermocatalytic systems remains largely the same; most systems are severely limited by the selectivity-conversion limit, independent of the catalyst employed, that restricts the achievable yield to an impractical limit. The first part of this talk critically examines recent developments in methane partial oxidation as they relate to progressing strategies for high-yield processes. From this analysis, we highlight the promising emergent strategies and motivate more directed science required to bridge existing gaps between the vast scientific knowledge in methane activation and the technological necessities of viable MtM processes.

In the following part of the talk, we describe recent advances from the group in the conversion of methane to an oxidation-resistant methyl ester, one of the most promising routes for high-yield methane conversion [2, 4, 5]. We introduce multiple solutions that target the key shortcomings of the conventional chemistry, namely its reliance on extremely aggressive acid solvents, economically impractical oxidants, and homogeneous catalysts, all of which pose issues for catalyst/product recovery and basic process economics [6]. We demonstrate an approach that uses a solid catalyst, air as an oxidant source, and a diluted acid solvent (< 15 wt%). We successfully developed manganese and cobalt-based heterogeneous catalysts with competitive performance on the basis of turnovers and production rates in comparison to previously-reported homogeneously-catalyzed systems that employ stronger oxidants and higher methane partial pressures. The improved performance of the supported transition metal catalysts combined with the advantages in catalyst/product recovery signify a promising advancement in direct methane partial oxidation technologies. The conclusion of the talk underscores impactful directions for further developing high-yield methane conversion processes.

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Identification and Characterization of Active Sites in Copper Exchanged Mordenite in Direct Methane to Methanol Oxidation

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The increasing amount of natural gas (containing methane as a primary component) from remote sources has animated research efforts to identify cost-effective methods to convert methane in small quantities into high-value products.[1,2] One particular approach, which has gained a lot of attention, is the direct, low-temperature oxidation of methane into methanol using copper-exchanged zeolites.[3] Although this process constitutes an excellent opportunity to transform methane into fuels and commodity chemicals in a sustainable manner, no commercial implementation has been realized so far.[4,5] One fundamental obstacle is the lack of knowledge about the identity and structure of the copper active sites in those materials as well as their redox properties and site-specific kinetic properties. This is further complicated by the fact that various active copper-oxo species may be present in a dynamic co-existence.[6]

In the present contribution, the copper speciation in copper-exchanged mordenite samples with different copper loadings was investigated by a combined spectroscopic and time-resolved approach. The general reactivity of specific sites towards methane as well as their redox properties were evaluated by tracing characteristic spectroscopic changes upon reaction with methane. Dimeric $[Cu_2O]^{2+}$ as well as monomeric $[CuOH]^+$ species were identified as active sites. In addition, direct evidence for the participation of bare Cu^{2+} ions adjacent to $[CuOH]^+$ sites in methane oxidation was delivered. In contrast to dimeric copper-oxo sites, methane oxidation was found to proceed in a more selective manner on monomeric copper species. Furthermore, insight into the kinetic properties of certain copper active centers was obtained on the basis of advanced *operando* spectroscopy methods. In comparison to monomeric copper sites, dimeric $[Cu_2O]^{2+}$ centers were characterized by a two-fold higher apparent activation energy and an approximately seven-fold faster reaction rate.

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Electrochemical Ruthenium-Catalysed C–H Activation in Water Through Heterogenization of a Molecular Catalyst

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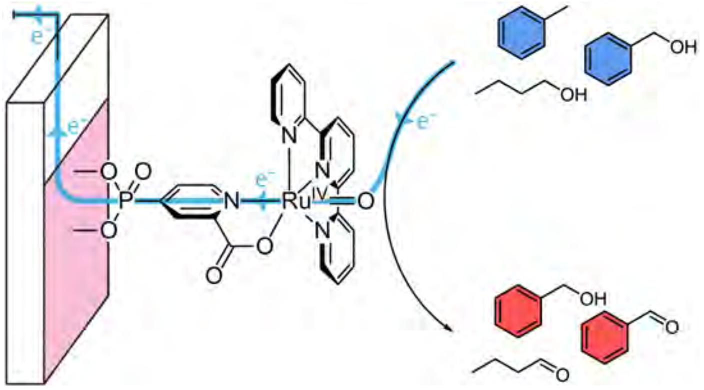
The catalytic oxidative activation of C–H bonds in organic substrates remains a hot topic in synthetic chemistry.[1] Classically, transition metal catalysis effects these transformations efficiently and with high selectivity.[2] Here, the combined advantages of molecular transition metal and heterogeneous catalysis are demonstrated by immobilisation of a ruthenium-based electrocatalyst [Ru(tpy)(pic-PO$_3$H$_2$)(Cl)] (where tpy is 2,2′:6′,2″-terpyridine, pic-PO$_3$H$_2$ is 4-phosphonopyrid-2-ylcarboxylic acid) on a metal-oxide surface.[3] Oxidation of toluene with the catalyst in aqueous media using ceric ammonium nitrate as terminal oxidant resulted in a rapid deactivation of the catalyst. Electrochemical regeneration of the catalyst circumvented some of the issues observed in solution resulting in an improved catalytic activity, which was further enhanced by immobilisation of the catalyst on a on a mesoporous indium tin oxide electrode surface through the phosphonate anchoring group. Using the heterogeneous catalyst system, the oxidation of a variety of organic substrates with varying bond dissociation energies (76–95 kcal mol^{-1}) was demonstrated with turnover numbers of up to 346.



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Operando insight of polycrystalline nickel in ethylene to syngas self-sustained oscillatory conversion

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As scientists, we have the responsibility to pave the way toward developing a sustainable economy that is based on renewable natural resources and to mitigate the emission of greenhouse gases. The catalytic process of large-scale conversion of short-chain hydrocarbons to syngas (CO and H_2) is critical for modern society and has the potential to significantly influence the future energy economy. Breakthrough research on fundamental catalytic processes is difficult to conduct since heterogeneous catalytic reactions are highly non-linear, multilevel chemical processes that operate far from thermodynamic equilibrium and are further complicated by competing non-catalyzed gas-phase reactions. The discovery of self-sustained oscillating reactions in the early 1970s revealed one of the most intriguing branches of catalysis, which has been observed in over 60 systems [1]. Non-noble metals are known for their catalytic activity in short-chain hydrocarbon partial oxidation and, under certain conditions, can exhibit self-sustaining oscillations. In order to shed some light on the coupled effect of different species in the gas-phase, the chemical state of the catalyst and resulting catalytic activity under relevant reaction conditions, we performed a correlative in-situ study based on the combination of operando microscopy and XPS spectroscopy. The objective is to obtain mechanistic insights into the role of surface species present in the catalytic process of partial oxidation of ethylene to syngas on a model polycrystalline nickel foil. The coupled and dynamic interplay between the gaseous environment and the surface chemistry strongly depends on the reaction conditions. Using a combination of operando scanning electron microscopy (OSEM) for real-time observation of structural dynamics and ambient pressure x-ray photoelectron spectroscopy (APXPS) [2] we are able to correlate the state of the catalyst with its activity. Although challenging to study, the self-sustained oscillating reaction mode enables detailed analysis of the successive elementary steps of the catalytic act. The obtained insights are envisioned to expand the research of self-regenerating operation of real-world catalysts. Our unique in-situ SEM setup allows us to visually observe the state of the active catalyst under reaction conditions in real-time, at high spatial resolution using a combination of dedicated secondary electron, high-temperature 3D backscatter- and an electron-beam absorbed current detectors. This enables surface-sensitive imaging and real-time observation of collective non-equilibrium dynamics under controlled atmosphere at pressures between 10^{-6} to 10^{+3} Pa and temperatures of up to 1250^{o}C. By maintaining a constant gas composition in isothermal conditions, a synchronized self-sustained oscillation mode was identified, in which the reaction`s product distribution was observed to reflect the catalyst morphology and chemical state. We have discerned the active species that generate protective surface intermediates in non-stoichiometric environments. We were able to trace the oscillatory behavior down to competing species that control the catalyst activity. The combination of spatially resolved real-time imaging [3, 4] with integral surface-sensitive spectroscopy enables the chemical identification of surface species and simultaneous visualization of their evolution as a function of reaction conditions. We were able to provide insight into structure sensitivity and coupling phenomena between reactive gas-phase and catalyst state that are related to the emergence of catalytic activity in a synchronized self-sustained oscillatory mode. The here described structure-activity correlations are not accessible through integral characterization techniques or by studying of steady-states alone, highlighting the importance of real-time, laterally resolved direct observation of active catalyst.

Bimetallic Gold-Zinc Catalysts for the Hydrogenation of CO_2 to Methanol

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In combination with the generation of hydrogen from renewable resources, the thermochemical hydrogenation of CO_2 to methanol is an appealing reaction for the mitigation of anthropogenic emissions, representing a strategy for the re-integration of CO_2 as part of a closed-carbon fuel cycle.[1,2] However, the development of active, selective and stable catalysts for this transformation remains challenging. For the most part, improvements are made on an empirical basis, through modification of metal, support, promoters and additives, which have been shown to have a profound influence on the observed reactivity and, consequently, selectivity for the desired product. In spite of intensive study of the aforementioned support and promoter effects, understanding of the precise function of the added components remains elusive.[3] One example where the choice of support/dopant is particularly pronounced is the case of Au-based CO_2 hydrogenation catalysts, where selectivity for methanol can be modulated through judicious selection of support.[4]

To confront this observation, and further explore the role of oxide support in driving selectivity for the Au-catalysed conversion of CO_2 to methanol, a surface organometallic chemistry (SOMC) approach was employed to generate supported Au-based nanoparticles on a Zn-doped silica support as a well-defined material amenable to spectroscopic study. Evaluation of this material under reaction conditions demonstrates that addition of Zn results in an enhanced methanol formation rate (1.16 $\text{mmol}_{\text{MeOH}}\ \text{mol}_{\text{Au}}^{-1}\ \text{s}^{-1}$) and methanol selectivity (64%) (vs. 0.63 $\text{mmol}_{\text{MeOH}}\ \text{mol}_{\text{Au}}^{-1}\ \text{s}^{-1}$ and 51% for Au/SiO_2). Study of the catalyst by *in situ* X-ray Absorption Spectroscopy (XAS) reveals the presence of an alloyed phase that is formed during hydrogen treatment, an observation that is consistent with insights from HAADF-STEM and diffraction experiments. Collectively these observations illustrate the importance of alloy formation in Au-Zn catalysts for CO_2 hydrogenation, enabling insights into related Au/ZnO CO_2 hydrogenation catalysts, as well as other alloy-containing catalysts used in CO_2 hydrogenation.

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Production of Jet-Fuel-Range Olefins via Catalytic Conversion of Pentene and Hexene over Mesoporous Al-SBA-15 Catalyst

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The oligomerization of biomass-based olefins offers potential for the synthesis of sustainable jet-fuels comprised of C_{10}-C_{18} hydrocarbons that are compatible with current infrastructures. However, the control of the oligomerization product distribution remains a challenge. In this contribution, the influence of process parameters comprising temperature, pressure, contact time, and feed composition on the catalytic conversion of a mixture of pentene and hexene over mesoporous Al-SBA-15 catalyst in continuous operations is thoroughly investigated. Kinetic evaluation resulted in the observation that pentene is more reactive than hexene, while selectivity to jet-fuel range products exceeding 98% was achieved at low-to-moderate conversion (<50%). Increasing the conversion to ca. 90% resulted in a decreased selectivity towards jet-fuel range products of ca. 75%. Notably, the product distribution of the oligomerization reaction is mostly independent of the process conditions under study, implicating that adjusting the conversion level is the primary way to tune oligomerization selectivity over the Al-SBA-15 catalyst. This understanding of the oligomerization process identifies the direction of research devoted to oligomerization of complex olefin mixtures mimicking the process stream of biomass-based olefins production units, with the goal to achieve and optimize the “biomass to jet-fuel” transformation.

Automated image analysis for single-atom detection in catalytic materials by transmission electron microscopy

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The visualization of atomically isolated metal species in solid catalytic materials, enabled through immense advances in (scanning) transmission electron microscopy (EM) technology, has ushered the advent of single-atom heterogeneous catalysts (SACs).[1] While EM images yield rich information that is key to confirm the elusive single-atom speciation, image analysis is subject to misinterpretation, lacks sample-wide representativity, and is work-intensive when performed manually. Herein, we tailor an off-the-shelf image recognition algorithm based on convolutional neural networks (CNN) to identify single platinum atoms in a non-model acetylene hydrochlorination catalyst.[2] The framework was trained on a subset of manually labeled images acquired under realistic and hence imperfect conditions. When properly parametrized, the atom detection accuracy of the CNN model (F1-score of 0.8) superseded simple image filters or a computer vision model, detecting up to 20’000 atomic positions. For the first time, a sample-averaged distribution of atomic densities, which agreed well with other techniques, could be obtained from statistical analysis of electron microscopy images. When sufficient labeled images were provided, the technique could be readily transferred to lower contrast images of other single-atom catalysts (iron on graphitic carbon nitride, Fe_1/GCN). This work sets the basis for the automated material analysis required for data-driven discovery of new catalytic materials.

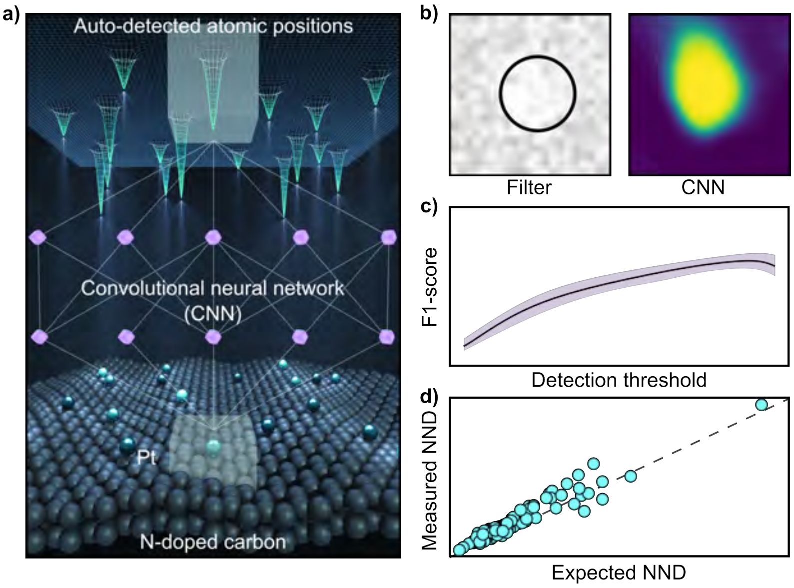

Fig. 1a Illustration of the single-atom detection workflow comprising of scanning transmission electron microscopy, CNN-driven image analysis, and statistical data evaluation. **b** Atomic feature identification is enhanced through the CNN compared to conventional image filters. **c** Model performance expressed as the F1-score can be carefully optimized through the detection threshold. **d** Sample wide metrics such as nearest-neighbor distance (NND) agree well with expected distributions.

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Reducing N_2O and NO_x emissions in Nitric acid plant with industrial Fe-zeolite catalysts

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Nitric acid is one of the most produced commodities worldwide. It is mainly used as an essential chemical for the synthesis of fertilizers and in 2013 the production reached 78 million tons [1]. In recent years, the higher awareness in the greenhouse effect and in the environmental pollution, have highlighted the importance of a new development in the nitric acid tail gas treatment, especially concerning the N_2O and NO_x species. Various metal oxide and zeolite catalysts have been developed for N_2O and NO_x abetment, each one with benefits and drawbacks. The state-of-the-art materials are based on Fe-zeolites which both show NO_x and N_2O abatement with the same catalyst. Numerous Fe zeolites have been explored, such as Ferrierite (FER), ZSM5 and BEA [2]. In this paper, the comparison of fresh and laboratory aged Fe-FER and Fe-ZSM5 industrial catalysts, has been carried out. Fe-FER catalyst is a proprietary catalyst of CASALE SA and ALSYS and is used in nitric acid plants [3]. The results from field and laboratory showed that Fe-FER will allow customers to benefit from a higher catalytic activity and greater stability compared to the current commercial solution with Fe-ZSM5. The extruded catalysts tested were prepared at industrial scale, from process production to quantity scale, by ALSYS. The catalytic tests were carried out in an Inconel reactor under industrial nitric acid plant conditions. The feed compositions are reported in figure 1 caption. The GHSV used was 25,000 h^{-1}. Very high space velocity was chosen with the purpose to highlight the differences in catalytic activity among the catalysts tested. The hydrothermal aging treatment was performed for 150 h at ambient pressure at two temperatures (600 and 700°C) with a feed of 12% of O_2 and 6% of H_2O with a GHSV of 5000 h^{-1}.

Two representative industrial catalysts were investigated in relevant industrial conditions before and after simulated aging treatments. Results showed that Fe-FER is the most stable catalyst and high performance that can be used for tail gas treatment in nitric acid plants. Moreover, Fe-FER is extremely selective in N_2 even after severe aging treatments. The Fe-FER catalyst for DeN_2O and $DeNO_x$ applications has superior performances compared to the Fe-ZSM5.

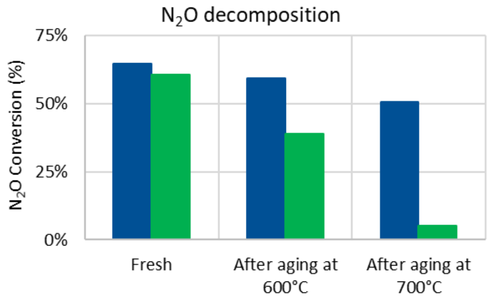

Figure 1. DeN_2O condition: NO 70 ppm, NO_2 30 ppm, N_2O 900 ppm, O_2 3.0%, H_2O 0.3% and N_2 balance. Fe-FER (blue bars), Fe-ZSM5 (green bars)

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Systematic investigation of the interaction between selected linear olefins and Zn-MOF-74

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Hydroformylation is an industrially important, homogeneously catalyzed reaction. Olefins react with a 1:1 mixture of H_2 and CO, promoted by cobalt or rhodium catalysts, to form branched and linear aldehydes [1]. Metal-organic frameworks are a class of highly porous, crystalline materials assembled from metal-containing nodes and organic linkers. Their chemical and structural flexibility enable their use in a plethora of applications [2]. The addition of Zn-MOF-74 to the cobalt-catalyzed reaction enhances the selectivity to 90 % in favor of the branched isomers. We showed by simulations that this effect is caused partially by the 14% higher density of 1-hexene within the channels of Zn-MOF-74 compared to its liquid density [3]. In order to support this finding and to gain a better understanding of the interaction between olefins and Zn-MOF-74, we investigated the system using multiple techniques among others attenuated total reflection infrared spectroscopy (ATR-IR), neutron powder diffraction (NPD) and temperature-programmed desorption (TPD). We used propene and 1-hexene as adsorbates to investigate the influence of the aliphatic part of the molecules. While ATR-IR reveals the part of the framework interacting with the adsorbates and TPD the number of different adsorption sites, their occupation, combined with the pore volume, allows the calculation of the density within the pores. In the case of propene, this value is peculiarly high. Furthermore, the NPD data show different adsorption modes depending on the olefin chain length.

This study improves our understanding of the adsorbate-MOF interaction and provides new insights in the adsorption properties of Zn-MOF-74.

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Promoted higher alcohols synthesis from syngas by inverse CuCo@ZrO_2 catalysts

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Higher alcohols (HA) have a large economic value and are important compounds in the chemical, pharmaceutical and energy sectors. Currently, they are mainly produced by sugar fermentation (ethanol and isobutanol), hydroformylation of light alkenes (propanol) or hydration of petroleum-derived alkenes (heavier alcohols), but their direct synthesis from syngas would comprise a more environmentally friendly, versatile and economical alternative.[1] A wide variety of heterogeneous catalysts have been evaluated in the direct conversion of syngas into HA, with modified Fischer-Tropsch synthesis systems like CuCo based catalysts showing the highest yield of HA. Herein, we report inverse ZrO_2 modified CuCo as a promising catalyst for direct conversion of syngas into HA. Under the optimized conditions, the inverse CuCo@ZrO_2 catalysts show ~3 times higher activity (*STY*) than the conventional CuCo catalysts (**Fig. 1a-b**) prepared by oxalate-gel coprecipitation method,[2] with the highest HA selectivity of ~22% in all products. The promotion effect of ZrO_2 might be attributed to the the enhanced ability of H_2 splitting and spillover, which was proved by the temperature-programmed reduction (TPR) of corresponding oxide precursors by H_2 (**Fig. 1c-d**). These findings provide a new insight into the design of efficient catalysis systems for direct HA synthesis from syngas.

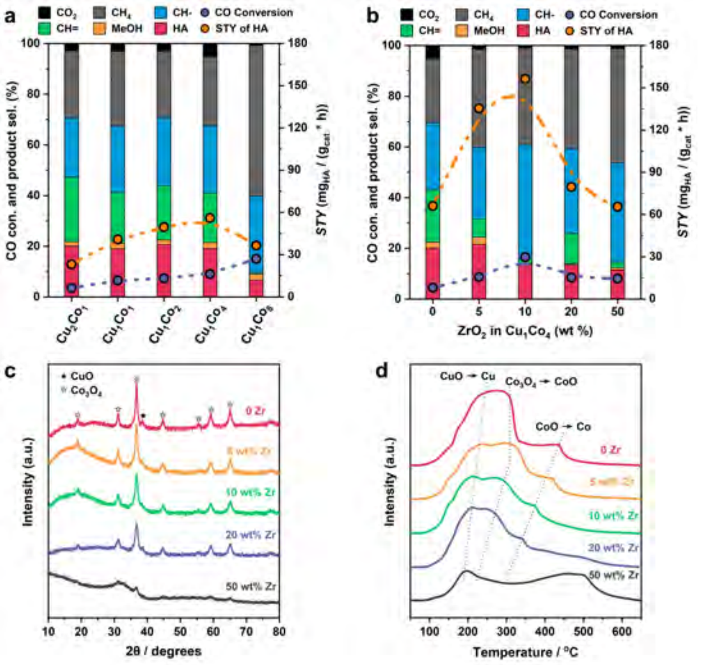

Fig. 1a Catalytic performance of CuCo catalysts with different Cu/Co molar ratio (543 K, 5 MPa, molar H_2/CO = 2, *WHSV* = 12000). **b** Catalytic performance of Cu_1Co_4@ZrO_2 catalysts with different weight percentage of ZrO_2 (543 K, 5 MPa, molar H_2/CO = 2, *WHSV* = 24000). **c** XRD patterns and **d** H_2-TPR curves of Cu_1Co_4@ZrO_2 oxide precursors with different weight percentage of ZrO_2. All catalysts were prepared by oxalate-gel coprecipitation method.

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Unveiling evolution of active oxygen species in ethylene epoxidation over silver foil by ambient pressure X-ray photoelectron spectroscopy

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Ethylene epoxidation (EPO) is one of the most important industrial catalytic reactions and silver-based catalysts have outstanding activities and selectivities in this reaction. Silver-based model catalysts (foils, powder, single crystals) have been extensively used to investigate the fundamental steps of EPO. It has been widely proven that surface oxygen species participate in the catalytic cycle and their property is a key factor in the selectivity of EPO. However, the influence of reaction conditions on the distribution of oxygen species is still unknown. In the current work, silver foil was characterized systematically as the starting step of a project aiming at the investigation of industrial catalysts. Ambient pressure X-ray photoelectron spectroscopy was used to investigate the effects of temperature and gas environment under both steady state and transient condition experiments. Three types of oxygen species correlated to different structure of AgO_x were unveiled on Ag foil. All of them were proved to be highly sensitive to temperature and ratio of reagent, and participate the reaction with ethylene. The key role of subsurface oxygen species was revealed over silver foil during the EPO process.

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^{51}V ssNMR Study for Surface Site of Vanadium-based Olefin Polymerization Catalyst Supported on $MgCl_2$

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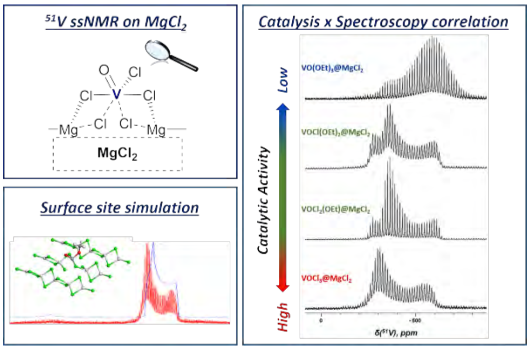
$MgCl_2$-supported vanadium-based catalysts (VMC) display high catalytic activity toward olefin polymerization, with complementary features with respect to the classical Ti-based catalyst.[1] However, the surface structure of VMC remains poorly understood.[2] We herein explored the surface structure of $VOCl_3$-based VMC by exploiting ^{51}V ssNMR, systematically tuning the ligand type of V precursors. Solid-state WURST-QCPMG $^{51}V\{^1H\}$ NMR successfully captured the surface vanadium site with differentiating its ligand environment, which was further linked with its catalytic activity emphasizing the crucial role of Cl-rich environment around vanadium center on catalysis. B3lyp/Def2TZVP level calculations, which were preliminalily validated by a library of vanadium molecular compounds, enable to resolve the structure of the surface species as shown by the good fit with the experimental spectrum. Herein the thus-obtained results draw parallel with the observation in Ti-based catalysts, which suggests the potential of this methodology as a evaluation tool for $MgCl_2$-supported catalysts.



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Cooperative PYE Complexes and their Application in Formic Acid Dehydrogenation

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The global transition towards green energy sources requires storage of intermittently produced energy. Formic acid (FA) is a promising carrier for this purpose and allows easy and safe storage of electrolytically produced dihydrogen. FA dehydrogenation has therefore been of growing interest and a variety of homogeneous complexes has been reported as highly active catalysts for this reaction.[1] Most systems so far rely however on air-sensitive phosphorous-based ligands and their replacement would be of high interest.[2] In this context Pyridylideneamines (PYEs), a class of electronically flexible ligands, known for their ability to stabilize a broad variety of transition metals in wide range of oxidation states, might be well suited candidates for enhancing dehydrogenation catalysts (Figure 1).[3]

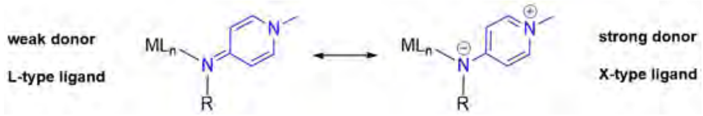

Figure 1 Electronic flexibility of PYEs

Here we present a series of air-stable ruthenium complexes featuring novel tridentate N,N,N ligand scaffolds that combine a cooperative site with the electronic flexibility of PYEs. We will demonstrate reversible protonation behaviour of the central nitrogen moiety (Figure 2) and rationalize the effect of different key parameters of ligand design such as ligand donor properties, cooperativity, and the role of ancillary ligands, en route to developing one of the most active complexes reported so far in FA dehydrogenation.

Figure 2. Reversible protonation behaviour of NNN ruthenium complexes (left) and dehydrogenation of formic acid (right)

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Activation of atomically-dispersed platinum in Pt/CeO$_2$ for the Water-Gas Shift reaction

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Oxide-supported noble metal catalysts have been extensively studied for decades for the water-gas shift (WGS) reaction. Discussions remain about the nature and reactivity of the active species, whether they are atomically dispersed or nanoparticles. In situ characterization techniques, such as ambient pressure photoelectron spectroscopy (AP-XPS), are excellently suitable for observing the changes in catalyst structure during activation and reaction. The challenge is how to couple the catalyst structure and performance under relevant conditions in the presence of the pressure gap. Here we show the characterization of atomically dispersed Pt/CeO$_2$ catalyst by in situ XPS under WGS operating conditions. Notably, we carried out ex-situ activity test in a flow reactor making use of a diluted reaction feed to match the partial pressures of reactants used during XPS measurement. The catalyst performance under such conditions is consistent with that in an AP-XPS chamber at mbar level pressure, which allows us to characterize and compare the activity and active sites under relevant working conditions. Atomically dispersed Pt(II) atoms exhibit no WGS activity. The onset of activity is paralleled by sintering into Pt(0) clusters. Once platinum clusters are formed, they no longer re-oxidise back to Pt(II), which allows the catalyst to remain active. This work highlights the structure–activity relationship in supported metal catalysts and proposes a suitable approach to correlate in situ XPS and activity test under relevant conditions.

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The hydrocarbon pool nature in the methanol-to-olefins process: an operando FT-IR spectroscopy study

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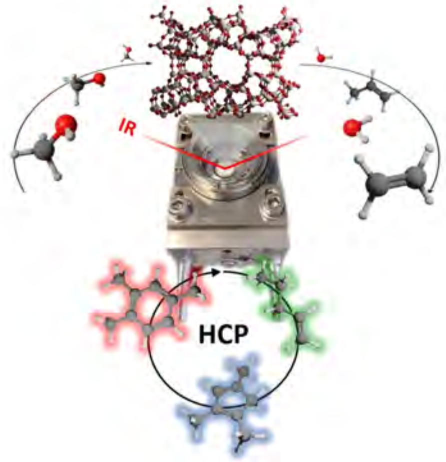
Sustainability and attention to the ecosystems are the drivers of today's chemical industry. Methanol is a promising direct link between sustainable feedstock, as CO_2, and commodity chemicals and fuels. In the specific case of the aircraft sector, sustainable fuels are highly sought after and a promising production pathway covers the methanol-to-olefins (MTO) process as intermediate step. In this work, ZSM-5 (MFI), SSZ-13 (CHA) and FER zeolites are tested as catalysts in the MTO process using operando diffuse reflectance IR spectroscopy. Transient experiments enable the observation of methanol-free spectra of the hydrocarbon pool built up by alternating the dosage and the removal of methanol while products quantification is carried out through gas chromatography. FER topology limits the formation of bulky unsaturated species and favors an aliphatic pool along with the production of higher olefins (C_{4+}). Conversely, ZSM-5, with a three dimensional 10-membered ring channels system, and SSZ-13, featuring small 8-membered ring pores and large cages, foster aromatics and unsaturated cyclic hydrocarbons formation while yielding ethylene and propylene other than C_4 – C_7 fractions. The presented method applied to the MTO process provides a desirable perspective on the evolution of hydrocarbon species residing in zeolite micropores and those produced during the first stage of the reaction and importantly it clarifies differences in terms of active sites nature and selectivity when employing various zeolite topologies.



Polarized nickel enables long-chain products in CO_2 electroreduction

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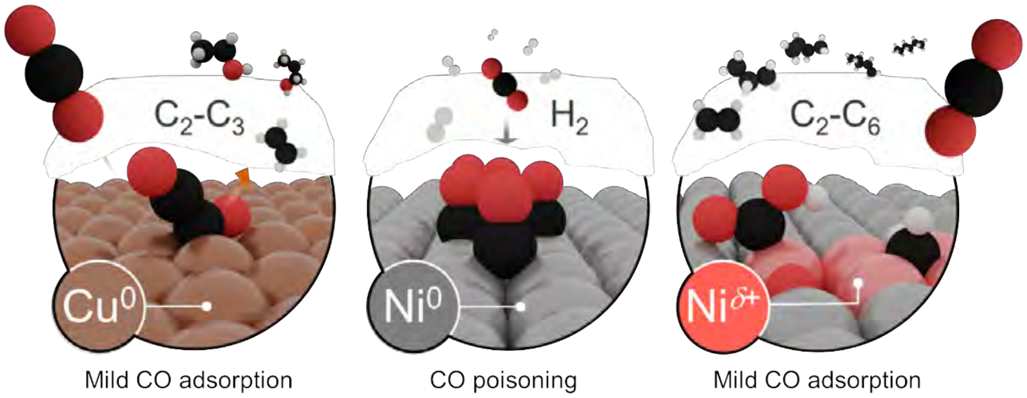
The electroreduction of CO_2 in combination with renewable electricity can be used to sustainably generate multicarbon products. To date, only copper-based materials can effectively promote carbon-carbon coupling giving rise mainly to C_2-C_3 products, despite vast efforts devoted to extend the scope of products reported by Hori et al. on this metal four decades ago.[1] Herein, we disclose that electrocatalysts derived from oxygenated nickel compounds can generate linear and branched C_3-C_6 hydrocarbons with sustained Faradaic efficiencies up to 6.5%, in contrast with the practically-inactive metallic nickel.[2] Electrochemical CO stripping, *operando* X-ray absorption spectroscopy, and density functional theory (DFT) pinpoint the presence of stable, polarized Ni^{d+} active sites, which bind CO moderately, associated with Ni-O bonds. The reduction of selected C_1 molecules and DFT simulations suggest that the Ni^{d+} sites promote an insertion mechanism reminiscent of Fischer-Tropsch synthesis: COOH + CH_x coupling followed by successive CH_x insertions. Our results disclose atom polarization as the key to prevent nickel from CO poisoning, extending the scope of the CO_2 electroreduction towards synthetic fuels.



Mild CO adsorption CO poisoning Mild CO adsorption

Fig. 1 Schematic representation of the main catalytic features associated to copper-based systems (left), metallic nickel (center) and nickel surfaces containing polarized sites (right). It is generally agreed that copper systems favor C-C coupling because of the mild CO adsorption enabling dimerization as the key step towards ethylene and C_2 and C_3 oxygenates. Metallic nickel is known to suffer from CO poisoning and thus exhibits poor catalytic performance towards carbon products. Polarization of nickel atoms makes them adsorb CO mildly and promote an insertion mechanism leading to long-chain hydrocarbons.

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The challenging interplay of catalyst, sorbent, and reactor in the sorption-enhanced methanol synthesis from CO_2

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The development of a methanol synthesis process from CO_2 brings significant new challenges compared to the standard process from syngas. Water is co-produced in the synthesis, resulting in a more stringent thermodynamic limitation (low CO_2 conversion) and in a lower activity of the catalyst (due to competitive adsorption). The scientific literature shows several examples of new catalytic materials, which can improve the course of the reaction [1]. However, an active catalyst is not the only requirement to make the CO_2 to methanol process a valid alternative to the current synthesis route. To overcome the thermodynamic limitation and increase the conversion per pass, the use of a sorption-enhanced reactor is an interesting option. However, the interplay of the catalyst and the sorbent is not trivial, and it is strongly affected by the properties of the reactor. In this presentation we show that the use of sorption-enhanced fixed-bed reactors for methanol synthesis are affected by significant heat transfer limitations, which tend to deactivate the reaction, due to operation at too high temperature (figure 1a). The conversion enhancement generates an excessive amount of heat, which cannot be effectively removed. We observed that this phenomenon can be significantly reduced by using a fluidized bed reactor, where the reaction heat is effectively distributed over the reactor. In this case, the methanol yield can be significantly increased. A further improvement can be achieved by combining the features of a fluidized bed and an entrained bed reactor (figure 1b). This means that the catalyst remains in the reactor, while the sorbent is entrained through the reactor and recirculated after regeneration. In this reactor, it is possible to achieve a continuous methanol production, while establishing an appropriate temperature profile to maximize the reaction yield.

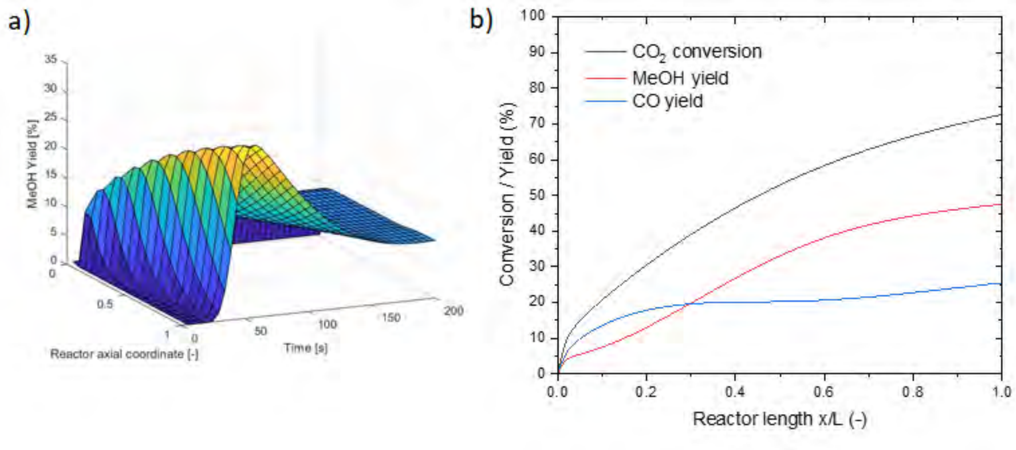

Figure 1 the methanol yield which can be achieved in: a) the fixed bed reactor; b) the entrained flow reactor (ratio sorbent: catalyst = 1:1, CO_2:H_2 at inlet = 1:3, P=30 bar).

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Droplet-based microfluidic platform for understanding metal stabilization in the design of single-atom heterogeneous catalysts

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One of the key challenges in single-atom catalyst synthesis is the controlled formation of atomically isolated metal species.[1] Despite the myriad of experimental approaches, only recently the focus has shifted towards mechanistic insights. Indeed, the understanding of single-atom catalysts fabrication through post-synthetic methods is limited, and the lack of knowledge of the metal uptake capabilities of the carriers mandates time-consuming parameter optimization. This study develops a high-throughput microfluidic technology to understand metal species' uptake and resulting nuclearity with different metal precursor-carrier combinations via wet impregnation, the most readily scalable and versatile approach for metal introduction. The microreactor environment created by a fast-mixing droplet-microfluidic reactor (**Fig. 1b**) permits precise control of the host material and metal precursor concentrations, mixing, and residence times, which enables correlation of the metal uptake and resulting speciation with the synthesis conditions. As a prototypical case study, the Pd/C_3N_4 system, well-described and highly relevant in alkyne semi-hydrogenation, is investigated.[2] The Pd uptake on optimized-size carbon nitride particles (**Fig. 1a**) before nanoparticle formation is repeatably determined to be around 0.32 Pd atom nm^{-2} (**Fig. 1c, Fig. 1d**). We expect this work to lead the way towards high-throughput microfluidic platforms for enhancing single-atom catalyst discovery and characterization through rapid screening of experimental conditions.

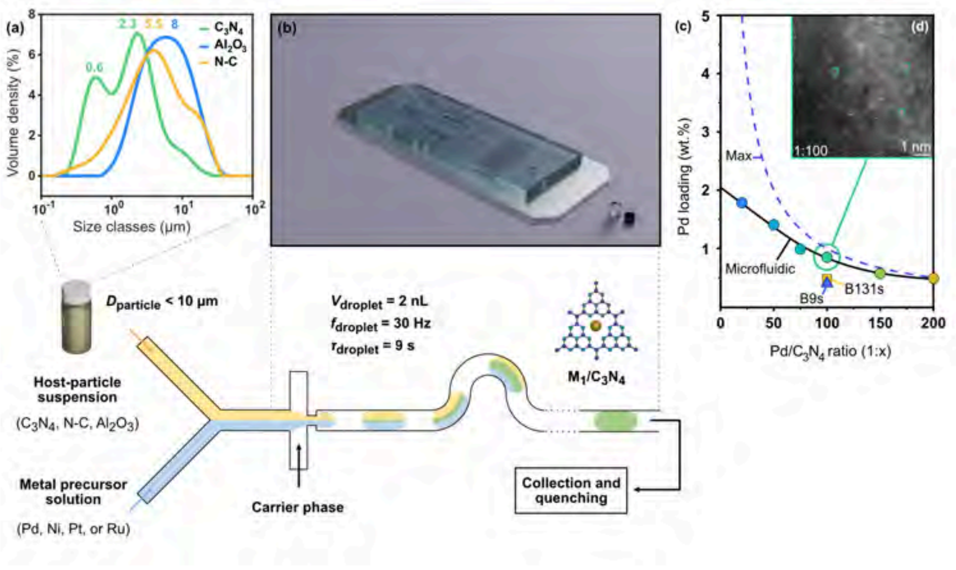

Fig. 1a Optimized size distributions for the particles used in the microfluidic reactor. Water-in-oil droplets form individual reaction vessels in which mass transfer and contact time between species is highly controllable, with rapid and efficient mixing. **b** Poly(dimethylsiloxane) microfluidic reactor. **c** Pd uptake determined with varying Pd/C_3N_4 ratio with an in-chip residence time of 9 s. **d** AC-STEM showing single Pd atomic centers (circled) for Pd/C_3N_4 = 1:100, corresponding to a density of 0.32 atoms nm^{-2}.

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A low Si/Al ratio in faujasites controls the selectivity in the catalytic fast pyrolysis of guaiacol

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Lignin can be converted into fine chemicals and fuels via catalytic pyrolysis.[1,2] Due to the poor selectivity towards targeted products, it becomes significant to understand the reaction mechanism to actively take control over the selectivity.[3,4] Besides understanding the decomposition mechanism of lignin in chemistry, the reaction mechanism on the catalyst's surface is equally important. Zeolites are common catalysts in lignin catalytic pyrolysis, which not only lower the reaction temperature but can also stabilize the reaction intermediates.[5] Zeolites have several unique features, such as Brønsted acid sites, providing the catalytically active protons, playing an important role in the reaction, and pore channels.

In this work, guaiacol as a lignin model compound was catalytically pyrolyzed over H-FAU catalysts with different Si/Al ratio. Experiments were carried out in a quartz tube reactor setup coupled with photoelectron photoion coincidence (PEPICO) techniques to detect reactive intermediates and stables products. The aim of this work is to disentangle the role of Brønsted acid sites, which are controlled by the Si/Al ratio, at operando conditions. We found that a low Si/Al ratio promotes the demethylation of guaiacol to catechol, by experimental detection of methyl radicals and methane, utilizing photoion mass-selected threshold photoelectron spectroscopy. By comparing intermediates quantitatively, we found that the low Si/Al ratio enables high selectivity towards phenol possible by quantitatively suppressing the catechol dehydration to the highly reactive fulvenone ketene, which makes this reaction uncontrollable otherwise.

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Assessing metal promotion in In_2O_3-catalyzed CO_2 hydrogenation using flame spray pyrolysis as a standardized synthesis platform

T. Pinheiro Araújo[1], J. Morales-Vidal[2], T. Zou[1], R. García-Muelas[2], P. O. Willi[1], K. M. Engel[1], O. V. Safonova[3], D. Faust Akl[1], R. N. Grass[1], C. Mondelli[1], N. López[2]*, J. Pérez-Ramírez[1]*

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A plethora of transition metals have been employed to boost the activity of indium oxide (In_2O_3) in CO_2 hydrogenation to methanol by improving its ability to activate H_2. However, the lack of systematic catalyst preparation and evaluation precludes a direct comparison of speciation and promotional effects among metal-promoted In_2O_3 catalysts, which is crucial to design an optimal system.[1] Herein, we apply flame spray pyrolysis (FSP) as a standardized synthesis method to introduce nine metal promoters (M = 0.5 wt.%) to In_2O_3. Methanol productivity generally increased on M-In_2O_3 with selectivity following Pd ~ Pt > Rh ~ Ru ~ Ir > Ni ~ Co > Ag ~ In_2O_3 > Au (**Fig. 1**). In-depth characterization, kinetic analyses, and theoretical calculations reveal a range of metal-dependent speciation which dictate catalyst architecture and degree of promotion (**Fig. 1**). Atomically-dispersed promoters (Pd, Pt, Rh, Ru, and Ir) grant the highest improvement in performance, particularly Pd and Pt, owing to the creation of In_3M and In_2M_2 ensembles, which strongly facilitate homolytic H_2 splitting and increase the availability of hydrides, which in turn participate in C-H hydrogenations. In contrast, metals in clustered (Ni and Co) and nanoparticle (Ag and Au) forms display moderate and no promotion, respectively, as the surface population of the active ensembles diminishes. This study provides an atomic-level understanding of In_2O_3 promotion based on a unified protocol, and highlights the potential of FSP to engineer complex catalytic systems applicable in diverse energy conversions.

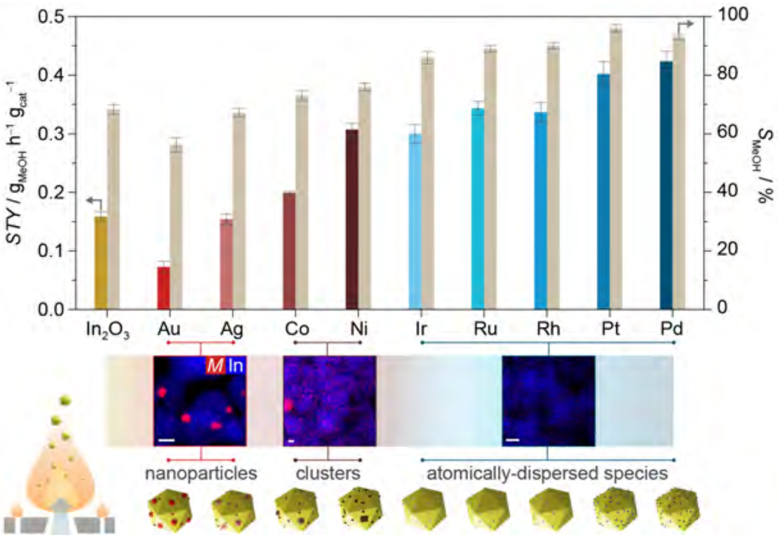

Fig. 1 Methanol space-time yield (*STY*, colored bars) and selectivity (S_{MeOH}, beige bars) during CO_2 hydrogenation over undoped In_2O_3 and M-In_2O_3 catalysts (0.5 wt.% of metal) prepared by FSP. The methanol *STY* was assessed at *GHSV* = 24,000 $cm^3\ h^{-1}\ g_{cat}^{-1}$, while S_{MeOH} at constant CO_2 conversion (*ca.* 3%) and variable *GHSV*. Averaged values measured over 24 h on stream are presented with their corresponding error bars. Reaction conditions: T = 553 K, P = 5 MPa, and H_2/CO_2 = 4. The representative EDX maps of M-In_2O_3 catalysts were collected after activation in CO_2 hydrogenation for 2 h under the same conditions as the catalytic tests. Scale bars are equivalent to 10 nm.

[1] T. Pinheiro Araújo, J. Morales-Vidal, T. Zou, R. García-Muelas, P.O. Willi, K.M. Engel, O. V. Safonova, D. Faust Akl, F. Krumeich, R.N. Grass, C. Mondelli, N. López, J. Pérez-Ramírez, *Adv. Energy Mater.* **2022**,*12*, 2103707.

Kinetic model of ammonia synthesis under industrial operating conditions

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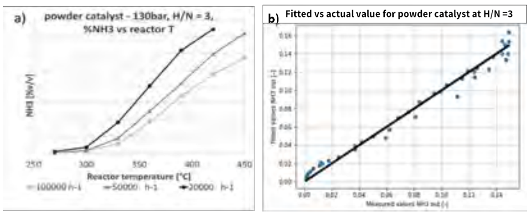
Catalytic ammonia synthesis from H_2 and N_2 still represents one of the most important industrial reaction. Despite the Haber-Bosch process is more than 100 years old [1], the reaction of ammonia synthesis continues to be one of the most studied. The present work focuses on the investigation of iron-based ammonia catalysts activity under different operating conditions, in order to capture and compare their performance with both a clean and poisoned feed (i.e. oxygenates compounds). As reported by Gramatica and Perinicone [2], the primary requirement in kinetic measurements is the collection of experimental data under conditions that are free of any deviating effects, such as flow maldistribution, mass and heat transfer phenomena and poisoning. However, the intrinsic rate constants determined in the laboratory must be combined with appropriate corrective factors for proper scale-up, design, and simulation of any industrial converter. For this reason, in the present work we propose an alternative strategy to study kinetics in different reaction conditions. The goal of the work is to collect experimental data useful for the development of a new kinetic model of NH_3 formation, with a more accurate function of the reaction rate depending on the temperature, ammonia and atomic oxygen contents in the inlet gas feed. The first experimental campaign has been carried out on a packed bed of iron powder catalyst diluted with SiO_2. The goal of these experiments is to measure the performance of the catalyst minimizing mass transfer limitations and hotspots inside the catalyst bed. Looking at the data reported in Figure, at low space velocities, the ammonia formation is higher as equilibrium is not reached. Moreover, the temperature inside the catalyst bed has been accurately measured by means of a multipoint thermocouple to know the actual temperature along the axial direction of the catalyst bed. The data generated by this experimental campaign has been used to refine the kinetic model, Figure b. After the successful model of the kinetics in clean feed, equal experimental campaigns have been conducted feeding NH3 in the feed and in presence of oxygenates. These data provide important information on the effect of catalyst poisoning in the early exposures, its effect overtime and the deactivation overtime due to thermal aging of the catalyst.



The approach developed in this study has considerable industrial importance because it has allowed to refine the kinetic model for iron-based catalysts suitable for NH3 synthesis in relevant industrial conditions such as wide range of temperature (270-510°C), pressure (100-150 bar) and space velocity (10’000-120’000 h-1). Moreover, it allows to discriminate the effect on the reaction rates of NH3 and atomic oxygen contents in the inlet gas feed. The development of a meaningful kinetic model will support the improvement of the industrial operating conditions, allowing to identify poisoning problems in real scale plants and supporting the definition of corrective actions in a due time to preserve the catalyst and the production of ammonia.

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Study of reactivity of NH3 synthesis via molecular modelling

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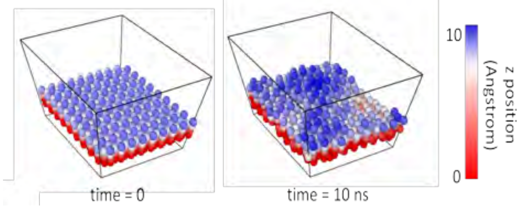
Ammonia (NH_3) is produced mostly via Haber-Bosch process. The reaction is conducted in the presence of iron-based catalysts working in the range of 650-750°K. Despite the reaction having been studied for 100 years, understanding at the atomistic level of the physical and chemical processes responsible for the catalyst activity is still to be discovered. This may provide important information to improve the efficiency of the process and reduce its environmental impact.

One aspect that needs to be clarified is the active catalyst surface morphology. Various studies [1–4] have been dedicated to investigating the Fe surface properties, mainly analyzing and correlating exposed surface orientations and catalytic activity. In these studies, the surface is always considered as a rigid, crystal-like structure. At 650-750 K, however, entropy may affect the surface dynamics, breaking the picture of an ordered Fe crystal surface also at short-range distances.

This work aims to study the properties of a (111) Fe surface at typical process conditions with molecular modelling. A further aim is to study the dissociation of a N_2 molecule over the surface. In order to obtain an accurate description of the Fe surface dynamics we constructed an *ab initio* quality potential with machine learning techniques.[5] Also, ab initio metadynamics was used to investigate N_2 dissociation at 700°K.



With these simulations the effect of the surface dynamics on the reactive steps and the structural and electronic contributions to the catalyst activity have been understood.

The (111) surface is considered the most active, however our simulations revealed that at 700°K it is not stable but becomes dynamically rough, exposing also other facets such as the (211) and (110) (see Fig 1.a). Our metadynamics simulations confirmed that in these conditions N_2 dissociation proceeds as reported in the literature[4]. Interestingly, we observed that the surface dynamics makes the high-coordinated Fe atoms (C7 sites) less easily accessible, thus decreasing the real reactivity of the (111) surface.

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Pd single-atom heterogeneous catalyst on nitrogen doped carbon for sustainable Sonogashira cross-coupling

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

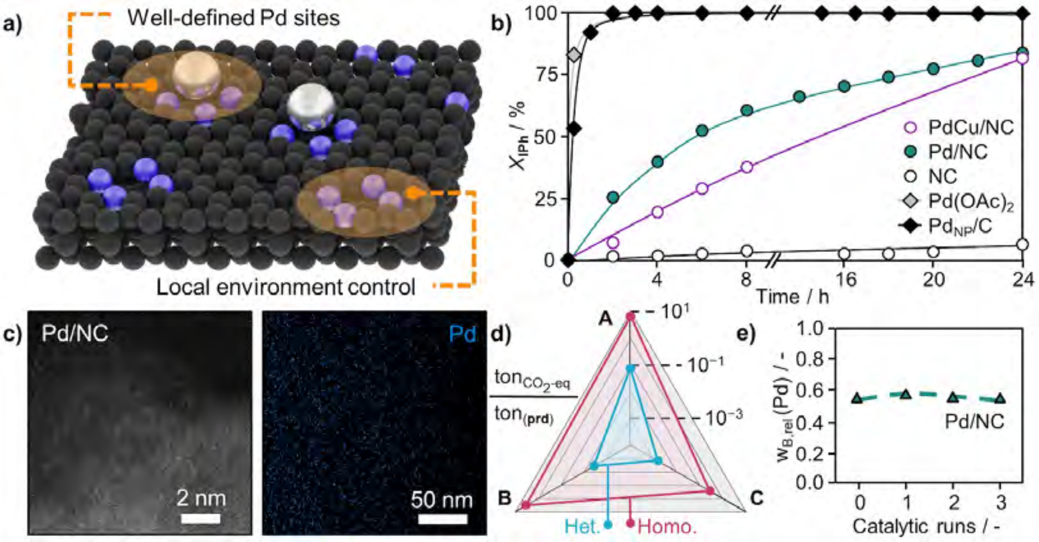

Fig. 1 a) Schematic representation of the surface of the Pd/NC catalyst (0.5wt% Pd loading). **b)** Catalytic performance of selected benchmark catalysts and Pd/NC.

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Towards parallel testing of CO_2 electroreduction to long-chain products

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The electrochemical conversion of CO_2 into fuels and valuable chemicals is attracting growing interest due to increasing climate and carbon management concerns. Current research mainly focuses on copper-based catalysts showing the propensity of C–C coupling and thus forming multicarbon products, mainly ethylene, ethanol, and *n*-propanol.[1] The distinct reaction mechanism on catalysts from inorganic Ni oxygenates (INO; e.g., phosphate, carbonate, borate) gives rise to various gaseous and liquid products, including linear and branched hydrocarbons up to C_6.[2] Going beyond the formation of C_2–C_3 products by using these INO-derived catalysts adds another degree of complexity and provides new challenges in terms of device engineering, product quantification, and upscaling. Herein, we provide refined protocols to access this complex product mixture of long-chain hydrocarbons and oxygenates at the lab scale using a gas diffusion electrode (GDE)-based setup combined with online GC and ^{1}H-NMR spectroscopy with an adapted WATERGATE suppression method. Whereas this set of protocols finally allows a reliable product quantification and a first exploration of Ni-based materials for C_{3+} product formation, large performance data sets combined with advanced data science methods will be required to decipher the entire complexity of INO-derived systems. In this manner, a novel 4-parallel CO_2 electrolyzer setup is presented, enabling the collection of large data sets under highly reproducible conditions and in an automated fashion. We foresee that this integrated approach will foster the exploration of Ni-based materials toward an application in the sustainable production of synthetic fuels.

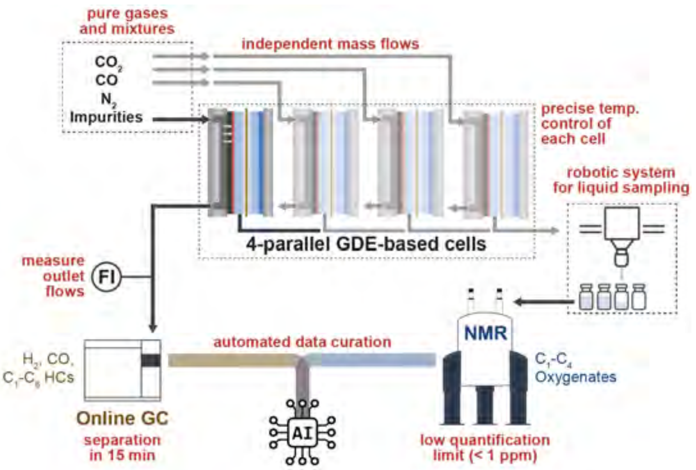

Fig. 1 Schematic illustration of a novel 4-parallel electrolyzer setup for CO_2 reduction. A unified control system allows the independent control of inlet gas flows, temperatures, and electrochemical parameters. The four GDE-based cells can be individually operated with pure gases, gas mixtures, and co-fed impurities (e.g., NO_x, SO_x, H_2S). All outlet mass flows are constantly monitored, allowing an accurate calculation of the carbon balance. A robotic system for liquid sampling combined with an automated curation of online GC, NMR, and electrochemical data will ensure the application of advanced data science methods.

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Insights into the Molecular Mechanism of Cobalt(II) Catalyzed C-O cross-Coupling Reaction: A DFT study

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O-arylation reactions represent a synthetically important class of reactions that are widely employed for the preparation of diaryl ethers [1]. Cobalt catalyzed cross-coupling reactions are gaining importance owing to the low cost, mild reaction conditions, and high chemoselectivity [2,3]. In the present work, a detailed computational investigation into the mechanism of the Co(II) catalyzed C-O cross-coupling of phenols with aryl iodides, is carried out for the first -time, using Density Functional Theory employing B3LYP-D3 functional [3] augmented with CPCM solvation model using acetonitrile as the solvent. The Co and I atoms are described using (LANL2DZ) for the inner electrons and its associated double-ζ basis set for the outer electrons. The C, H, N, O, and Cl atoms were described by a 6-31+G(d) basis set. L-valine is the ancillary ligand used in this study. The active catalyst species is tetrahedral, L-valine ligated cobalt (II) phenoxide complex. The investigated O-arylation reaction proceeds through a **σ** – bond metathesis mechanism involving the concerted breaking of the Csp^2 – I bond and the formation of the Csp^2 – O bond proceeding through a four-centered transition state. Frontier Molecular Orbital (FMO) analysis was performed to investigate the effect of functional groups at the *para* position of the substrates. The substitution by electron-withdrawing groups (EWG) considerably decreases the energy of FMO's involved. The presence of EWG on aryl iodides tends to favor the reaction by reducing the energy of its LUMO. However, for the phenolic substrates, a decrease in the energy of the HOMO by the electron-withdrawing groups leads to an increased HOMO-LUMO gap [5].

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Locating aluminum in zeolite frameworks by exploiting anomalous X-ray powder diffraction at the Al absorption edge

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

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The aluminum in a zeolite framework introduces a negative charge balanced by the extra-framework cation (the active site). If the extra-framework cation is a proton, the zeolite becomes a solid acid active in Brønsted-acid catalyzed reactions. Unfortunately, a proton is too light to be observed by X-ray diffraction directly. Consequently, only by locating aluminum in a zeolite structure the determination of accessibility and geometry of the active sites is enabled.

The number of different techniques was put through this problem, however they brought only partial information that did not allow on identification which T sites in a zeolite framework structure are occupied by aluminum. Most zeolites bear low aluminum content (typical zeolite catalysts have Si:Al ratios larger than 5) and the scattering power of this element does not differ much from silicon.

We have recently developed a method that exploits the anomalous scattering of Al X-ray absorption edge [1]. At X-ray energy far from the edge, the X-ray atomic scattering factor is primarily a function of the number of electrons in the element (e.g. 14 for Si and 13 for Al), but as the energy approaches an element's edge, the anomalous contributions to the scattering factor of that element become significant which changes dramatically. At the Al absorption edge (1.56 keV), the scattered signal for aluminum decreases while that for silicon remains unchanged (Figure 1). This difference affects the intensities of the Bragg reflections and allows the aluminum positions in the structure to be found.

Two **FER**-type zeolites with identical compositions ($|H_{2.2}|$ $[Si_{33.8}Al_{2.2}O_{72}]$), but different catalytic activities, were investigated. They were synthesized under conditions that aimed to alternate the Al distribution. The materials appeared to be ideal candidates to test the viability of the method its limits of detection (Si:Al ratios ca. 15). One sample was more active and selective in the isomerization of *n*-butene to *i*-butene than the other, but it also deactivated faster [2]. The aluminum can be located at the four different T sites in **FER**-type structure. One sample exhibited an even distribution, while the other showed a clear concentrated aluminum on the T1 and T3 sites. More aluminum located in the T2 site lead to the higher activity and faster deactivation of the first sample.

The AXPD method can be applied to zeolites with Si:Al ratios as high as 15 to achieve a quantitative and unambiguous picture of the catalytically active sites. This method is a major advance in our fundamental understanding of the relationship between zeolite structure and catalytic activity. We believe that AXPD at the Al X-ray absorption edge could become the technique of choice for zeolite scientists interested in pinpointing the active catalytic sites in their materials.

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Tin dendrite electrocatalyst for CO_2 reduction to formate over a broad potential window in a hybrid flow cell

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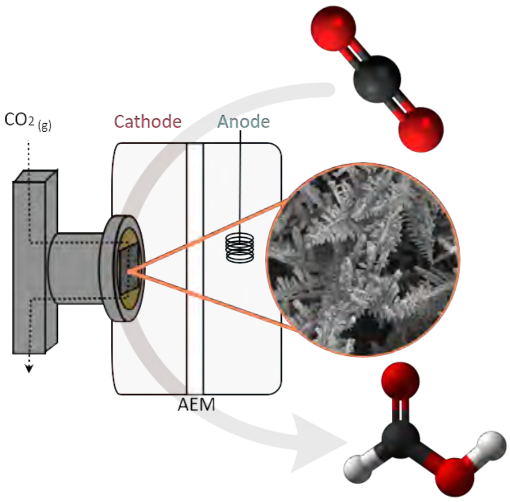
It is of the utmost importance that anthropogenic CO_2 emissions are reduced in order to decelerate climate change and its harmful effects. Using CO_2 as a chemical feedstock is a promising solution that could simultaneously produce valuable chemicals and fuels without fossil or biomass resources. Formic acid has the highest market value of typical CO_2 reduction products, however, there remains a need for formate-selective catalysts to be optimised in high-performance electrolysers. Most studies employ H-cells, which are limited by CO_2 mass transport due to the low solubility of CO_2 in aqueous electrolytes. This imposes a theoretical maximum on performance. Herein we report the use of a "hybrid" flow-cell with an intermediary design between the traditional H-cell and flow-cell, allowing easier transition and scale-up. A tin dendrite catalyst was immobilised onto a gas-diffusion electrode and showed high selectivity for formate (> 80%) over an exceptionally broad potential range.



Mechanistic Investigations of the Iron–Catalyzed Synthesis of Pyrrolidines by Intramolecular C–H Amination

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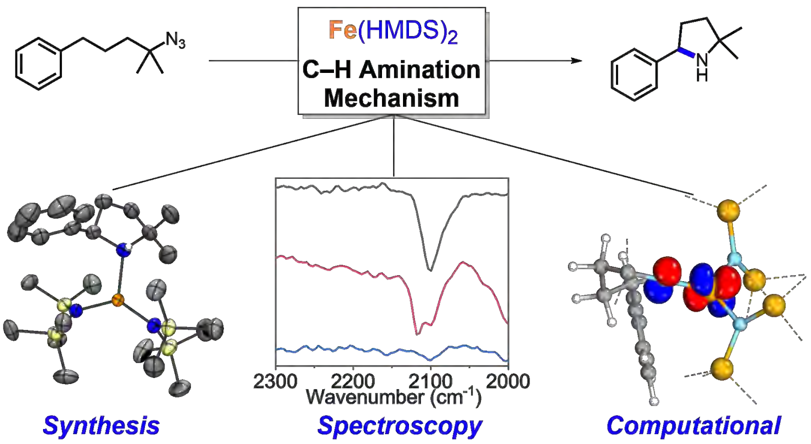
The formation of N-heterocycles is of paramount importance for synthesis of pharmaceuticals, agrochemicals and natural products.[1] Due to its atom-economy, direct C–H amination is a very attractive method to synthesize this class of compounds. Especially when using azides as nitrene precursors, N_2 is produced as the only side product. Only very few complexes are known to catalyze this transformation,[2] and much effort has been made to improve their turnover numbers (TONs). Recently, we reported an iron complex that reaches 7600 TONs in this transformation, an order of magnitude higher than any previously reported system.[3] While improvements in activity have been accomplished in recent years, elucidation of the mechanism has been difficult, especially for iron complexes.

In this contribution we will discuss the ability of $Fe(HMDS)_2$, which is synthesized in only one single step, to catalyze the formation of pyrrolidines from alkylazides. Moreover, mechanistic investigations using a combination of synthetic (stoichiometric experiments, kinetics), spectroscopic (NMR, FTIR, XRD) and computation methods (DFT, NEVPT2-CASSCF) allows now a detailed mechanism to be postulated, including off-cycle intermediates and main decomposition pathways. These insights are useful for further improving the catalytic activity and for designing new catalytic systems.



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Ceria-supported gold nanoparticles as a superior catalyst for nitrous oxide production via ammonia oxidation

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Direct oxidation of NH_3 into N_2O comprises an effective approach towards the affordable manufacture of this versatile and highly selective oxidant, offering a unique solution to a long-standing challenge of selective conversion of hydrocarbons into value-added oxygenates. However, the lack of a suitable catalyst precludes its industrial implementation. Instead, N_2O is produced *via* thermal decomposition of NH_4NO_3, rendering it too expensive and limiting its prospective uses.[1] Herein, we report CeO_2-supported Au nanoparticles (**Fig. 1a**, 2–3 nm) as a highly selective catalyst for low-temperature NH_3 oxidation to N_2O, exhibiting two orders of magnitude higher space–time yield than the state-of-the-art Mn-Bi/Al_2O_3 and remarkable stability over 70 h on stream (**Fig. 1b,c**). The reaction is revealed to proceed *via* a Mars-van Krevelen mechanism (**Fig. 1d**), with the density of interfacial $Au^{\delta+}$ species and the oxygen storage capacity of CeO_2 identified as the key performance descriptors (**Fig. 1e,f**). The latter could be further enhanced by cobalt doping, improving the catalytic activity and setting a new benchmark for N_2O productivity (**Fig. 1b**).[2] These findings establish NH_3 oxidation as a viable technology for N_2O manufacture and facilitate its broader utilization in selective oxidations.

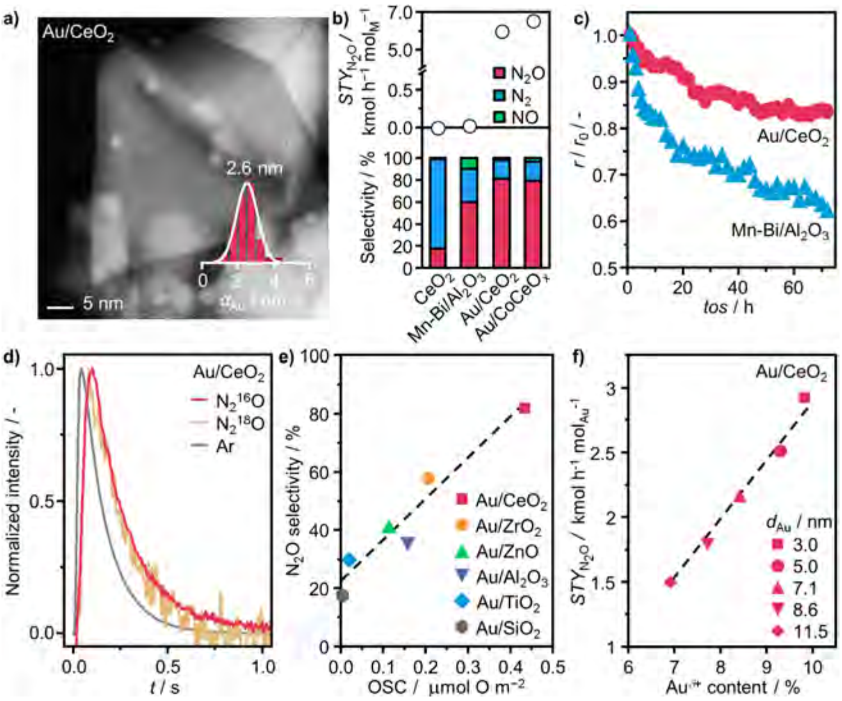

Figure 1a Micrograph of Au/CeO_2. **b** Catalytic performance of selected NH_3 oxidation catalysts. **c** Stability test of Au/CeO_2 and benchmark Mn−Bi/Al_2O_3. **d** Transient response upon pulsing of 1:1:1 NH_3:18O_2:Ar mixture over Au/CeO_2 at 573 K. **e** Oxygen storage capacity (OSC) and **f** $Au^{\delta+}$ content as performance descriptors of Au/CeO_2 in NH_3 oxidation to N_2O. Sample code: M/support.

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Sinter resistant nickel catalyst for lignin hydrogenolysis achieved by liquid phase atomic layer deposition of alumina

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Lignin hydrogenolysis is an important step in sustainable production of aromatic chemicals and fuels from lignocellulosic biomass. Inexpensive catalysts containing nickel have led to high yields but tend to rapidly deactivate due to nanoparticle sintering and carbonaceous deposit formation. While condensation can be removed by regeneration methods, sintering is an irreversible structural change of the catalyst. Here, we used a simple, recently-developed method called stoichiometrically liquid phase atomic layer deposition (ALD) to deposit alumina layer on a Ni/C catalyst to protect nickel nano particles from sintering. With both hydrogen chemisorption tests and microscopic images, we proved that this layer can prevent sintering during reduction up to 600°C. Besides gas phase tests, this catalyst was evaluated for hydrogenolysis of propionaldehyde extracted lignin in batch and continuous mode. In batch mode, 250°C and ca 80 bar, the catalyst overcoated with alumina maintained high monomer yields with low sintering over 4 cycles of reuse while the yield for the catalyst without alumina reduced to half and severe sintering occurred. In a continuous flow reactor at 200°C and 60 bar, deactivation rates were three times lower for the catalyst with an alumina overcoat vs. the uncoated catalyst. Meanwhile, microscopic images confirmed that the alumina layer largely preserved the size of nickel particles after 10 days of operation. Our results demonstrate alumina deposition prevents sintering during lignin hydrogenolysis leading to lower deactivation rates, which could facilitate the development of continuous lignin upgrading.

Effect of particle size in dibromomethane hydrodebromination over SiO_2-supported Pd nanoparticles

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Bromine-mediated functionalization of methane is a promising route for natural gas upgrading into fuels, with CH_3Br as the key platform toward higher hydrocarbons.[1] However, direct bromination of methane yields large quantities of dibromomethane (DBM) as a byproduct, hindering the implementation of this technology. A possible solution to this is the valorization of DBM. Nevertheless, (*i*) direct conversion of DBM into light olefins and (*ii*) catalyst stability remain major hurdles. In a former study,[2] the ability of SiO_2-supported Pd nanoparticles (NPs) to promote the hydrogenative oligomerization of DBM into hydrocarbon mixtures *via* formation of a Pd carbide phase was demonstrated. Herein, we explore the catalytic properties of this novel class of catalysts for DBM hydrodebromination. To this end, the influence of the Pd NPs size in the fresh catalysts is investigated (**Fig. 1a, b**). Though the formation of C−C coupling products is affected only to a lesser extent, the degree of unsaturation of the latter increases with particle size (**Fig. 1c**), being negligible in NPs of approximately 1 nm. This effect is ascribed to a stronger adsorption of alkene intermediates on the surface of smaller NPs, likely richer in electron-poor Pd atoms favoring full hydrogenation. Furthermore, the catalysts remain stable over 10 h on stream, exhibiting unaltered product selectivity (**Fig. 1d**). These findings highlight the potential of Pd catalysts for DBM valorization.

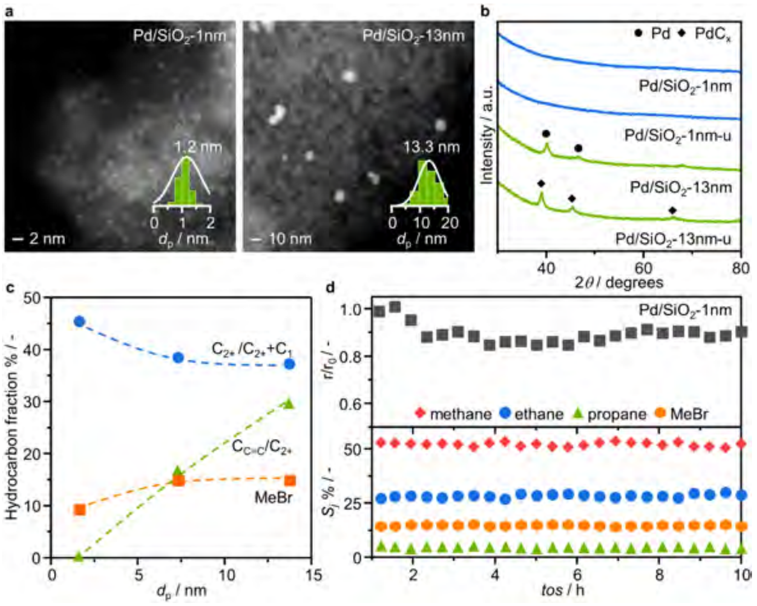

Fig. 1a Electron micrographs of SiO_2-supported Pd NPs. Sample code: Pd/SiO_2-average particle size. **b** Corresponding X-ray diffraction patterns of the fresh and used (-u labelled) catalysts, showing the formation of a Pd carbide phase. **c** Size-dependent selectivity patterns. **d** Relative rate of DBM hydrodebromination (top) and corresponding product selectivity (bottom) as a function of time on stream.

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Unravelling the effect of bimetallic co-catalyst and reaction conditions on the photocatalytic conversion of methane to oxygenates over TiO_2

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The direct oxidation of methane into more energy-dense liquid derivatives, such as methanol, is a promising route to realize a sustainable chemical industry. However, the process is very demanding, as the high C–H bond strength of methane requires harsh conditions (high temperature and pressure to be activated. Photocatalysis have emerged as a promising alternative to traditional used thermocatalysis. Upon photo-excitation, very energetic charge carriers are generated that activate methane and substantially reduce the activation energy, allowing to drive chemical process under mild conditions [1]. Typical oxide semiconductors (TiO_2, ZnO, WO_3) loaded with active co-catalysts, such as metals (Pt, Pd, Au, Ag) and metal oxides (FeO_x, CoO_x) have demonstrated good photocatalytic activity in the selective oxidation of methane [2]. Nevertheless, little is known about the mechanism behind the photocatalytic conversion of methane and the role of reaction conditions and the role of the metal co-catalyst.

Here, we present the selective photocatalytic oxidation of methane to oxygenates over a photocatalytic system composed of TiO_2 as semiconductor and metallic or bimetallic nanoparticles as co-catalysts (Au, Pd and Au-Pd). The photocatalytic systems were synthesized via a simple sol-immobilization method. The photocatalytic conversion of methane was carried out in a custom-made flow-through reactor cell using molecular oxygen or H_2O_2 as an oxidant under specific light irradiation. A wide range of operating conditions (co-catalyst loading, temperature, oxidant concentration, residence time) and photo-triggers (visible or ultraviolet light irradiation and dark experiments) were used to evaluate the influence of these parameters on the photocatalytic activity and selectivity. Additionally, in situ quick-scanning XAS studies at the Au L_3-edge and Pd K-edge combined with reactant cut-off or addition or light on/light off experiments allowed to obtain a complete picture of the structure activity/selectivity relationships.

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Electrocatalytic generation of metal hydrides promoted by concerted proton electron transfer mediators

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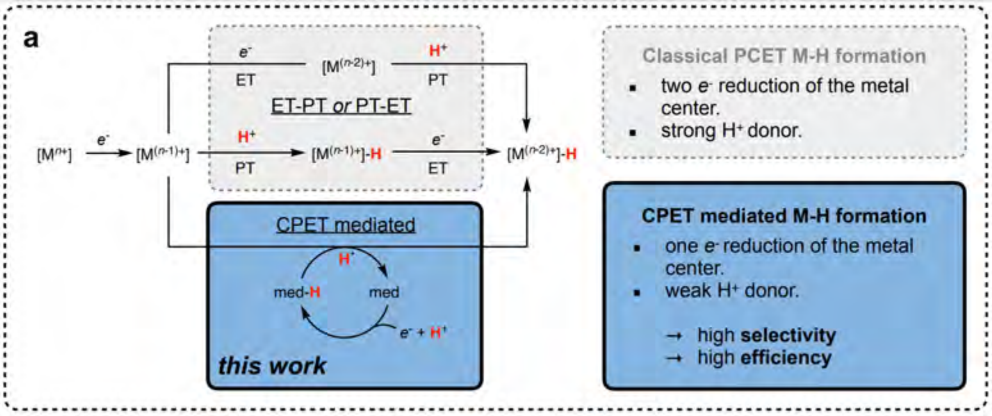
Transition metal hydrides (M-H) have been identified as key intermediates in a variety of catalytic transformations ranging from the conversion of energy in biological systems to industrial processes. As such, M-H are involved in the electrochemical or thermochemical reduction of CO_2 to formic acid[1], the reversible interconversion of H^+/H_2[2] and in a wide number of hydrogenation reactions. In this context, the facile generation of M-H species presents one of the main limitations for the catalytic transformation of small molecules by utilizing renewable energy. Particularly, in the reduction of CO_2 to formic acid one of the main activation pathways involves the reactivity of CO_2 with M-H bonds.[1] Current classical strategies for electrochemical M-H formation necessitate the initial reduction of a metal center followed by the sequential transfer of a proton and an electron in either a proton transfer-electron transfer (PT-ET) or an ET-PT mechanism. This stepwise process often requires considerably high cathodic potentials to promote the reaction and the use of a strong acid as proton source. Alternatively, generation of M-H species may occur in a single kinetic step, based on the homolytic coupling of a singly reduced metal center with a hydrogen atom (concomitant proton and electron transfer) in a so called concerted proton-electron transfer (CPET) mechanism (Figure 1a, bottom).

We have recently identified a novel strategy for the electrocatalytic generation of M-H species via a proton coupled electron transfer mechanism utilizing CPET mediators to promote the formation of a manganese hydride species.[3] Utilizing this approach, we are exploring the extension of this concept to a variety of transition metal based catalysts to acquire a fundamental understanding of the thermodynamic boundary conditions and the kinetic limitations which govern electrocatalytic M-H generation. The electrochemical CO_2 reduction reaction (CO_2RR) was investigated to understand the product selectivity and develop a mechanistic understanding of the reaction.



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Pd/ZSM-5 materials for continuous liquid phase catalyzed methane oxidation to oxygenates

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The direct oxidation of earth-abundant methane into liquid derivatives, such as methanol, has triggered significant research interest over the years because of both environmental and economic implications. In particular, due to its molecular structure, methanol is very reactive and thus more useful as a chemical building block for the production of fuels and high value-added chemicals [1]. Recently, a number of low temperature approaches have been explored for the conversion of methane, each with some disadvantages and limitations, including low reaction rates, the need for an additional activation step and environmental concerns. The low temperature oxidation of methane over metal-containing (Fe or Cu) zeolites with O_2, H_2O or N_2O as gaseous oxidants allows to avoid overoxidation of methane [2]. However, after formation of uniquely anchored oxygen species using oxidants they are rapidly consumed by CH_4 and require a regeneration step at high temperature. Thus, the transformation of CH_4 to methanol by oxide species is rather an oxidation reaction instead of continuous catalytic process. In contrast to solid-gas reactions, the conversion of CH_4 to CH_3OH, or even formic acid, do not require a regeneration step. The main challenge is still the activity and selectivity towards methanol, which is below the requirements for industrial production. In order to address those challenges a catalytic system with high activity and selectivity towards methanol or even ethanol as well as fundamental understanding of the reaction mechanism is necessary.

The aim of this study was to determine the influence of reaction conditions (flow rate, concentration of oxidant (H_2O_2) and temperature) on the performance of Pd/ZSM-5 catalysts in the liquid phase oxidation of methane to methanol. The flow rate was varied from 0.1-1.0 ml/min, the H_2O_2 concentration from 1-10 mmol and the temperature from 50-90℃. All catalytic tests were performed at a pressure of 34 bar. The catalysts were synthesized by both ion-exchange and impregnation methods to compare the Pd dispersion and were characterized using XRD, elemental analysis, low temperature N_2 sorption, TEM and XAS. The obtained results will allow us to optimize the process parameters and catalysts synthesis enhancing the selectivity and stability of the studied materials towards methanol, ethanol and other oxygenates.

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Boosting the formation of ethanol from CO_2 hydrogenation over Rh-based catalysts generated via SOMC

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The continuous increase in the concentration of atmospheric CO_2 has started to raise serious concerns with major impact for the environment like the greenhouse effect and ocean acidification. CO_2 hydrogenation by using renewable H_2 is viewed as a highly promising route to mitigate the CO_2 emission. Ethanol is considered as an ideal fuel additive, promising hydrogen carrier, and versatile building-block chemical.[1] Therefore, selective production of ethanol from CO_2 hydrogenation is highly appealing but challenging due to the high kinetic barrier of C-O bond scission and C-C coupling.[2] Among the reported catalyst systems including Rh-, Cu-, Co-, and Mo-based catalysts employed for CO_2 hydrogenation, Rh-based catalysts present the promising selectivity towards ethanol.[3] Normally, promoters like alkali metals and transition metals are needed to shift the product to ethanol over Rh-based catalysts. However, molecular-level understanding the role of promoters is missing. In addition, the reaction mechanism is still mostly unknown due to the ill-defined structure of classic Rh-based catalysts.

Herein, we adopted the surface organometallic chemistry (SOMC) approach to design the well-defined model Rh-based catalysts modified by different promoters (Zn, Mn, and Fe) (Fig. 1a). This model catalyst amenable to spectroscopic study allows us to clarify the role of promoters at molecular level. Evaluation of these model catalysts indicates that $RhFe@SiO_2$ shows the highest formation rate of ethanol among different promoted catalysts (Fig. 1b). By further optimizing the ratio of Rh/Fe, the formation rate of ethanol can reach up to 0.15 g g_{Rh}^{-1} h^{-1}, which is three times that of the classic $RhFe/SiO_2$ catalyst. Study of in situ X-ray Adsorption Spectroscopy (XAS) suggest that the isolated Fe^{2+} strongly interact with Rh nanoparticles to form the interface as the active sites for ethanol synthesis. This established structure-activity relationship would help us to rationally design the classic catalysts for ethanol synthesis from CO_2 hydrogenation as well as syngas conversion.

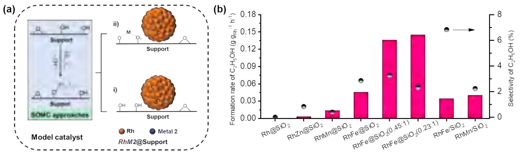

Fig. 1. a) Scheme for SOMC approach to generate the well-defined model catalyst; b) catalytic performance over different catalyst.

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SOMC-Derived Cobalt Nanoparticles as Model for Conventional Heterogeneous Catalysts in CO_x Hydrogenation

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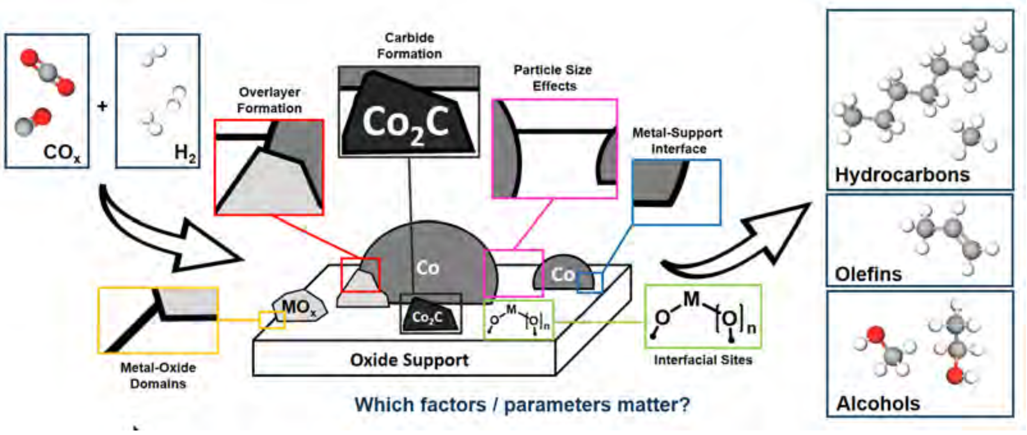
Cobalt is commonly used in heterogeneous catalysis. Typically, cobalt-based catalysts are made from the cobalt nitrate which are deposited on various oxide supports, calcined to the respective Co oxides and eventually treated under H_2 to yield supported Co nanoparticles. The synthesis of cobalt metal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



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

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Revisiting Structure-Performance Relationships of Ni-Ga/SiO_2 Catalysts for the Hydrogenation of CO_2 to Methanol

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Through the catalytic hydrogenation of CO_2 to methanol (MeOH) a greenhouse gas is converted into a valuable product that can be used as a fuel or a platform chemical.[1] Using density-functional theory calculations, Ni-Ga intermetallic phases have been identified as promising catalysts for the hydrogenation of CO_2 to MeOH. Specifically, a high catalytic activity was predicted for intermetallic δ-Ni_5Ga_3 and α'-Ni_3Ga surfaces.[2] Yet, experimentally α'-Ni_3Ga was found to be inactive and hence the structure – performance relationship in this system remain debated.[3,4] Here, we investigate a series of Ni-Ga/SiO_2 catalysts with varying Ni:Ga ratios by operando X-ray absorption spectroscopy (XAS) and pair distribution function (PDF) analysis of total scattering data which allowed us to correlate the structure (electronic and geometric) to the performance of these catalysts.

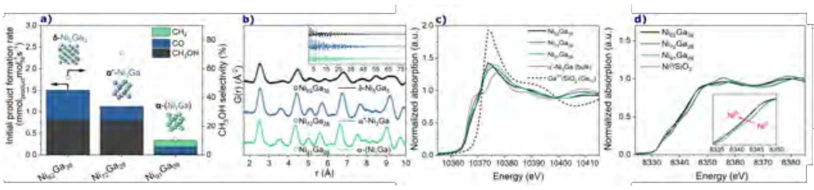

Figure 1 a) Initial MeOH formation rate and selectivity, 230 °C, 25 bar $CO_2:N_2:H_2 = 1:1:3$, GHSV = 60000 ml $gcat^{-1}$ h^{-1}. b) d-PDF, c) Ga and d) Ni XANES of $Ni_xGa_{(100-x)}$ under reaction conditions (230°C, 20 bar $CO_2:N_2:H_2 = 1:1:3$).

SiO_2 supported $Ni_xGa_{(100-x)}$ catalysts were prepared by the co-deposition of Ni and Ga nitrates onto colloidal SiO_2 under hydrothermal conditions,[5] followed by H_2 treatment (700 °C, 1 bar). Our catalytic tests showed a strong dependence of the MeOH yield and selectivity on the Ni:Ga ratio (Fig. 1a). The highest MeOH yields were observed for $Ni_{62}Ga_{38}$ and $Ni_{72}Ga_{28}$ (0.81 and 0.79 $mmol_{MeOH}molNi^{-1}s^{-1}$) whereby the MeOH selectivity decreased in the order $Ni_{72}Ga_{28}$ (71%)>$Ni_{62}Ga_{38}$ (54 %)>$Ni_{91}Ga_{09}$ (9 %). This trend was reproduced during operando X-ray-based experiments. Furthermore, the suppression of CH_4 formation was observed even for relatively low Ga contents ($Ni_{91}Ga_{09}$). Difference PDF (d-PDF) analysis identified the nanocrystalline (ca. 6 nm) phases of $Ni_{62}Ga_{38}$, $Ni_{72}Ga_{28}$ and $Ni_{91}Ga_{09}$ under reaction conditions as, respectively, δ-Ni_5Ga_3, α'-Ni_3Ga and a Ni-rich (Ni, Ga) disordered alloy (Fig. 1b). X-ray absorption near edge structure (XANES) revealed that the electronic structure of Ni and Ga in $Ni_{62}Ga_{38}$ and $Ni_{72}Ga_{28}$ differs from that of the monometallic reference, i.e. there is an electron transfer from Ga 4p to Ni 3d, resulting in $Ni^{\delta-}$ and $Ga^{\delta+}$ (Fig. 1c-d). Ni in $Ni_{91}Ga_{09}$ is predominantly present in the form of Ni^0, i.e., there is no (or only very little) electronic modification in this system. In $Ni_{62}Ga_{38}$, 4-coordinated Ga^{3+} species were also detected, presumably present as isolated sites or small clusters dispersed in/on the SiO_2 support. In conclusion, using XAS and X-ray total scattering we found that catalysts containing either δ-Ni_5Ga_3 and Ga^{3+} species or α'-Ni_3Ga exhibited superior catalytic performance in the hydrogenation of CO_2 to MeOH when compared to catalysts containing a random alloy or monometallic Ni. We demonstrate that a high MeOH selectivity and MeOH yields are not limited to the δ-Ni_5Ga_3 intermetallic phase. In fact, alloying Ni with Ga forming an α'-Ni_3Ga phase can yield highly active and selective catalysts. The strong modification of the electronic structure of Ni and Ga in α'-Ni_3Ga and δ-Ni_5Ga_3 based catalysts may play a critical role for obtaining high rates of MeOH formation and selectivities.

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Highly selective and stable $ZnZrO_x$ catalysts prepared by flame spray pyrolysis for CO_2 hydrogenation to methanol

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Mixed metal oxides are a promising class of catalysts for the hydrogenation of carbon dioxide to methanol due to their controlled vacancy chemistry and CO_2 activation ability. While zinc oxide-zirconia ($ZnZrO_x$) solid solutions have been reported to be stable and selective to methanol formation using pure CO_2 and hybrid CO-CO_2 feeds,[1,2] the nature of the active sites is less well-known, with the required multi-step synthesis procedures also complicating its optimal design. Herein, flame spray pyrolysis (FSP) was employed as a one-step method to systematically investigate the $ZnZrO_x$ catalyst family while maintaining uniform synthesis conditions (**Fig. 1a**).[3] Catalysts prepared by FSP showed an increasing trend in methanol space-time yield (*STY*) with Zn content up to 5 mol%, outperforming counterparts prepared by co-precipitation which follow a different volcano trend (**Fig. 1b**). In-depth characterization reveals highly dispersed Zn species interacting with different ZrO_2 polymorphs in FSP catalysts depending on Zn content, and surface restructuring (**Fig. 1c**). Computational modelling further highlights the important role of CO_2 adsorption over the ZnO_x-ZrO_x interface in its selective activation, and the positive effect of Zn on oxygen vacancy formation in ZrO_x. This study offers new insights in understanding the active nanostructure of $ZnZrO_x$ systems, showing that a bulk solid solution is not necessary to convert CO_2 to methanol.

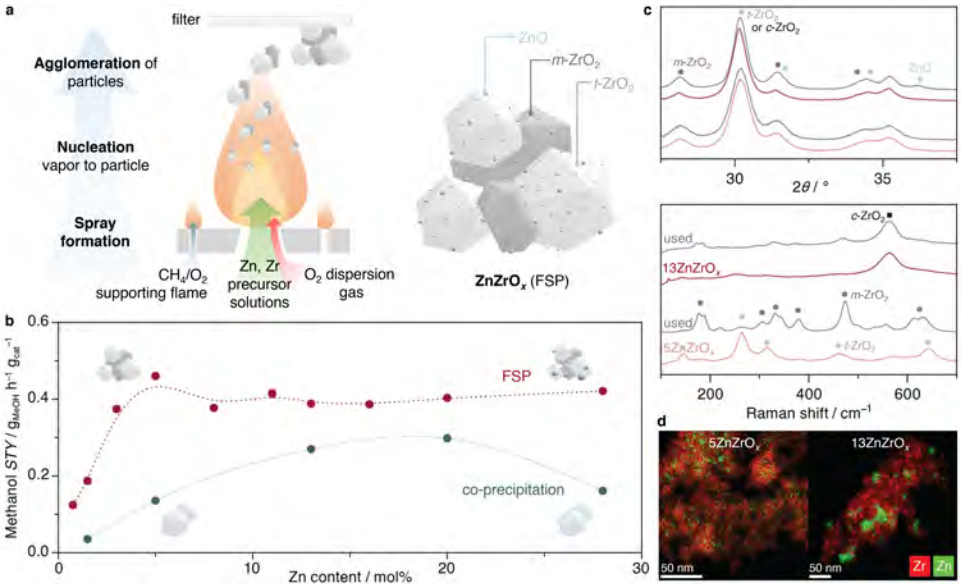

Fig. 1a Schematic of the FSP synthesis procedure for $ZnZrO_x$ catalysts and the resultant ZrO_2 polymorphs. **b** Methanol *STY* over $ZnZrO_x$ catalysts prepared by FSP and co-precipitation with varying Zn content. **c** X-ray diffractograms and Raman spectra of catalysts containing 5 and 13 mol% of Zn prepared by FSP, denoted as $5ZnZrO_x$ and $13ZnZrO_x$, respectively. **d** Energy dispersive X-ray maps of used catalysts. Reaction conditions: 593 K, 5 MPa, $H_2/CO_x = 4$, $CO/CO_x = 0–0.5$, time on stream = 24 h, *GHSV* = 24 000 $cm^3_{STP}\ h^{-1}\ g_{cat}^{-1}$.

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