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## Selectivity and stability of zeolite catalysts in methanol-to-hydrocarbons reaction

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Zeolites (microporous crystalline aluminosilicates) represent one of the most prominent types of heterogeneous catalysts. Zeolites are characterized by regular pores, channels, and cages of molecular dimensions (0.3 - 1 nm). The microporous structure of zeolites allows for the stabilization of various active sites, intermediates, and products that would otherwise be unstable. A unique feature of zeolites is fascinating hydrocarbon pool chemistry, in which confined co-catalytic intermediates actively participate in the catalytic cycle. Methanol-to-hydrocarbons (MTH) is the prime example of a reaction following the hydrocarbon pool mechanism.[1] In addition to being a chemically intriguing reaction, MTH is an industrially relevant method to produce valuable light olefin and aromatic building blocks from virtually any carbon source (gas, coal, CO<sub>2</sub>, biomass) via the methanol intermediate.

With all these opportunities also come challenges, because the chemistry in confinement differs from the conventional chemistry. The processes, taking place inside the zeolite pores during conversion of a relatively simple methanol molecule to olefins and aromatics, are extremely complex. Entangled dynamic effects of co-catalytic intermediates, active sites, spectating and deactivating species, and diffusion limitations, define the MTH reactivity. Our understanding of these processes is deficient and the control that we can exert over them to tune the selectivity and stability of MTH catalysts is limited.

In this lecture, selected aspects of the reactivity of zeolite catalysts in the MTH reaction will be discussed. More specifically, I will focus on two strategies to control the reaction selectivity and catalyst stability: co-feeding of furanics to produce more aromatics [2] and modification of zeolites with alkaline earth cations to produce more propylene and decrease the deactivation rate [3]. These cases will also illustrate an effective toolbox of characterization techniques (operando FTIR, operando XRD, operando TG-MS, <sup>13</sup>C/<sup>1</sup>H NMR, pulse reaction technique, and isotopic labelling) for investigating the chemistry of MTH catalysts.

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## Consequence of Alloying and metal-oxide interface in bimetallic PtGa Propane Dehydrogenation catalysts prepared via Surface Organometallic Chemistry on Carbon

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The non-oxidative propane dehydrogenation (PDH) reaction has become an intense field of research in both academia and industry, due to the increase in demand of propylene combined with the emergence of shale gas as a major chemical feedstock.<sup>1</sup> Due to its industrial relevance, numerous supported Pt-based bi- and multi-metallic model systems have been investigated with the goal to understand the effect of promoters.<sup>2</sup> In recent years, surface organometallic chemistry (SOMC) combined with thermolytic molecular precursor (TMP) approach has proved to be a powerful tool to prepare tailored, highly active and well-defined silica-supported bimetallic PDH catalysts based on PtGa<sup>3</sup>, PtZn<sup>4</sup>, as well as PtMn<sup>5</sup> nanoparticles. In these Pt-based systems, the major role of the promoters was attributed to the formation of alloyed nanoparticles, resulting in Pt-site isolation, improved propene selectivity and increased stability against coking. However, the effect of the oxide support, is typically disregarded, since it is considered to be inert to the reaction conditions.

In this work, we make use of the SOMC/TMP approach to investigate PtGa-based PDH catalysts on carbons with the goal to better understand the effect of Ga as a dopant and the role of the nanoparticle-oxide interface on the catalytic performance. The decomposition of the ligand sphere of the grafted precursors, allows for the tailored introduction of an oxide interface, which enables to study interfacial effects of oxide interfaces on the catalytic performance in the PDH reaction.

We show, that alloyed, bimetallic PtGa nanoparticles supported on carbon can be generated via this methodology with almost identical spectroscopical features and catalytic properties as observed for SiO<sub>2</sub> supported analogues.<sup>3</sup> We were able to show that thus prepared carbon-supported, monometallic platinum nanoparticles are highly crystalline. In contrast, bimetallic PtGa particles were found to be less crystalline or even amorphous. These results further consolidate the role of Ga in Pt site-isolation and in enhancing of the surface atom mobility. Additionally, while not necessary for the stabilization of the nanoparticles against sintering, the presence of an oxide interface was found to promote the rate of reaction.

Overall, the strategy for the preparation of tailored bimetallic materials on carbon offers a platform for the preparation and study of interface and dopant effects in thermal catalysis, and can be readily extended to electrochemical applications.

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## Advancing Strategies for Methane Partial Oxidation to a Methyl Ester with Heterogeneous Catalysts

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Direct methane partial oxidation to liquid oxygenates (e.g. methanol) is a highly desired valorization pathway with limited actionable progress due to numerous challenges and despite decades of research [1-3]. For thermocatalytic systems, a steep selectivity-conversion trade-off remains independent of the catalyst that severely limits product yields. The first part of this contribution critically examines the current strategies to break through these limits and achieve high product yields, comprising work in catalyst design, additional co-reactants/protecting agents, and cycling schemes. From this, we highlight the most successful strategies and identify crucial gaps in bridging the vast scientific knowledge in methane activation and the technological necessities of viable methane valorization.

In the second part of the contribution, we describe recent advances from the group in the conversion of methane to an oxidation-resistant methyl ester, one of the most effective routes for high-yield methane conversion [2, 4]. We first introduce an improved system that targets key shortcomings in the conventional chemistry, namely the reliance on extremely aggressive acid solvents, economically impractical oxidants, and homogeneous catalysts [6]. Notably, we synthesize the first solid catalysts that can perform this chemistry using air as the oxidant. Under our improved reaction conditions, facilely synthesized Co/SiO<sub>2</sub> and Mn/TiO<sub>2</sub> display competitive performance on the basis ester production rates ( $\sim 250$  and  $\sim 610 \mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$ , respectively) with negligible metal leaching in comparison to previously reported homogeneously catalyzed systems that employ stronger oxidants and higher methane partial pressures [5, 6]. Furthermore, we find that high metal dispersion is associated with high activity in this system, and the most efficient utilization of cobalt or manganese is realized at the lowest metal loadings. The conclusion of the contribution underscores impactful directions for further developing this high-yield strategy beyond conventional approaches.

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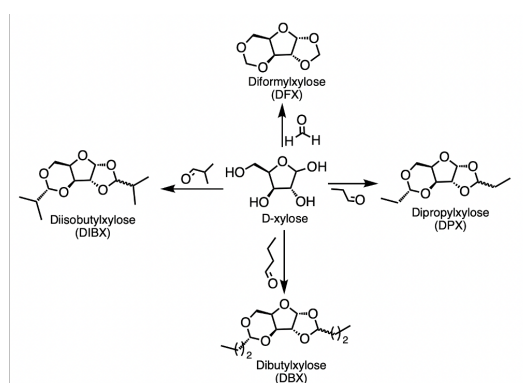


## Sustainable Bio-Based Solvents with Acetal Functionalized Carbohydrate Core Produced from Renewable Biomass

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The manufacturing and disposal of chemicals are among the primary contributors to carbon emissions and environmental pollution. Over 99 % of the most common chemicals are still not produced sustainably. Addressing this challenge requires a collective effort to develop and adopt environmentally friendly and safe chemical processes and products. Biomass plays an important role in this transition since it is the largest source of renewable carbon on Earth. Key to further progress in the industrial implementation of biomass conversion practices is the large-scale production of platform chemicals. We recently discovered Diformylxylose (DFX), a xylose-based platform chemical that can be isolated from lignocellulosic biomass in high yield by a relatively simple process [1]. DFX demonstrated potential as a polar aprotic solvent in model reactions with comparable performance to toxic and environmentally harmful solvents such as NMP, DMAc, and DMF, whose use in industry is currently restricted [2]. In this work, we further expanded DFX application as a solvent for biomass pretreatment, exfoliation of nanoparticles, and as a component of deep eutectic solvents. We also showed the potential of other acetal-functionalized xylose molecules as solvents, namely Dipropylxylose (DPX), Dibutylxylose (DBX), and Diisobutylxylose (DIBX) that we isolated from biomass. We demonstrated the application of these solvents in alkylation reactions and in enzymatic polycondensation to produce sustainable polyesters. Notably, we proved that these new ether solvents are not flammable and non-peroxide forming, which are the main concerns over ether solvents in industry.



We performed the pilot-scale production of DFX from pure xylose and from agricultural waste, specifically corn cobs. We also provided insights into the techno-economic viability of DFX production at different scales and scenarios. We conducted a preliminary life-cycle assessment and revealed that production of the acetal-functionalized solvent offers a very low global warming potential as well as minimal environmental impact. Finally, we showed that DFX is inherently biodegradable under aqueous aerobic conditions which facilitates its disposal. Overall, this study provides a practical example of how waste biomass can be sustainably transformed with low cost and high efficacy into valuable platform chemicals that can be applied as solvents.

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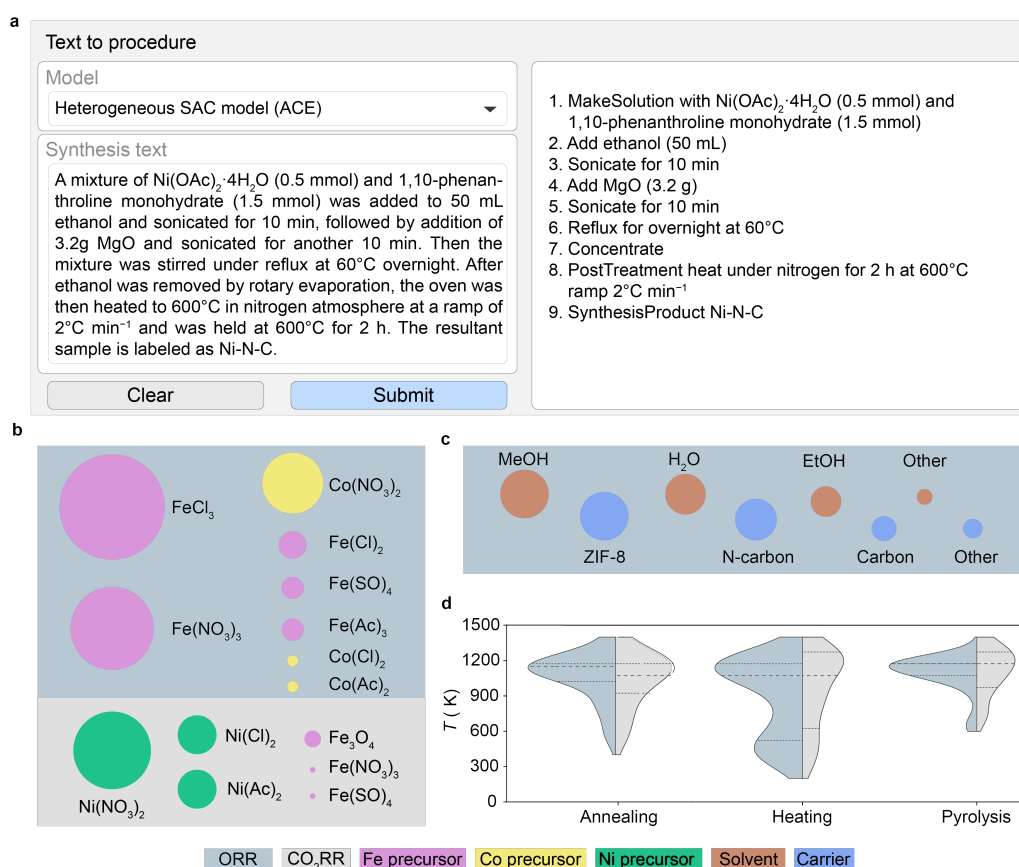
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## Digitally-guided synthesis of single-atom heterogeneous catalysts by leveraging language models and protocol standardization

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The synthesis of single-atom catalysts (SACs) is rapidly evolving, offering precise nanoscale control over structures optimized for diverse applications<sup>1</sup>. However, keeping up with new developments is challenging due to the vast number of publications and lack of data standards. We develop a transformer-based language model that extracts synthesis protocols of SACs from texts and converts them into action sequences along with their associated parameters, reflecting all procedures necessary to replicate the corresponding synthesis<sup>2</sup> (**Fig. 1a**). We use the output of the model to perform statistical analysis of the trends in SAC synthesis conditions for the widely investigated oxygen reduction and carbon dioxide reduction reactions (**Fig. 1b-d**) and demonstrate the model's generalizability to other families of heterogeneous catalysts. Our analysis highlights a lack of standardization in reporting synthesis procedures, which limits machine-reading capabilities. We take vital steps toward implementing data-driven synthesis in heterogeneous catalysis by providing guidelines on machine-readable formats and open-source our technology as a web app for greater access by the research community.



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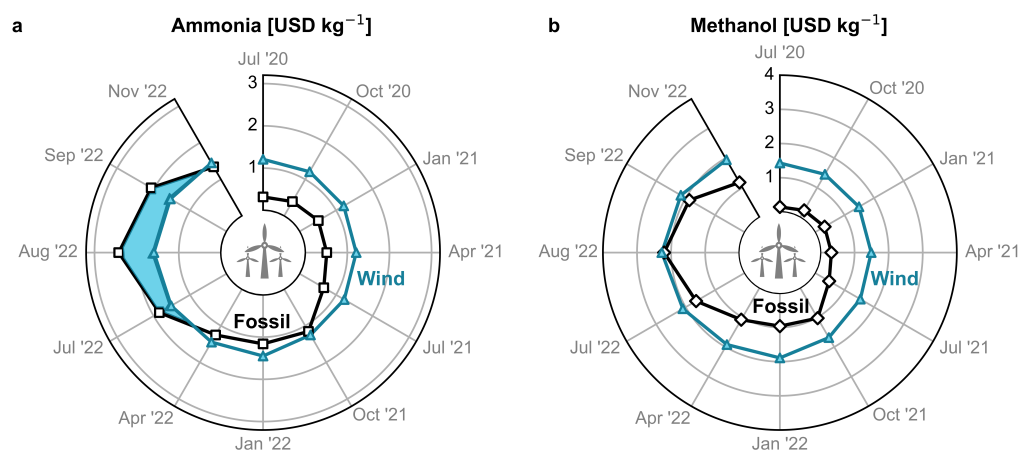
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## Green Chemicals: The Ultimate Win-Win Solution Amidst Europe's Energy Crisis

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The chemical industry strongly depends on fossil fuels, responsible for approximately 10% of global greenhouse gas emissions.<sup>[1]</sup> Ammonia and methanol are essential platform chemicals that serve as primary building blocks for producing a myriad of products with diverse applications in various industrial sectors. Currently, 60–70% of global ammonia and methanol are produced from syngas, primarily obtained through steam reforming of natural gas, contributing to GHG emissions of 0.8 Gt CO<sub>2</sub>-eq yr<sup>-1</sup>.<sup>[1]</sup> Previous studies have demonstrated the technical feasibility and potential climate benefits of using green hydrogen in ammonia and methanol production.<sup>[2]</sup> However, the fundamental barrier towards implementation has always been the higher production costs than their fossil-based counterparts. The current geopolitical scenario has dramatically altered this situation, leading to a surge in natural gas and electricity prices, resulting in higher production costs for fossil-based ammonia and methanol in Europe. Consequently, under this scenario, low-carbon ammonia and methanol production could potentially become economically (in addition to environmentally) appealing. In this study, we employ process simulation and techno-economic assessment tools to examine the extent to which the ongoing energy crisis in Europe has affected the economic competitiveness of green ammonia and methanol. According to our study, fossil ammonia and methanol reached production costs of 2.4 and 2.2 USD kg<sup>-1</sup>, respectively, during the peak of natural gas spot prices in August 2022 (**Fig. 1**). These high prices, *i.e.*, 3–4 times higher than in the same period in 2021, made green ammonia and methanol from on-shore wind electricity economically competitive during the same period (**Fig. 1**). Wind-based ammonia, in particular, exhibited a significant advantage, with costs ranging from 1.3 to 1.6 USD kg<sup>-1</sup>, clearly outperforming its fossil counterpart (blue shaded area in **Fig. 1a**). Our study highlights the tremendous potential for Europe to lead the grand transition towards a sustainable chemical industry, given the evident uncertainty in natural gas supply and the price fluctuations.



**Fig. 1** Temporal evolution of estimated production cost for wind-based **(a)** ammonia and **(b)** methanol in Europe compared with their fossil counterpart in USD kg<sup>-1</sup>. The blue shaded area in **(a)** demonstrates the economic viability of wind-based ammonia.

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## How to overcome challenges in Green Ammonia through a multidisciplinary research in catalysis

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Nowadays, most of the ammonia produced worldwide derives from fossil-based hydrogen. As a result, the Haber-Bosch process represents the biggest emitter of carbon dioxide among all industrial chemical syntheses [1]. In light of The Paris Agreement, emission regulations will become progressively stricter over the following decades, thus making necessary the device of sustainable manufacturing pathways to meet the decarbonization targets. As a result, chemical companies are already developing greener processes to comply with the new policies and decarbonize their activities. For this reason, the research of sustainable production of ammonia, replacing fossil fuels with green or zero-carbon, is fundamental for academia, industries and governments. Green ammonia (gNH<sub>3</sub>) production involves the use of green hydrogen in the Haber-Bosch process using renewable electricity [2]. Therefore, due to the nature of the renewable energy sources, it is crucial to precisely characterize the converter functioning when undergoes fluctuations under operating conditions [3]. Moreover, also the behavior of ammonia synthesis catalyst must be verified, since its behavior at non-stationary conditions, is a missing information and no experimental evidences are currently available in the scientific literature.

The goal of the work is to present the challenges of the process and how to overcome these challenges through different strategies that involve catalyst studies, modelling of the process and utilization of optimizers to calculate the levelized cost of ammonia (LCOgNH<sub>3</sub>) taking into account the available renewable energy during the year.

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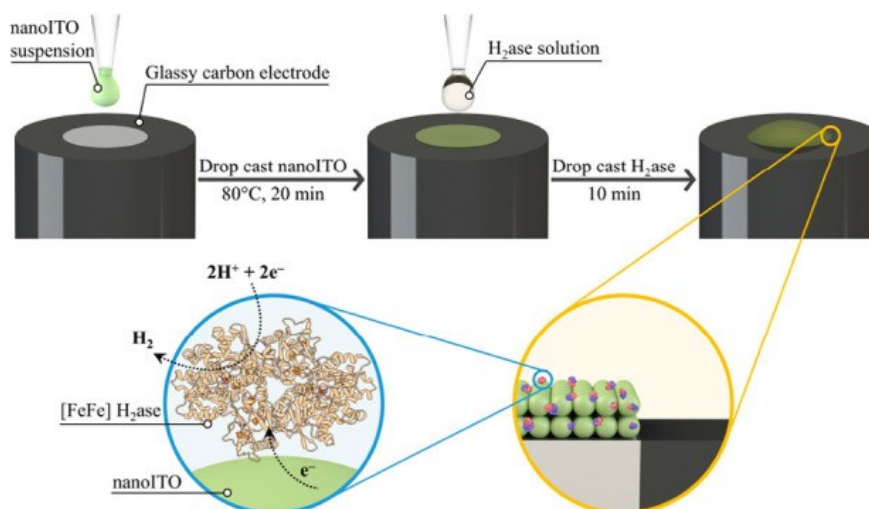
## Understanding enzyme-nanoparticle interactions during bioelectrocatalytic hydrogen formation

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The demand for renewable fuels such as H<sub>2</sub> continues to rise during the climate crisis. Metalloenzymes such as [FeFe]-hydrogenase offer an attractive option for electrocatalytic H<sub>2</sub> evolution as they operate under mild conditions. To produce hydrogen electro-enzymatically, the biocatalyst can be immobilized on (and electronically wired to) an electrode surface, where a potential is applied to drive H<sup>+</sup> reduction. However, these bioelectrocatalytic systems often suffer from reduced stability.

We recently reported a technique for the facile functionalization of carbon electrodes with an In:Sn oxide (ITO) nanostructured architecture, onto which [FeFe]-hydrogenase was directly immobilized.<sup>1</sup> H<sub>2</sub> production by the bioelectrode was recorded by cyclic voltammetry to high current densities of > 8 mA cm<sup>-2</sup> at -0.8 V vs. SHE (pH 7), and maintained ~92 % of the original current density after 5 days of continuous potentiostatic operation. Interestingly, the current density for H<sub>2</sub> production on ITO was > 38x higher than when [FeFe]-hydrogenase was immobilized on planar glassy carbon (GC). We hypothesize there may be stabilizing interactions between the enzyme and ITO surface which can account for this enhanced performance.



In this work, we further investigate properties of the ITO architecture which may contribute to the high performance of this bioelectrode. The electrocatalytic activity of the enzyme during H<sub>2</sub> production is compared between nanostructured and planar ITO to understand if the nanostructured surface stabilizes the hydrogenase. The thickness of the ITO surface is varied in order to understand the impact on enzyme loading and performance. This is realized using a quartz crystal microbalance (QCM), coupled with electrochemistry, to following the adsorption process of the enzyme and to calculate its loading. We anticipate that these results can be utilized in combination with rotating ring disk electrochemistry to aid a deeper kinetic investigation of the bioelectrochemical system.

We anticipate that further investigation of the ITO architecture can aid in the application of this 'nanoITO' electrode in a combination with other (metallo)enzymes of interest to electroenzymatic biotechnologies which are harder to study electrochemically.

## Biocatalytic reduction of six-membered ring heterocyclic imines in continuous flow

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Heterocyclic amines are a key structural motif in the backbone of medicinal natural products (i.e. antibiotics) as well as pesticides and flavors. For this reason, and the lack of general synthetic routes, many efforts are still ongoing towards using more efficient alternatives [1]. In this regard, imine reductases (IREDs) have recently emerged as highly selective and sustainable biocatalysts for asymmetric reductive aminations [2]. Herein, we have tested 4 known IREDs and 2 newly characterized IREDs for the reduction of heterocyclic imines containing S, O, or N. Most of the IREDs showed the highest catalytic activity towards the newly reported sulfur-containing heterocyclic amine. Since IREDs are NADPH-dependent enzymes, a cofactor-regenerating enzyme was added to the catalytic system with the glucose dehydrogenase from *Bacillus megaterium* (BmGDH). The bi-enzymatic system achieved full conversion at a 10 mM scale of the S-containing heterocyclic imine in less than 2 h and using only 2% w/v of biocatalyst. To further improve the efficiency and sustainability of the system, we have carried out enzyme immobilization on porous microparticles (inSEIT technology). In fact, immobilization of IREDs is very challenging due to the decrease of enzyme activity upon immobilization, thus it has barely been explored until now [3]. By using CapiPy bioinformatic tools,[4] we quickly developed an immobilized biocatalyst that retains up to 90% of its initial activity. This enables the integration of the biocatalytic system into a continuous-flow reactor for process intensification. In this project, the multidisciplinary synergy between academia and industry allowed the development of a synthetic technology platform that gives access to new molecules in a green and efficient manner (Figure 1).

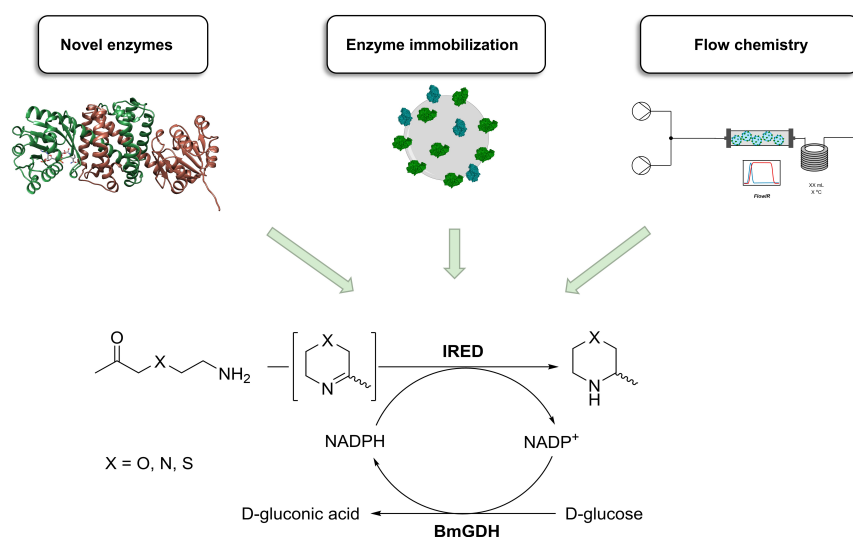


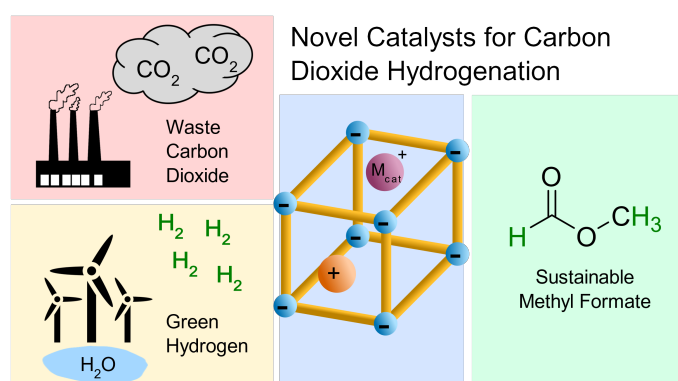
Figure 1. Enzymatic catalysis by IRED towards the synthesis of six-membered ring heterocyclic imines. On the top, the key enabling technologies for this project are highlighted. On the bottom, the reaction scheme including the cofactor recycling system is depicted.

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**CO<sub>2</sub> Hydrogenation to Methyl Formate using CO<sub>2</sub> as the Sole Carbon Source**R. C. Turnell-Ritson<sup>1</sup>, P. J. Dyson<sup>1\*</sup><sup>1</sup>École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

The atmospheric concentration of CO<sub>2</sub> is still increasing, despite international efforts to curb emissions. The removal of CO<sub>2</sub> from the atmosphere is a high-cost endeavour, necessitating economic incentives for carbon capture. More importantly, the use of the near-unlimited C<sub>1</sub> resource of atmospheric CO<sub>2</sub> as a building block for process chemicals is essential to a sustainable future.<sup>1</sup> We have developed efficient catalysts for the hydrogenation of CO<sub>2</sub> to formic acid (FA) and methanol. Additionally, we have combined these C<sub>1</sub> building blocks into methyl formate (MF) in one system. Our catalysts are based on the encapsulation of noble metal complexes and sub-nanoparticles in the pores of zeolites, leveraging the acidity of the support and the principle of nanoconfinement to accelerate these multi-step reactions.



A Ru-based catalyst was developed for the hydrogenation of CO<sub>2</sub> to FA, and simultaneously facilitates fast esterification to MF (TOF > 100 h<sup>-1</sup>), comparable to similar catalysts which operate at higher temperatures and pressures.<sup>2,3</sup> A second series of catalysts, both from the literature and developed in our lab, are capable of CO<sub>2</sub> and FA hydrogenation to MeOH under the applied conditions. Combining two appropriate catalysts, MF in which both C atoms derive from CO<sub>2</sub> is formed. In the presence of a methoxide additive, the MF can be decarbonylated to give high CO concentrations (>20%) at a much lower temperature than traditional reverse water gas shift reactions.<sup>4</sup> The structures of these catalysts will be discussed, and the reaction mechanisms will be explored to understand the key catalyst features which enable their reactivity. The present work allows the formation of three major C<sub>1</sub> synthons widely used in industry using CO<sub>2</sub> under relatively mild conditions. An outlook on coupling CO<sub>2</sub> hydrogenation with C-C bond-forming reactions will be described, as we progress towards the sustainable and selective synthesis of C<sub>2+</sub> products from atmospheric carbon.

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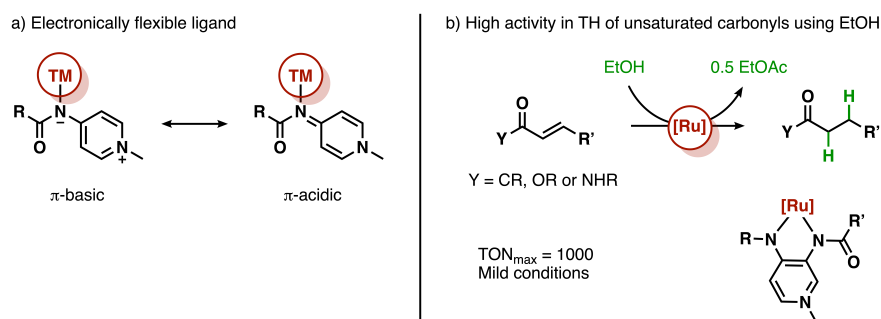
## Selective olefin transfer hydrogenation of unsaturated carbonyls with ethanol using a PYA ruthenium(II) complex

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Hydrogen production is one of the most polluting processes in chemistry generating about 900 million tons of CO<sub>2</sub> each year, or more than 2% of world CO<sub>2</sub> emissions.<sup>[1]</sup> Alcohols, applied in transfer hydrogenation reactions, are known alternatives to H<sub>2</sub> that can be sourced from renewable feedstock. Historically, isopropanol has been widely investigated but is limited in terms of utilization, safety, and production. In this context, ethanol has found an increasing interest in the past few years, but its use is still limited by its ability to form stable carbonyl compounds<sup>[2]</sup> and side reactions such as  $\alpha$ -alkylation under basic conditions.<sup>[3]</sup>

Here, we propose the use of pyridylidene-amide (PYA) complexes as efficient catalysts to propel ethanol-based transfer hydrogenation. PYAs are unique ligands featuring electronically flexible properties that can stabilize the metal center during a catalytic cycle and thus increase its activity and robustness in a variety of reactions, e.g. olefin and water oxidation (Fig. 1a).<sup>[4]</sup> Here, we will present a novel N,N-bidentate ruthenium(II) complex that is readily accessible with high stability towards air and moisture. Excellent activity and selectivity in the reduction of  $\alpha,\beta$ -unsaturated compounds were obtained in mild conditions for a wide range of substrates (Fig. 1b). The use of ethanol as hydrogen source at room temperature combined with catalytic use of common laboratory base makes the system cost-effective and attractive for industrial and pharmaceutical applications.



**Figure 1.**

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## Mixed-metal Ionothermal Synthesis of Metallophthalocyanine Covalent Organic Frameworks for CO<sub>2</sub> Capture and Conversion

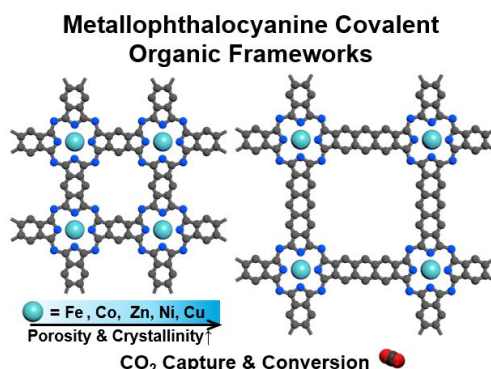
K. Song<sup>1</sup>, P. W. Fritz<sup>1</sup>, D. F. Abbott<sup>2</sup>, L. N. Poon<sup>2</sup>, C. M. Caridade<sup>1</sup>, V. Mougel<sup>2\*</sup>, A. Coskun<sup>1\*</sup>

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Phthalocyanines (PCs) are macrocyclic compounds containing nitrogen-bridge, and their chemical property and stability are tuned by the coordinated metal ions. The metallophthalocyanines (M-PCs) have been investigated in various chemical reactions including electrical-photochemical CO<sub>2</sub> reduction since the coordinated metal atom acts as a catalytic active site in the reaction. Therefore, their polymeric counterparts featuring extended conjugated backbones have gained significant interest as heterogeneous catalysts and PC-containing frameworks such as covalent organic frameworks (COFs) have been widely investigated for CO<sub>2</sub> capture and conversion [1].

General solvothermal reaction methods for PC-based frameworks cause low-crystallinity of frameworks due to the high stability of the linkers, and require an expensive catalyst, organic solvent, and additional work-up steps to purify it. Therefore, a novel and environmentally friendly synthetic approach for high crystallinity of PC-based frameworks is required.

Herein, we show the innovative synthesis strategy using the mixed metal salt (MCl<sub>2</sub>/ZnCl<sub>2</sub>, M = Cu<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, and Fe<sup>2+</sup>) in the ionothermal synthesis of Phthalocyanine based Covalent Organic Frameworks (COFs) which called PPC (Porous polyphthalocyanines). We hypothesized that mixed metal salt mixtures (MCl<sub>2</sub>/ZnCl<sub>2</sub>) would result in PPC including desired metal ions, which has a higher complex stability than that of the Zn-phthalocyanine according to the Irving-Williams series, which predicts the relative stability of complexes formed by transition metals that increases when moving in the periodic table from Fe<sup>2+</sup> to Cu<sup>2+</sup>. In the end, we found a clear correlation between the Irving-Williams series and the metal content, surface area, and CO<sub>2</sub> adsorption capabilities of PPCs. This result provides a tunable approach to designing these polymer properties. Noticeably, with surface areas as high as 2043 m<sup>2</sup>g<sup>-1</sup> and CO<sub>2</sub> uptake capacities up to 7.6 mmol g<sup>-1</sup>, these polymers exhibit significant potential for CO<sub>2</sub> application. In addition, We also investigated the growth of the Co-pPPC and Co-anPPC on highly conductive carbon nanofibers and demonstrated their high catalytic activity in the electrochemical CO<sub>2</sub> reduction, which show Faradaic efficiencies towards CO of up to 74% at -0.64 V vs. RHE.



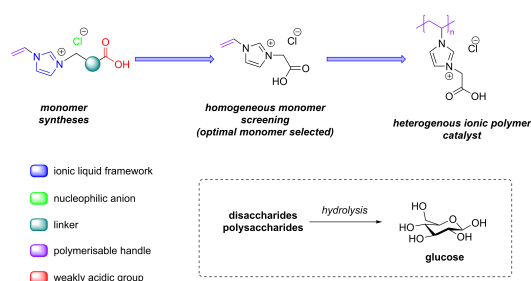
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## Catalytic polysaccharide hydrolysis using separable Brønsted acidic imidazolium salts and ionic polymers in water

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Catalytic polysaccharide hydrolysis is a key step in the valorisation of cellulosic and starchy biomass, as glucose is a key intermediate in potential biorefineries<sup>1</sup> for the production of fuels and platform chemicals (e.g. dimethylfuran, levulinic acid,  $\gamma$ -valerolactone)<sup>2</sup>. Carrying out this hydrolysis with heterogeneous catalysts in water is desirable as it improves catalyst separation and avoids organic solvents. We report the systematic design of imidazolium salts containing pendant carboxylic acid groups and their use in cellulose and starch depolymerisation in water as well as the design and preparation of a cross-linked weakly acidic polymer network that heterogeneously catalyses starch depolymerisation to glucose in water.



Acidic imidazolium compounds were screened in the hydrolysis of the model compounds cellobiose and maltose (as homogeneous models of cellulose and starch, respectively). A vinylimidazolium salt containing a pendant carboxylic acid group was found to be effective in the depolymerisation of cellulose and starch. This monomer was then polymerised to create a cross-linked insoluble acidic polymer network for the heterogeneous cleavage of saccharides. The heterogeneity of the polymer catalyst and the hydrothermal stability of the polymer was investigated and humins deposition onto the polymer surface is proposed as a possible catalyst poisoning pathway.

With the most active vinylimidazolium monomer, good yields of glucose were obtained from model saccharides, cellulose, and potato starch. Subsequent polymerisation yielded a heterogeneous ionic polymer catalyst which was active for the conversion of model saccharides and potato starch to glucose in water. Gratifyingly, the yields obtained with the polymer catalyst are similar to those obtained with the monomer catalyst and are obtained in water at relatively mild temperatures (120–140 °C). Catalysis with the polymer network was tested for its heterogeneity and the catalyst remains active even at low (1:10 catalyst:potato starch, by mass) loadings.

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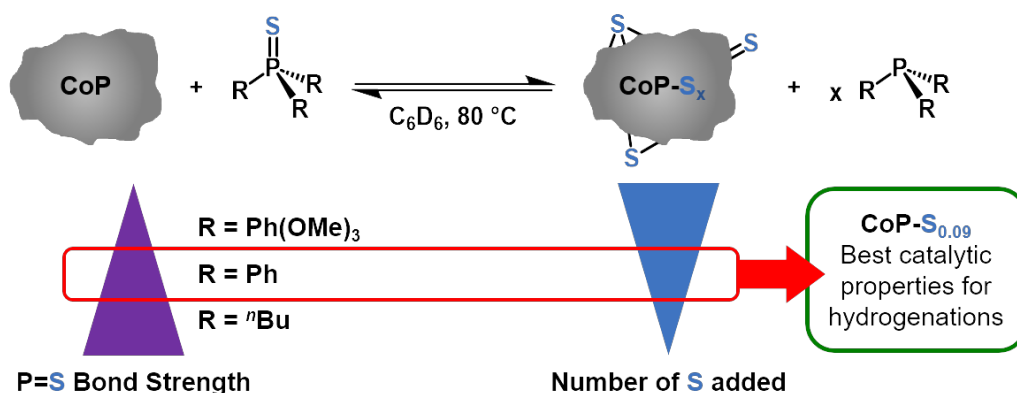
## Controlled Modification of Cobalt Phosphide by Sulfur for Tuned Catalytic Properties in Hydrogenation

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Transition metal phosphides have shown promise as alternatives to the typical noble-metal based catalysts of water splitting and hydrotreating applications.<sup>1-2</sup> A small amount of sulfur incorporated into the transition metal phosphide has been shown to significantly improve their catalytic performance.<sup>3-5</sup> This sulfur effect is not well understood. This is in part because conventional synthesis methods of sulfur-doped phosphides typically result in a wide distribution of chemical environments for sulfur both inside and on the surface of the phosphide, which is challenging to analyze.<sup>4-5</sup>

Here, we present a novel approach to modify transition metal phosphides with sulfur. We used phosphine sulfides ( $\text{SPR}_3$ ) as molecular reagents to transfer sulfur to cobalt phosphide (**CoP**). This enabled the addition of controlled amounts of sulfur to the surface of **CoP**. Furthermore, variation of the P=S bond strength of the  $\text{SPR}_3$  reagents revealed that there is a distribution of different S-sites on the surface of **CoP** with a range of surface binding strengths between 69 and 84 kcal/mol. We probed the effect of different amounts and types of sulfur on **CoP** on its catalytic performance in the hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes. Our results suggest that an intermediate amount of sulfur on **CoP** leads to the best catalytic performance. The fundamental information about the surface chemistry of **CoP** and its relationship with catalytic properties found herein shows important new routes for catalyst design.



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## Co/Co oxide Foam Catalysts for Sustainable Nitrate to Ammonia Electroreduction

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Electrochemical nitrate reduction (NO<sub>3</sub>RR) is an energy-efficient method to remove harmful nitrate from wastewater while producing valuable ammonia. Catalyst selection is crucial for accelerating NO<sub>3</sub>RR and directing the process towards the target product. This process addresses environmental concerns by reducing nitrate through electrochemical reactions, generating ammonia with high added value.<sup>1</sup> By utilizing electrochemical nitrate reduction and suitable catalysts, simultaneous nitrate removal and ammonia synthesis can be achieved, promoting sustainable wastewater treatment and resource utilization. **Ongoing research aims** to optimize this promising approach for efficient and environmentally friendly nitrate valorization.

In this study, we synthesize novel Co foam catalysts using additive-assisted electrodeposition in combination with the dynamic hydrogen bubble template method and followed by thermal annealing at 300 °C for 6 h. The resulting three-dimensional foam morphology significantly influences the catalyst's overall process performance. The foam structure provides a high active surface area, an improved mass transport, and enhanced utilization of active sites, leading to enhanced catalytic activity.

Oxidized Co foams exhibit a remarkable selectivity in the electroreduction of nitrate. Within the specific low potential range of -0.1 to -0.3 V vs. RHE, the Faradaic efficiency (FE<sub>NH<sub>3</sub></sub>) for ammonia production exceeds 95%. Notably, this efficient conversion process from nitrate to ammonia occurs with hydrogen as a minor by-product, and no other nitrogen-containing products (e.g., NO, N<sub>2</sub>O, or N<sub>2</sub>) are formed during electrolysis. These findings underscore the exceptional selectivity and efficiency of Co based foam catalysts in driving the conversion of nitrate to the targeted ammonia.

To elucidate the active chemical states/species contributing to the superior efficiency of ammonia production, we employed *operando* Raman spectroscopy and synchrotron-based *operando* X-ray diffraction (XRD) techniques. These analytical approaches enabled us to investigate the potential-dependent alterations in the chemical states of Co species prior to and during the nitrate reduction reaction (NO<sub>3</sub>RR). Intriguingly, **our findings reveal that** the active phase responsible for the reduction of NO<sub>3</sub><sup>-</sup> to NH<sub>3</sub> is not metallic Co or Co<sub>3</sub>O<sub>4</sub>. Instead, **it comprises a composite of Co(OH)<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub>**, which forms only during the nitrate to ammonia conversion. These results underline the importance of oxidized Co<sup>2+</sup> and Co<sup>3+</sup> ions as active catalyst species for the efficient transformation of nitrate into ammonia.

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**Local structure of PdO/Al<sub>2</sub>O<sub>3</sub> catalysts during aqueous phase reduction**

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Pd catalysts are widely used in catalysed hydrogenation reactions for the synthesis of fine and bulk chemicals, which are often conducted in liquid phase. Since the Pd active phase is commonly deposited in its oxidised form on the support, previous works sought to study how the catalyst activation procedure affects the reducibility of the PdO phase, as well as the properties of the supported Pd nanoparticles (dispersion, particle size, morphology, interaction with the support, structural order, and surface properties), and how these factors correlate with the catalyst behaviour during hydrogenation [1].

In this work, we investigated the isothermal reduction of PdO (5 wt%) supported on different polymorphs of Al<sub>2</sub>O<sub>3</sub> and their combinations using aqueous solutions of common reducing agents (NaBH<sub>4</sub>, HCOONa), thus mimicking the procedure adopted by the catalyst manufacturer. For comparison, water saturated by H<sub>2</sub> was also used. In order to follow reduction at 65°C and ambient pressure, we used high-energy X-ray diffraction (HE-XRD) and pair distribution function (PDF) analysis at beamline ID15A of the ESRF to identify and quantify Pd components in both average and local structure, and thus separate long-range from short-range structural effects.

Analysis of HE-XRD data (Rietveld) suggested that most of the supports are made of a low-symmetry, inter-grown composite phase and not a mixture of the ideal structures of the various polymorphs [2]. Both HE-XRD and PDF analysis were able to clearly follow the isothermal consumption of the PdO phase upon reduction, the subsequent formation of metallic Pd and the nucleation of the Pd hydride phase with a time resolution of 1-2 s. The results reveal that the rate of the reduction process is influenced by the nature of the Al<sub>2</sub>O<sub>3</sub> polymorph at constant PdO particle size. For example,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> delayed significantly the formation of Pd hydrides under these experimental conditions. Reduction by H<sub>2</sub> was also slow probably as a result of the low solubility of H<sub>2</sub> in water. Chemically different reducing agents proved to require different concentrations in order to provide comparable extents of hydride formation, suggesting a different extent of reducing ability.

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## Inverted RDE for True OER Catalyst Degradation Assessment

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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 materials. However, to be able to characterize the performance of these new catalysts, it is also needed to consider using the adequate screening methods. It has been recently demonstrated that the conventional rotating disk electrode (RDE)-based studies are not suitable for gas evolving processes due to bubbles uncontrollably blocking catalytic active sites. [1] To overcome this issue, an upward facing configuration of the instrument allows the formed gaseous product to escape the catalyst surface as demonstrated among others for metal deposition and CO<sub>2</sub> reduction reaction. [2,3] Therefore, the true catalyst performance can be screened and assessed. In the current work, we used this so-called *inverted* RDE (*i*RDE) for the OER with Ir nanoparticles supported on commercially available Sb-doped SnO<sub>2</sub> (Ir/ATO). The test consisted in cycling the potential between 1.2 and 1.7 V vs RHE at rate of 10 mV s<sup>-1</sup>. The evolution of the current densities at 1.5 V vs RHE over the number of cycles obtained with the *i*RDE is compared to the one obtained with the conventional RDE setup (Fig. 1a). Rapid decline of the catalyst activity was observed in the RDE setup, while the catalyst activity demonstrates a rather stable behavior in the *i*RDE setup. The fast activity drop observed in the RDE setup is to some extent due to accumulation of O<sub>2</sub> bubbles on active sites. However, the main reason for catalyst deactivation is the gradual passivation of the catalyst back contact. [4] This latter issue can be overcome by employing a non-porous catalyst that prevents contact between back contact material and electrolyte. Moreover, the oscillations observed in the *i*RDE are accounted for short live bubble retention and detachment as depicted in Fig. 1b-c.

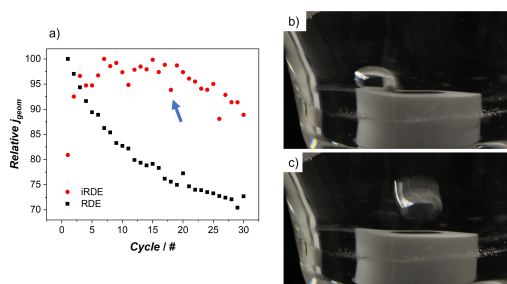


Figure 1. (a) Evolution of the relative current densities at 1.5 V vs RHE over the number of cycles employing the *i*RDE (red) and the RDE (black) setup. (b-c) Photographs of O<sub>2</sub> bubble detachment from Ir/ATO at cycle 18 (blue arrow).

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## Combinatorial neutron imaging for in-situ alkane adsorption analysis over C<sub>1</sub>-C<sub>4</sub> coupling catalysts

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Hydrocarbons are essential commodity chemicals used in various applications and crucial for our society. However, their dependence on fossil sources puts pressure on the environment. Hence, the production of these molecules from renewable sources is crucial for the advancement of a sustainable society. Currently, the most promising routes rely on the activation and subsequent oligomerization of small molecules (C<sub>1</sub>-C<sub>4</sub>) into longer chain hydrocarbons over heterogeneous catalysts. Nevertheless, these systems suffer from poor selectivity towards a single target product,<sup>[1]</sup> as well as rapid deactivation.<sup>[2]</sup> These transformations are largely governed by the ability of the reagents and products to diffuse through the catalyst pore network. Therefore, a complete understanding of the sorption kinetics is beneficial for the establishment of descriptors that aid the design of catalytic materials with optimized properties. Such investigations are traditionally performed by infrared radiation (IR) in combination with Raman spectroscopy or by simple gravimetric methods.<sup>[3]</sup> While these methods provide valuable information on the properties of a system, the in-situ optical visualization of the material changes during the adsorption/desorption process remains challenging due to interferences with the source light. In addition, the design of suitable cells is required for the application of these techniques under realistic temperatures and pressures. Herein, the uptake and desorption kinetics of *n*-hexane as probe molecule over commercial zeolite catalysts under catalytically relevant conditions is studied using the combinatorial neutron imaging method.<sup>[4]</sup> The large interaction between neutrons and hydrogen leads to significant changes in contrast when H-containing molecules are adsorbed on the materials. This property enables the in-situ adsorption/desorption visualization, and the quantification of the hydrocarbon species adsorbed. In addition, the custom designed experimental setup used in this study allowed the simultaneous investigation of up to 69 samples.<sup>[4]</sup> For temperatures below 473 K, the observed radial diffusion profiles in most porous materials indicate that the diffusion of long chain products plays a critical role in the catalyst deactivation under typical reaction temperatures (423-523 K). Overall, the findings provide new insights on the adsorption kinetics of hydrocarbons over systems with varying porosity and pore connectivity, facilitating the design of optimized catalysts for oligomerization reactions.

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**Low-Cost CuX Catalyst from Blast Furnace Slag Waste for Low-Temperature NH<sub>3</sub>-SCR**L. Chen<sup>1,2</sup>, S. Ren<sup>1</sup>, Q. Liu<sup>1</sup>, D. Ferri<sup>2</sup><sup>1</sup>Chongqing University, <sup>2</sup>Paul Scherrer Institut

The presence of nitrogen oxides (NO<sub>x</sub>) in industrial flue gas is a major concern due to their negative impact on the environment and human health [1]. Selective catalytic reduction with NH<sub>3</sub> (NH<sub>3</sub>-SCR) is the primary technology for reducing and controlling NO<sub>x</sub> emissions [2]. As one of the primary solid wastes generated from blast furnace iron production, blast furnace slag (BFS) contains an adequate quantity of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> that could serve as raw material for zeolite synthesis. Zeolite X with low Si/Al ratio was successfully prepared by the seed-hydrothermal method [3].

In this study, we investigated the low-temperature NH<sub>3</sub>-SCR activity and surface acidity of a series of Cu-exchanged zeolite X (derived from blast furnace slag) catalysts with various Cu/Al ratios (mole ratio of Cu/Al=0.13, 0.28, 0.4, 0.45, 0.46, 0.47). Based on the NH<sub>3</sub>-SCR performance of these CuX catalysts, the CuX-0.28 catalyst exhibited the highest NH<sub>3</sub>-SCR activity across the entire temperature range, exhibiting NO conversion above 93% from 150 °C to 400 °C and N<sub>2</sub> selectivity higher than 91%. The catalytic tests towards the oxidation of NH<sub>3</sub> revealed that NH<sub>3</sub> was oxidized to NO or N<sub>2</sub>O above 300 °C. NH<sub>3</sub>-TPD measurements showed that the CuX-0.28 catalyst had the highest surface acidity in the series and most of surface acidity was attributed to Lewis acid sites. During in situ DRIFTS of the NH<sub>3</sub>-SCR reaction, both Lewis and Brønsted acid sites were identified on the CuX-0.28 catalyst, with Lewis acid sites playing the primary role in the NH<sub>3</sub>-SCR reaction.

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## A Surface Organometallic Chemistry Platform for Efficient Deoxygenation of Small Molecule Oxygenates

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Current chemicals and fuels are mostly derived from fossil fuels and are thus not sustainable due to the limited resources and the emissions of CO<sub>2</sub> associated with their production and use. Moving to biomass-derived feedstocks would offer several advantages: they are renewable, (more) carbon neutral, already available as a waste byproduct of various industries.<sup>1</sup> However, biomass intrinsically contains a large variety and number of oxygen-containing functional groups, that need to be converted to bridge the gap with most value-added chemical products, hence the need for synthetic methodologies for selective and efficient deoxygenation while leaving the carbon skeleton intact.<sup>2</sup> Ideally, this transformation can be achieved using only (green) dihydrogen as a reactant, rendering it both atom economical and forming only water as benign byproduct. In this context, bimetallic catalysts are privileged materials by displaying bifunctional properties, enabling dihydrogen activation and acid-catalyzed reactions from the co-existence of metallic nanoparticles and metal oxide — e.g., the combination of group XI-X metals and a group VI-VII metal oxide such as MoO<sub>3</sub>.<sup>3,4</sup> However, the mechanism and exact role and synergies between the two metals and the support is poorly understood. In order to be able to study these materials and establish meaningful structure activity correlations, well-defined model catalysts are required. We have thus developed a platform of organometallic precursors based on diisopropylamidinate ligands for the metals Rh, Ir, Ni, Pd, and Pt, that can be employed to generate size-homogeneous supported nanoparticles on oxide-based supports, via surface organometallic chemistry.<sup>5,6</sup> We have examined bimetallic materials synthesized from a Mo-doped SiO<sub>2</sub> support to evaluate their activity in deoxygenation. During this study, we have identified catalyst materials active in the deoxygenation of primary, secondary, and tertiary alcohols, various ketones, and  $\alpha$ -ketoesters. Almost quantitative yields can be achieved for some substrates, and functional group tolerance towards both electrophilic and nucleophilic functional groups was observed, allowing for a synthetic handle for further diverse functionalization of the products.

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**Operando transient EPR spectroscopy of N<sub>2</sub>O activation and reaction on Fe-zeolites**

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Control of N<sub>2</sub>O emissions from stationary anthropogenic sources and novel fuel technologies is mandatory due to its large global warming potential. Catalysts based on Fe exchanged in silico-aluminates (zeolites) represent a major class of technologies currently used to remove N<sub>2</sub>O from exhaust gases. While Fe-zeolite catalysts are active for this reaction, the nature of the active site remains debated because of the difficulty to obtain homogeneously dispersed Fe sites. Spectroscopy as a tool of characterizing the active sites during reaction suffers from the need to disentangle complex signals of species probably not involved in the reaction. In this contribution we show that electron paramagnetic resonance (EPR) spectroscopy coupled to transient experiments is able to provide information on the structure of the active sites of N<sub>2</sub>O activation and reaction going beyond what was obtained so far.

We have analyzed a commercial Fe-zeolite catalyst comprising a number of Fe species of different degrees of agglomeration (monomers in different environments and clusters) by exposing it to pulses of N<sub>2</sub>O in Ar, NO/Ar and NO+NH<sub>3</sub>+O<sub>2</sub>/Ar at 400°C while measuring products evolution with a mass spectrometer.

The EPR spectra of the catalyst exposed to N<sub>2</sub>O at 400°C clearly showed that N<sub>2</sub>O oxidizes all Fe species to Fe<sup>3+</sup>. However, it is by repeatedly adding/cutting-off N<sub>2</sub>O that only specific Fe<sup>3+</sup> sites can reversibly activate N<sub>2</sub>O and break the N<sub>2</sub>-O bond. These species coincide with Fe coordinated in beta-exchange positions of the zeolite structure. Other species such as Fe coordinated to gamma-positions of the framework and also clusters can perform reversible Fe<sup>2+</sup>/Fe<sup>3+</sup> red-ox only when a reducing agent is added to the reaction, as in the case of the N<sub>2</sub>O+NO and N<sub>2</sub>O+NO+NH<sub>3</sub>+O<sub>2</sub> environments. The work helps rationalizing the contribution of different Fe species in the mechanism of the simultaneous removal of N<sub>2</sub>O and NO from exhaust gases that we have studied using X-ray absorption spectroscopy, EPR and infrared spectroscopy under identical experimental conditions to those shown here.

These results show that the transient nature of the experiments allows extraction of key mechanistic details that would remain otherwise hidden. This is even more important for a technique highly sensitive to the local environment of different Fe species such as EPR spectroscopy.

**Cation effect on electrocatalytic nitrate reduction to ammonia**J. Forner<sup>1</sup>, Y. Wang<sup>1</sup>, A. Dutta<sup>1</sup>, P. Broekmann<sup>1\*</sup><sup>1</sup>Department of Chemistry, Biochemistry and Pharmaceutical Science, University of Bern, Freiestrasse 3, 3012 Bern, Switzerland

The electrochemical reduction of nitrate to ammonia (NO<sub>3</sub>-RR) is a sustainable approach to mitigate nitrate pollution. Previous studies have shown that alkali metal cations play a significant role in electrochemical reduction processes. The influence of alkali metal cations on the activity, selectivity, and mass transport during NO<sub>3</sub>-RR was investigated in this work.

In previous research <sup>[1][2]</sup>, it was observed that the electric field induced by solvated cations can modulate the activity and selectivity in the electrochemical reduction of CO<sub>2</sub> by affecting the electrochemical double layer, particularly the outer Helmholtz plane. As the cation size increases, the hydration sphere radius decreases, resulting in a decrease in hydration energy and an increase in mobility (Li<sup>+</sup> < Na<sup>+</sup> < K<sup>+</sup> < Cs<sup>+</sup>) <sup>[3]</sup>. This trend allows for tuning of activity, selectivity, and mass transport by selecting the appropriate supporting cation.

In this study, a porous Cu-foam catalyst deposited onto a copper mesh support using the dynamic hydrogen bubble template method was employed to examine the influence of alkali metal cations (Li<sup>+</sup> < Na<sup>+</sup> < K<sup>+</sup> < Cs<sup>+</sup>) on NO<sub>3</sub>-RR. By adjusting the composition and concentration of the supporting electrolyte, the effects of different alkali cations were investigated.

The results revealed that the partial current density, and consequently the nitrate removal rate, increased following the order Li<sup>+</sup> < Na<sup>+</sup> < K<sup>+</sup> < Cs<sup>+</sup>. These consistent trends in NO<sub>3</sub>-RR emphasize the pivotal role played by the electrostatic effect, which stabilizes negatively charged species at the electrode interface. The experimental surface coverages of alkali metal cations align with their free energies of hydration, following the order Li<sup>+</sup> > Na<sup>+</sup> > K<sup>+</sup> > Cs<sup>+</sup>. The conversion rate of nitrate to ammonia increases according to the coverage of specifically absorbed alkali metal cations that exhibit lower degrees of hydration. These findings suggest that the extent of dehydration of alkali metal cations at the electrode-electrolyte interface significantly influences their ability to facilitate nitrate reduction.

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## Boosting Nitrate to Ammonia Electroconversion through Hydrogen Gas Evolution over Cu-foam@mesh Catalysts

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The hydrogen evolution reaction (HER) is often considered parasitic to numerous cathodic electro-transformations of high technological interest, including but not limited to metal plating (e.g., for semiconductor processing), the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR), the dinitrogen→ammonia conversion (N<sub>2</sub>RR), and the nitrate reduction reaction (NO<sub>3</sub><sup>-</sup>RR).

Herein, we introduce a porous Cu foam material electrodeposited onto a mesh support through the dynamic hydrogen bubble template method as an efficient catalyst for electrochemical nitrate→ammonia conversion. To take advantage of the intrinsically high surface area of this spongy foam material, effective mass transport of the nitrate reactants from the bulk electrolyte solution into its three-dimensional porous structure is critical. At high reaction rates NO<sub>3</sub><sup>-</sup>RR becomes, however, readily mass transport limited because of the slow nitrate diffusion into the three-dimensional porous catalyst. Herein, we demonstrate that the gas evolving HER can mitigate the depletion of reactants inside the 3D foam catalyst through opening an additional convective nitrate mass transport pathway provided the NO<sub>3</sub><sup>-</sup>RR becomes already mass transport limited prior to the HER onset. This pathway is achieved through the formation and release of hydrogen bubbles facilitating electrolyte replenishment inside the foam during water/nitrate co-electrolysis. This HER mediated transport effect “boost” the effective limiting current of nitrate reduction, as evidenced by potentiostatic electrolyses combined with an *operando* video inspection of the Cu-foam@mesh catalysts under operating NO<sub>3</sub><sup>-</sup>RR conditions. Depending on the solution pH and the nitrate concentration, NO<sub>3</sub><sup>-</sup>RR partial current densities beyond 1 A cm<sup>-2</sup> were achieved.

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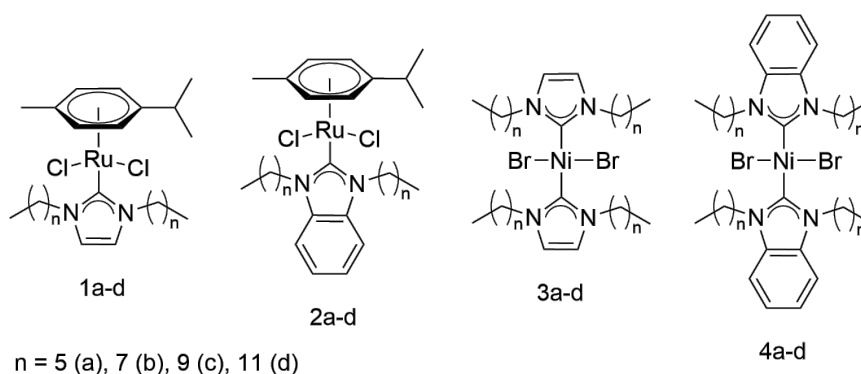
## Design of organometallic complexes as precursors for catalysts with tuneable properties

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Coreshell nanoparticles (CSNPs) show excellent stability and selectivity for catalysis due to the presence of a protective shell encapsulating the active nanoparticle surface.<sup>1</sup> The increased stability and selectivity have proven beneficial for biomass conversion to value-added chemicals<sup>2</sup> – an important topic for a more sustainable future. However, there are major challenges with reproducibility and control over nanoparticle properties, particularly in the field of heterogeneous catalysis.<sup>3</sup> Herein we propose a strategy for the reproducible synthesis of nanoparticles with adjustable properties to help bridge the gap between catalyst preparation and catalyst properties. By correlating the nature of the organometallic precursors and CSNP preparation method parameters with the structure of the resulting CSNPs, we are developing a methodology for preparing CSNPs with tuneable physical properties. Studying the relationship between CSNP physical and chemical properties allows us to identify key features that indicate greater stability and higher activity in C-O bond hydrogenolysis.

A variety of ruthenium and nickel complexes featuring *N*-heterocyclic carbene (NHC) ligands (Ru-NHC and Ni-NHC) were prepared and used to generate NPs. NHC ligands featuring alkyl side chains (Fig. 1) were chosen to emulate the carbon chains of many surfactants previously used to generate stabilized NPs.<sup>4</sup> The length of the carbon chain was varied to study the effect on shell thickness and porosity, and, as a result, the activity, selectivity, and stability of the NPs. After a sequential chemical reduction and pyrolysis of the organometallic precursors, the physical properties, such as shell thickness, can be related to the precursor nature and variables in the NP synthesis method. After application to the C-O bond hydrogenolysis of lignin model compounds (diphenyl ether, benzylphenyl ether, and phenethyl phenyl ether) under mild conditions (140 °C and 15 bar H<sub>2</sub>), structure-activity relationships identify the most important physical properties for predicting catalytic activity, stability, and selectivity.



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**Aging of DeNO<sub>x</sub> and DeN<sub>2</sub>O catalysts for Nitric Acid plant**A. Garbujo<sup>1</sup>, F. Oldani<sup>1</sup>, R. Lanza<sup>2</sup>, A. Lahougue<sup>3</sup>, E. Rohart<sup>3</sup>, P. Biasi<sup>1</sup><sup>1</sup>Casale SA, Lugano, Switzerland, <sup>2</sup>Verdant, Stockholm, Sweden, <sup>3</sup>Alslys, Ploemeur, France

Nitrous oxide (N<sub>2</sub>O) is one of the most impacting greenhouse gases that significantly contributes to climate change. In 2017, Europe alone emitted around 18 million tonnes of N<sub>2</sub>O, mainly from agricultural activities and the production of nitric acid. [1] Scientist are constantly searching for effective new deN<sub>2</sub>O catalysts that can be used in real-world applications. One crucial aspect of this research is the industrial aging of catalysts. This process simulates the conditions under which catalysts will be exposed to in industrial environments, including high temperatures and exposure to pollutants. By conducting representative industrial aging tests, researchers can gain a better understanding of how catalysts will perform over time in real-world settings and make necessary adjustments to improve performance and lifetime. Additionally, this process allows researchers to identify potential degradation mechanisms and optimize catalyst design, thus reducing N<sub>2</sub>O emissions in the final stages of catalyst use. Industrial Fe-FER and Fe-ZSM5 catalysts were prepared by the French company ALSYS on an industrial scale. [2] The catalysts were exposed to a simulated accelerated aging procedure, which was created to model a specific catalytic aging process. This was done to study the deNO<sub>x</sub>/deN<sub>2</sub>O catalytic behavior at the end of the catalyst's life. The deNO<sub>x</sub>/deN<sub>2</sub>O catalytic performance was tested under relevant industrial conditions... A very high space velocity was used to stress the differences in catalytic activity between the catalysts that were tested. The aging treatments were conducted for 150 hours at two temperatures, 600 and 700°C. This study compares the catalytic activity of Fe-FER and Fe-ZSM5 catalysts for NO<sub>x</sub> and N<sub>2</sub>O abatement in a simulated nitric acid process. The study examines the structural, through XRD, and catalytic evolution of the catalysts upon aging under representative industrial conditions. The results show that Fe-FER has higher catalytic activity and structure stability than Fe-ZSM5, particularly after the aging procedure. Fe-ZSM-5 experiences loss in deN<sub>2</sub>O activity, while Fe-FER retains its catalytic activity under these conditions. The stability of the Fe-FER catalyst is believed to be responsible for its higher catalytic activity and better preservation of deN<sub>2</sub>O activity. The study highlights the importance of using representative industrial aging treatments and real industrial test conditions when studying new catalysts, as these conditions can greatly affect the catalytic activity and structure of the materials.

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**Evolution of active species in ethylene epoxidation over silver foil revealed by ambient pressure X-ray photoelectron spectroscopy**

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The 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 nature of oxygen species and their roles in EPO are still unclear. In the current work, silver foil was characterized systematically as the starting step of a project aiming at chemical looping process of EPO. 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 structures of AgO<sub>x</sub> were unveiled on Ag foil. All of them proved to be highly sensitive to temperature and ratio of reagent, and participate in the reaction with ethylene. The key role of subsurface oxygen species was revealed over silver foil during the EPO process. Dichloroethane was cofed at a ppm level in the end to investigate the significant effect of chlorine on the selectivity of ethylene oxide

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## Titanium Surface Sites in Ziegler-Natta Pre-Catalysts from $^{47/49}\text{Ti}$ solid-state NMR Signatures

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The initial development of the heterogenous Ziegler-Natta (ZN) polymerization catalyst dates back to the mid-1950s<sup>1</sup>. Despite the industrial importance of the ZN catalysts towards the world production of polyethylene (HDPE & LLDPE) and polypropylene (iso-PP)<sup>2,3</sup>, the structure-activity relation until now remains elusive. As a result, decades of development targeted towards performance gains of the highly complex heterogenous catalytic system were primarily empirical. In the 1970s, the usage of magnesium chloride ( $\text{MgCl}_2$ ) as support of the active site was found to significantly enhance the activity of Ti-based ZN catalysts<sup>2</sup>. However, in order to promote a more rational catalyst design, a detailed molecular-level understanding of Ti surface sites of the ZN pre-catalyst,  $\text{TiCl}_4/\text{MgCl}_2$ , which is known to form active sites under polymerisation conditions, is required.

For the evaluation of the Ti surface sites, we turned to  $^{47/49}\text{Ti}$  NMR, which is highly sensitive towards the ligand environment of Ti, altering the local charge distribution and electronic structure. The applications of  $^{47/49}\text{Ti}$  NMR are nonetheless often limited, due to (i) low Ti content in the catalyst (ca. 2 wt%), (ii) the low natural abundance of the NMR nuclei (< 10 %), (iii) the presence of two NMR active isotopes with small resonant frequency difference ( $\Delta\delta_{^{47/49}\text{Ti}} = 267$  ppm) and (iv) the quadrupolar nature of both isotopes. In this work, we addressed these challenges by (i) combining high magnetic field (900 MHz), fast magic angle spinning (MAS) and low temperature (100 K)  $^{47/49}\text{Ti}$  NMR measurements, in order to decrease the linewidth and increase sensitivity, (ii) performing state-of-the-art density-functional theory (DFT) computations, and (iii) using  $\text{BCl}_3$ -treated ZN pre-catalyst<sup>3</sup>, which was expected to contain fully chlorinated Ti species, hence a more symmetric electric charge distribution around Ti, associated with more favourable NMR properties, and shown to increase the amount of the active sites.<sup>4</sup> The obtained NMR spectroscopic signatures of Ti surface sites of the ZN catalyst and the application of DFT modelling allowed us to resolve the structure of  $\text{TiCl}_4$  on  $\text{MgCl}_2$ , a representative industrial pre-catalyst. Analysis of chemical shift and quadrupolar coupling constant helped to highlight the influence of the local environment and  $\text{MgCl}_2$  morphology on the electronic structure of the Ti sites.

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## Decoding Solid-State NMR Descriptors of Group(VI)-Metal and Ligand Nuclei using Machine Learning

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Understanding the structure-reactivity relationship in catalytic species requires spectroscopic techniques capable of accessing and rationalizing this connection. In solid-state NMR spectroscopy, chemical shift tensors (CSTs) provide valuable information about local chemical environments and their connection to frontier molecular orbitals.<sup>[1]</sup> However, current methods relying on orbital analysis to connect experimentally accessible NMR descriptors of ligands<sup>[2]</sup> and metal nuclei<sup>[3]</sup> to reactivity face limitations due to computational expense and time-consuming solid-state NMR measurements. To overcome these challenges, we employ data-driven methods to uncover trends between NMR descriptors (CST and electric field gradient tensor for quadrupolar nuclei) and electronic structure in a broader chemical space. Our goal is to develop a machine learning model that maps global and local descriptors of ligands and metal complexes<sup>[4]</sup> to the chemical shieldings of d<sup>0</sup> group(VI) Mo and W complexes, an important class of precatalysts for olefin conversion processes such as metathesis and oligomerization.

We generated a dataset of 29'000 penta- and hexacoordinated complexes combinatorically with a d<sup>0</sup> metal (Mo or W) and various ligands, with each molecule bearing a dianionic ligand (oxo, imido, sulfido, selenido), four monoanionic ligands (e.g. halogenides, alkoxides, alkyls) and up to one neutral ligand (e.g. THF). Using semiempirical geometry optimization and high-level DFT calculations, we obtained the CST values for the dataset. Featurization of the dataset involved 125 local and global descriptors, including steric and electronic parameters. Through hierarchical clustering, we reduced the feature space to 15-30 uncorrelated features suitable for regression algorithms. By training a Random Forest Regressor on a subset of the data, we achieved accurate predictions (R<sup>2</sup> of 0.7-0.9) for the metal and dianionic ligand isotropic chemical shieldings, with mean absolute errors of 200-400 ppm for the metal (<sup>95</sup>Mo, <sup>183</sup>W) and 20-40 ppm for the ligand (<sup>15</sup>N, <sup>17</sup>O).

Analysis of the dataset revealed trends consistent with previous case studies, such as the linear correlation of <sup>95</sup>Mo and <sup>183</sup>W chemical shifts for metals in the same coordination environment and the influence of ligand electronegativity on metal nuclei chemical shifts. Additionally, we uncovered unexplored trends related to the influence of metal  $\sigma$ - and  $\pi$ -bonding with the dianionic ligand and the impact of ligand steric bulk on NMR parameters. This approach demonstrates the potential of machine learning in providing novel insights into NMR-based descriptors and advancing our understanding of the relationship between NMR spectroscopy and electronic structure across a broad composition space.

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**Metal-Like Molecule for Stable Oxygen-Evolution: Natural Mimic by Integrating  $\text{Co}_4\text{O}_4$  Cubane into Polypyrrole**S. Li<sup>1</sup>, Z. Zhang<sup>1</sup>, G. R. Patzke<sup>1\*</sup><sup>1</sup>University of Zurich

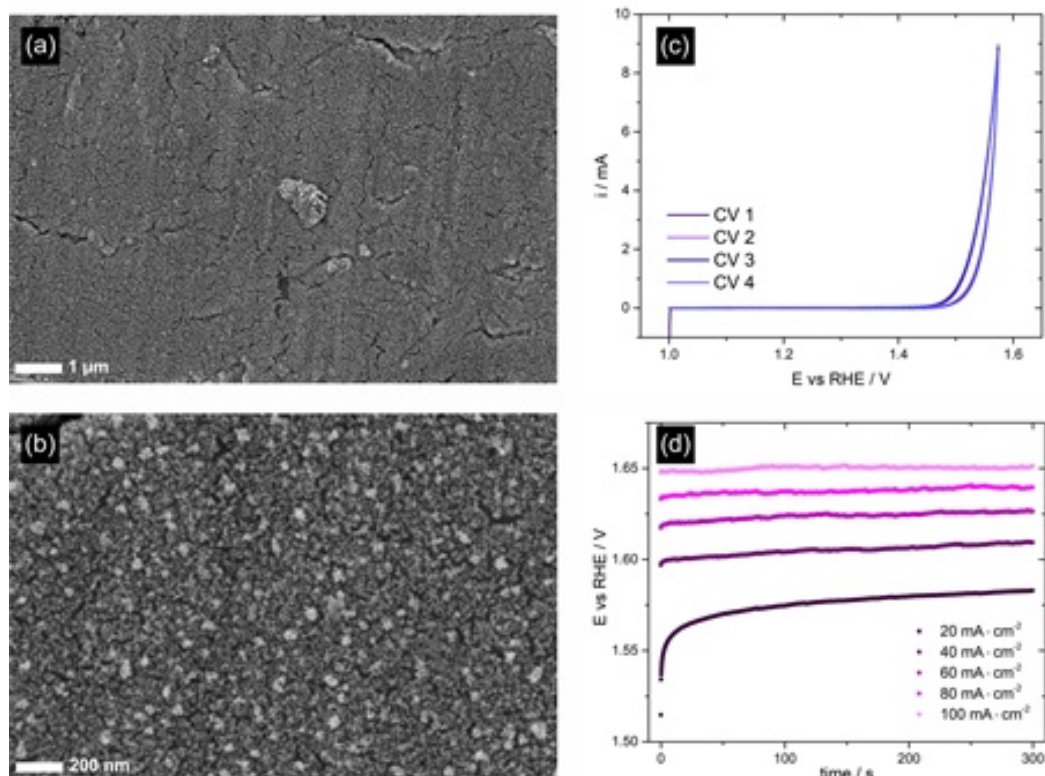
Exploration of efficient and stable water oxidation catalysts based on polynuclear metal-oxo clusters remains the primary challenge in conversion of renewable energy sources into fuels. The cubic  $\{\text{Co}_4\text{O}_4\}$  complexes, inspired by the natural inorganic core of photosystem II (PSII), have continuously attracted interest as molecular water oxidation catalysts combining features of both heterogeneous and homogeneous catalysis. However, further application remains impeded by the instability during oxygen evolution reaction (OER) and missing knowledge of the design concept in molecular level. Photosystem II (PSII), as a protein complex, shows asymmetric structure and ligand-protein environment for stabilizing the catalytic cubic core. Here, we present a molecular synthetic strategy for stabilization of the  $\text{Co}_4\text{O}_4$  cubane oxo by both the asymmetric design and the integration with conjugated polypyrrole, thus avoiding the intermolecular aggregation during the OER process. The asymmetric design not only prevents the catalyst decomposition, but also increases the catalytic efficiency by providing the directed cofacial dihydroxide motif. In addition to the protection, polypyrrole is a p-type conducting polymer that promotes the holes transfer during the OER process, resulting in a high turnover frequency (TOF) to the  $\{\text{Co}_4\text{O}_4\}$  molecular catalyst. By a combination of experimental and theoretical results, different oxygen evolution pathways, affected by intramolecular hydrogen bond (IHB), are proposed. This study follows the natural feature and provides an elegant design concept for stabilizing the polynuclear oxo and improving the efficiency of  $\{\text{Co}_4\text{O}_4\}$  cubane for long-term OER.

## Novel Iridium-Based Electrocatalyst on Titanium Substrates for the Oxygen Evolution Reaction

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The oxygen evolution reaction (OER) is the critical half-cell reaction in proton exchange membrane water electrolysis (PEMWE) that still needs improvement for the practical development of sustainable hydrogen production<sup>1-2</sup>. The most developed OER electrocatalyst materials used for acidic water electrolysis are based on Iridium or Iridium oxides<sup>1-2</sup>. Due to the scarcity and high material cost of Ir<sup>1</sup>, there is a demand for catalyst materials with both a high electrochemical active area and an exceptionally high robustness towards mechanical and chemical degradation.



(a), (b) Top-down SEM images of as deposited Ir on Ti foil. (c) Cyclic voltammograms acquired prior to (CV 1-2) and after (CV 3-4) electrochemical stressing through stepped galvanostatic OER (d).

In this project, a novel and facile synthesis concept for Ir-based catalysts deposited on Ti substrates is developed. Different experimental parameters of electrodeposition are screened and correlated to the morphologies of the resulting catalyst layers through scanning electron microscopy (SEM). The catalysts are characterized electrochemically to determine their activity in the OER as well as their stability under the applied harsh anodic and acidic reaction conditions. The deposition parameters are optimized to obtain a minimal Ir loading on Ti supports without losses in activity or stability of the catalyst.

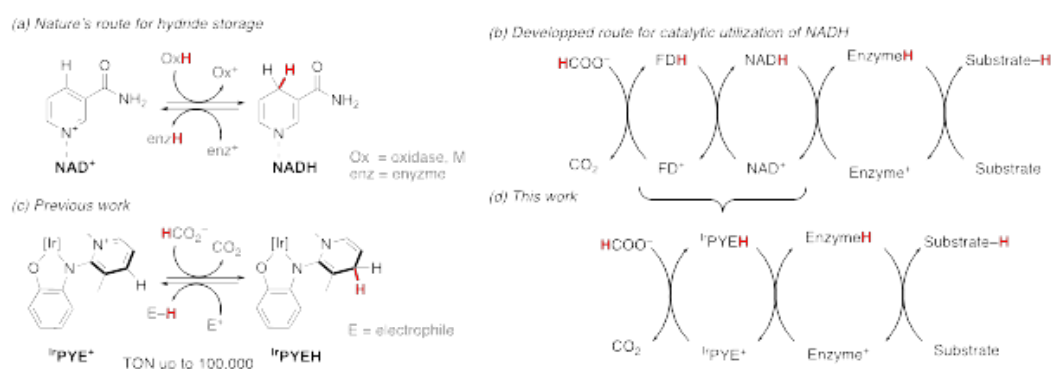
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**$\text{IrPYE}^+$  /  $\text{IrPYEH}$  complex as self-regenerated NADH cofactor**L. Monte<sup>1</sup>, N. Lentz<sup>1</sup>, F. Paradisi<sup>1\*</sup>, M. Albrecht<sup>1\*</sup><sup>1</sup>Department of Chemistry, Biochemistry and Pharmaceutical Sciences, University of Bern, Freiestrasse 3, CH-3012 Bern (Switzerland)

NADH is an important cofactor that plays a critical role in most oxidoreduction enzymatic processes relying on reversible storage of the hydride on the nicotinamide moiety (Fig. 1a). However, NADH is limited by its high cost, low stability, and stoichiometric utilization.<sup>[1]</sup> In the past years, several groups investigated different cofactor regeneration systems as well as the use of synthetic cofactors aiming to reduce the cost associated with NADH-dependent reactions.<sup>[2], [3]</sup>

Our group recently developed an iridium complex bearing a pyridylidene-amine (PYEs) ligand that was successfully applied in the dehydrogenation of formic acid.<sup>[4]</sup> Interestingly, ligand optimization showed a unique functional ligand-type reactivity where the hydride is stored on the heterocycle ring, mimicking an NADH-type reactivity (Fig. 1c).<sup>[5]</sup> Herein, we are investigating the possible application of the iridium complex into chemoenzymatic processes in a multidisciplinary way, combining a computational, biocatalytic and organometallic approach (Fig. 1b and 1d).



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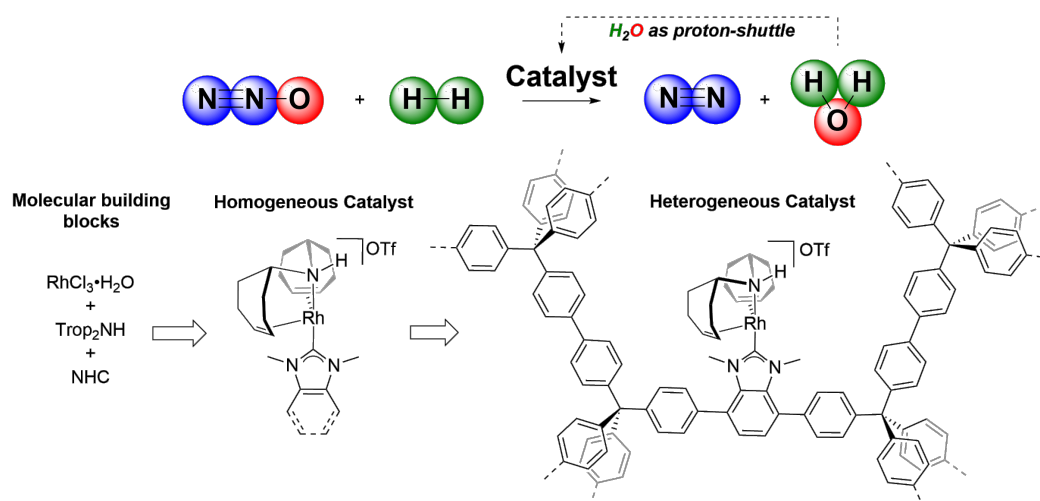
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## Metal-ligand Cooperative Rhodium Complexes as Highly Active N<sub>2</sub>O Hydrogenation Catalysts

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Nitrous oxide (N<sub>2</sub>O), more commonly known as laughing gas, is no laughing matter in view of its significance as an atmospheric pollutant. In recent times, N<sub>2</sub>O has been identified as the most ozone depleting agent of the 21st century (comparable to that of CFC's) and a potent greenhouse gas.<sup>[1]</sup> The 'simple on-paper' reaction: N<sub>2</sub>O + H<sub>2</sub> → N<sub>2</sub> + H<sub>2</sub>O can be a promising mitigation strategy, but in reality this reaction is difficult to perform. Activation of N<sub>2</sub>O is challenging, in addition, the catalyst must remain robust and selective towards the oxidizing (N<sub>2</sub>O) and reducing (H<sub>2</sub>) conditions. N<sub>2</sub>O have been, and generally still is, broadly overlooked compared to its isoelectronic and isostructural more well known molecule, CO<sub>2</sub>. In the past decades we have seen strong research forces yielding several CO<sub>2</sub> hydrogenation catalysts with turnover numbers (TON's) up to millions.<sup>[2]</sup> Meanwhile the homogeneous N<sub>2</sub>O hydrogenation catalysts in the scientific literature today are very few in numbers and only reaches TON's of hundreds.<sup>[3]</sup>



We can now report that we have found a catalyst that shows unprecedented activity (~ 200'000 TON's) in the hydrogenation of N<sub>2</sub>O at mild conditions (2-5 bars, 65 °C). Rhodium as the metal and NHC's as ancillary ligands combined with a tridentate bis-olefine amine ligand<sup>[4]</sup> was found to be the best among the tested candidates. The credit cannot be given to the catalyst design alone as evidence suggests a more holistic process. Our combined experimental and theoretical study of the reaction mechanism concludes that the process is autocatalytic. In a bottom-up approach the catalyst could be heterogenized, and the activity and stability of the well-defined single-site heterogeneous catalyst was evaluated and compared with the molecular version.

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## Understanding the catalytic pyrolysis mechanism of lignin constituents: the importance of functional groups

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Lignin, rich in aromatic compounds, is renewable and cheap, which makes it an ideal raw material for producing fuels and chemicals.<sup>1</sup> It is a complex and amorphous polymer, and its complex catalytic pyrolysis mechanism results in challenging product-selectivity control. Understanding the reaction mechanism in lignin catalytic pyrolysis is, thus, key to improving product selectivity.<sup>2</sup>

Lignin can be described as a condensate of smaller aromatic units (*p*-hydroxyphenyl and guaiacyl, etc.) with linkages, such as the  $\beta$ -O-4 bond, between them.<sup>3,4</sup> Therefore, lignin model compounds, such as guaiacol, vanillin, eugenol, and linkage-bound dimers offer a tractable avenue to investigating the reaction mechanism. We have applied advanced Photoelectron Photoion Coincidence spectroscopy (PEPICO) to investigate a broad variety of lignin model compounds and derived comprehensive reaction pathways based on detecting reactive intermediates isomer-selectively.<sup>5</sup>

In this contribution, we discuss and summarize the influence of the hydroxyl, methoxy, aldehyde, and allyl functional groups on the reaction temperature and the pyrolysis mechanism based on experiments of mono- to tri-substituted aromatics. The goal is to construct a coherent picture based on these model compounds and to reveal universal rules driving lignin catalytic pyrolysis. This will open up new ways to optimizing lignin valorization.

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## Tandem Carbon Capture and Catalysis over Amine-Functionalized Metal-Organic Frameworks for CO<sub>2</sub> Hydrogenation to Methanol

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Methanol is one of the most critical chemicals, with a broad range of industrial applications. When produced from CO<sub>2</sub>, methanol promises to be a key molecule to reaching carbon neutrality. Current catalysis for CO<sub>2</sub> hydrogenation to methanol is carried out at high temperatures and pressures over heterogeneous catalysts. The demand for a high-purity CO<sub>2</sub> feed at high pressures implicates high energy and, therefore, environmental costs. Current scrubbing technologies for CO<sub>2</sub> capture often require high temperatures for sorbent regeneration, further adding energy penalties to the cycle. Carbon capture processes using solid sorbents, in general, hold many promising advantages compared to conventional aqueous amine scrubbers.

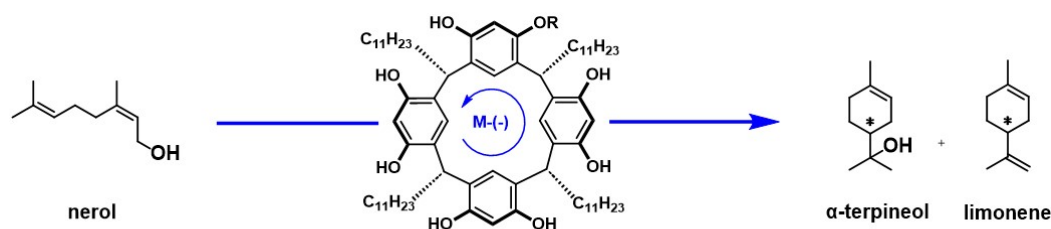
In this work, we report bi-functional systems that combine CO<sub>2</sub> adsorption at low partial pressures with its conversion to methanol by hydrogenation with H<sub>2</sub>. The materials are made from amine-functionalized metal-organic frameworks (MOFs) that can adsorb and activate CO<sub>2</sub> in form of carbamates. The captured CO<sub>2</sub> is subsequently converted to methanol by means of PNP- or PNN-pincer transition metal complexes. Preliminary tests at low CO<sub>2</sub> partial pressures have shown that amine-functionalized MOFs produce methanol with H<sub>2</sub> at low temperature and mild pressures in the presence of the PNP-pincer ruthenium complex RuH(BH<sub>4</sub>)(CO)(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>) (Ru-MACHO-BH).

## Exploration of Novel Optically Active Resorcin[4]arene Capsule Derivatives for Enantioselective THT Cyclizations

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Mimicking the capabilities of terpene cyclases in the tail-to-head terpene cyclizations (THT) represents a great challenge in asymmetric catalysis. Molecular containers, by entrapping guests in a closed cavity, are able to mimic to some extent the enzymatic pockets of natural enzymes. The hydrogen-bond-based resorcin[4]arene capsule, first reported by Atwood in 1997,<sup>[1]</sup> is able to catalyze the THT cyclization of terpenes by stabilizing the cationic intermediates formed during the reaction cascade.<sup>[2]</sup> In this context, our group recently reported the first examples of optically active mono-alkylated resorcin[4]arene capsules and their application as supramolecular catalysts in the asymmetric THT cyclization of nerol.<sup>[3]</sup> Therefore, demonstrating that the chirality transfer from a rather large molecular container (approximately 1400 Å) onto the encapsulated substrate is possible. In this work we enlarged the scope of this supramolecular catalyst reporting 14 novel optically active resorcin[4]arene capsule derivatives, exploring the tolerance of the self-assembling of such systems towards structural modifications. Furthermore, the effects that these modifications have on the enantioselectivity of the THT cyclization studied are presented.



R: Alkyl, Propargyl, Allyl, Alcohols, Ethers, Esters.

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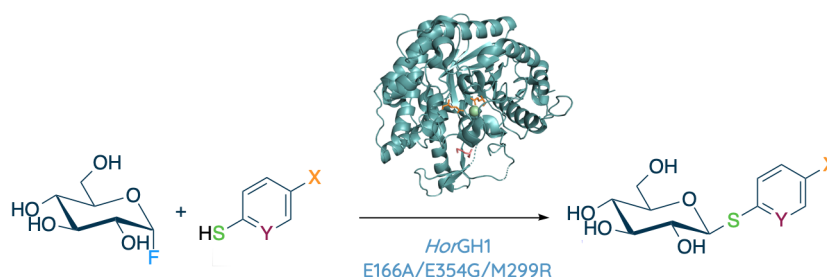


## Novel triple mutant of an extremophilic glycosyl hydrolase enables the rapid synthesis of thioglycosides

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Due to their low susceptibility to hydrolysis, thioglycosides are highly interesting molecules that have been used as enzyme inhibitors and in carbohydrate-based therapeutics. A plethora of chemical synthesis to access thioglycosides have been reported, however, these procedures are complex, offer limited stereochemical control and often require non-sustainable reagents.<sup>[1]</sup> Selective and sustainable biosynthetic methods relying on mutant forms of glycosidases which have had their catalytic residues replaced by neutral ones have been reported. While thiooligosaccharides have been synthesized via these strategies,<sup>[2]</sup> enzymatic syntheses of thioglycoconjugates are scarce. Moreover, attempts to translate these elegant proof-of-concepts to industrial processes are often plagued by the poor resistance of enzymes to the organic solvents that are often required to dissolve thiols. In order to expand the range of reaction conditions suitable for biocatalytic preparation of thioglycosides, we selected a  $\beta$ -glycosyl hydrolase (GH1; EC 3.2.1.21) from *Halothermothrix orenii* (*HorGH1*), an extremophilic enzyme with a high tolerance to extreme temperatures, pHs and organic solvents. We previously engineered this enzyme towards thioglycosidase activity and highlighted the key role of an arginine residue (M299R mutation) in the recognition of thioglycosides.<sup>[3]</sup>



Herein, we present the first example of an extremophilic glycosyl hydrolase engineered towards thioglycosynthase activity with a novel combination of mutations.<sup>[4]</sup> Among the 8 *HorGH1* variants resulting from a combination of the E166A (acid/base residue), the E354G (nucleophilic residue) and the M299R mutation, the triple mutant *HorGH1* M299R/E166A/E354G gave access to a range of high-value thioglycosides with exquisite stereoselectivity and good to excellent conversions (61-93%). Aside from being easy to handle and cofactor independent, this robust catalyst remained active for 48 hours despite the presence of 30 % DMSO. Overall, this work expands the repertoire of mutant glycosidases available for thioglycoside synthesis and provides an innovative, safe, green and profitable synthetic route for the construction of S-glycosidic linkages

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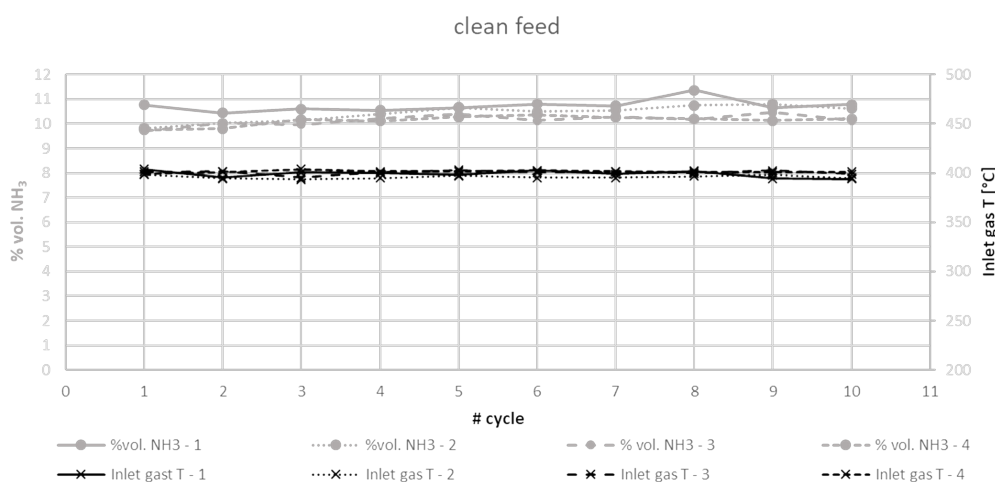
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## Validation of the Iron Catalyst for green ammonia application

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Ammonia is a fundamental feedstock for both agriculture and energy sectors [1]. For this reason, the research of sustainable production of ammonia, replacing fossil fuels with green or zero-carbon, is fundamental for academia, industries and governments. Green ammonia (gNH<sub>3</sub>) production involves the use of green hydrogen in the Haber-Bosh process using renewable electricity [2]. Therefore, due to the nature of the renewable energy sources, it is crucial to precisely characterize the converter functioning when undergoes fluctuations under operating conditions [3]. Moreover, also the behavior of ammonia synthesis catalyst must be verified, since its behavior at non-stationary conditions, is a missing information and no experimental evidences are currently available in the scientific literature. The goal of the present work is the assessment of the catalyst activity under accelerated green NH<sub>3</sub> conditions, characterized by frequent oscillations of the main operating variables including catalyst bed temperature, pressure, space velocity, as well as changes in the inlet gas feed composition. This allows to achieve a deep understanding on how to use the current ammonia synthesis catalyst in green NH<sub>3</sub> process. It is also very important to understand how to prevent abnormal catalyst behavior in these unexplored operating conditions. Indeed, robustness of catalyst over long-lasting applications during operations is not known yet and these information will have an impact on the understanding of operative costs.



Experiments were performed by varying the selected parameters as temperature, pressure and GHSV in cyclic alterations. Preliminary results of fast cycles of temperature in clean conditions reveals that the catalyst is stable. Moreover, the effect of oxygenated compound at the same conditions, was studied. After a first partial deactivation due to the poisoning effect of oxygenates, the ammonia productivity stabilizes, without any further decline in %vol. NH<sub>3</sub>. The loss in catalyst activity in presence of oxygenating compounds is proportional to the O content in the feed; higher the amount, higher the effect on iron catalyst. However, once the catalyst is submitted to clean syngas treatments at 450°C after poisoning, its catalytic activity results always restored. In addition, it was found that the recovery time is dependent on the O ppm content maintained during the “deactivation stage”. Therefore, it can be concluded that cyclic alterations of the temperature combined with different atomic oxygen content in the syngas mixture do not cause a permanent and irreversible deactivation of the catalyst.

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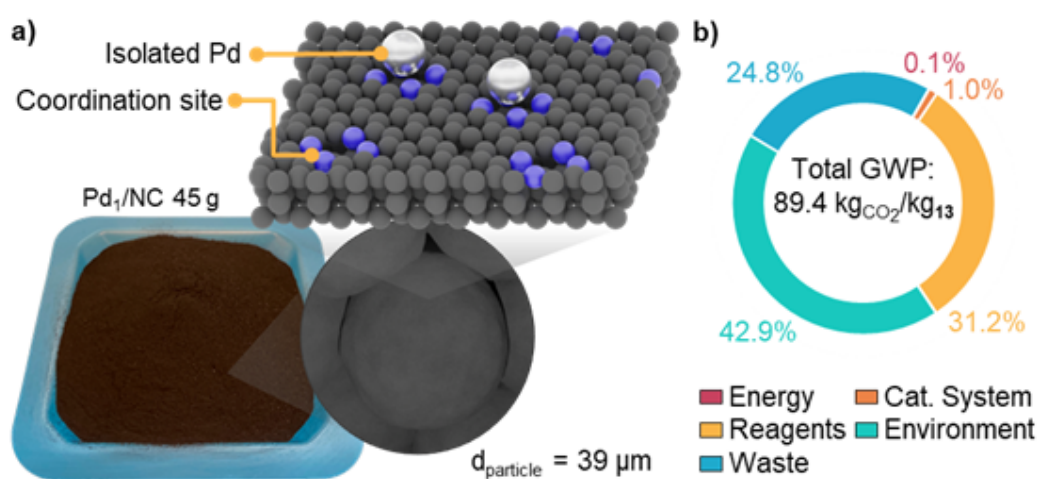
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## Pd single-atom heterogeneous catalyst for sustainable Sonogashira cross-coupling on scale

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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.<sup>[1]</sup> 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.<sup>[2]</sup> 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 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. 1b**).



**Fig. 1 a)** Photography of the Pd<sub>1</sub>/NC and schematic representation of its structure at particle and nanometer scale. Color code: blue, nitrogen; black, carbon; gray, palladium. **b)** Donut chart expressing the component classes' shares of the Sonogashira reaction's total GWP. Pd<sub>1</sub>/NC is assumed to be used for 10 consecutive batch reactions. *Energy*: Electricity and heat; *Cat. System*: Pd<sub>1</sub>/NC, CuI and PPh<sub>3</sub>; *Reagents*: Aniline **11** and Ethin **12**; *Environment*: MeCN and NEt<sub>3</sub>; *Waste*: Incineration of generated waste.

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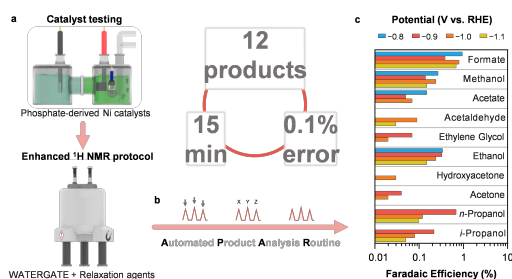
## Liquid product quantification *via* NMR in CO<sub>2</sub> electrocatalytic reduction over phosphate-derived nickel catalysts

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The emergence of Ni-based catalysts that enable the production of diverse multicarbon products necessitates the development of highly sensitive and flexible quantification techniques for accurate catalyst evaluations.<sup>[1]</sup> In response to this need, we have developed robust <sup>1</sup>H NMR protocols that possess the desired characteristics. These protocols include optimized water suppression using an adapted WATERGATE method<sup>[2]</sup> and a significant reduction in NMR experiment time achieved by incorporating a relaxation agent (**Fig. 1a**). By combining these protocols with an Automated Product Analysis Routine (APAR) developed in Python and accessible to all catalysis practitioners (**Fig. 1b**), we have established a comprehensive approach for samples containing up to twelve liquid products. Faradaic efficiencies can be obtained within a time frame of 15 min, including NMR analysis and data processing. This approach exhibits low quantification limits ranging from 0.3-3.2 μM, enabling the determination of Faradaic efficiencies as low as 0.1%.

Employing these powerful tools on phosphate-derived Ni (PD-Ni) catalysts, we have made notable discoveries. Specifically, we have identified four previously unreported eCO<sub>2</sub>RR products, namely acetate, ethylene glycol, hydroxyacetone, and *i*-propanol. Furthermore, we have uncovered performance trends associated with varying potential, electrolyte buffer capability, and bulk pH (**Fig. 1c**). For example, long-chain products exhibit a positive response to lower overpotentials and near-neutral pH. Additionally, we have observed that low bicarbonate concentrations promote the concurrent formation of methane along with other carbon products while favoring oxygenates over hydrocarbons. This work establishes a solid foundation for the advancement of this new class of materials by providing sensitive and flexible tools for quantifying liquid products. Furthermore, these tools can be directly applied to evaluate other catalysts that generate complex liquid mixtures, including copper-based catalysts.



**Fig. 1a** Complex liquid mixtures generated by CO<sub>2</sub> electroreduction over phosphate-derived Ni catalysts can be accurately quantified by <sup>1</sup>H NMR using water suppression *via* WATERGATE and relaxation agents. **b** Raw NMR data is automatically processed by a developed routine (APAR) to provide **c** Faradaic efficiencies for a set of 12 products revealing performance trends. 15 min are required from the start of NMR analysis until Faradaic efficiencies are available with errors below 0.1%.

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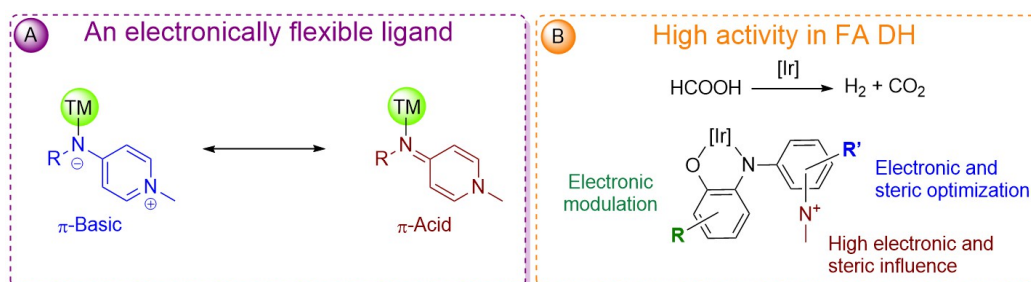
## Investigation and optimization of iridium complexes bearing O-functionalized PYE ligands for efficient formic acid dehydrogenation

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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.<sup>[1-3]</sup>

Our group recently propelled FA dehydrogenation using an iridium complex containing a simple and inexpensive O-functionalized pyridylidene-amine (PYE).<sup>[4]</sup> The PYE moiety features unique donor flexibility (Fig. 1a) known to stabilize transition metals resulting in high catalytic activity, e.g. olefin oxidation.<sup>[5]</sup> Here I will present our efforts to understand electronic and steric influence of the ligand on the catalyst performance. We will demonstrate that structurally similar iridium complexes lacking donor flexibility are inactive in FA dehydrogenation. Moreover, simple ligand modifications led to a library of complexes with varied steric and electronic properties arising from (i) positional PYE isomers, (ii) PYE functionalization, and (iii) the phenolate functionalization (Fig. 1b). We will discuss the catalytic impact of these modifications and disclose some useful correlations.



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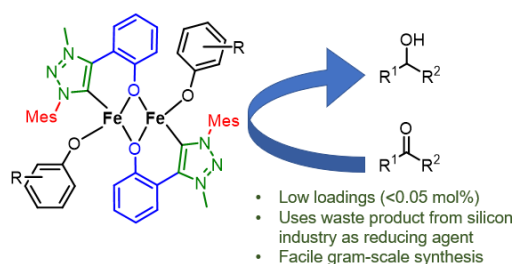
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## Highly Efficient Hydrosilylation of Ketones and Aldehydes Catalysed by an Iron-Mesoionic Carbene Complex

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Reduction of unsaturated bonds is a well-established organic transformation, mostly performed by hydrogenation utilizing high pressure of dihydrogen gas. Alternatively, hydrosilylation can offer safer, selective, catalytic alternatives to these reduction processes by going through a silane-based intermediate.<sup>1</sup> Industrially, hydrosilylation is often performed with platinum complexes, driving up the cost of this transformation as well as posing concerns due to the scarcity and toxicity of this metal.<sup>1</sup> Consequently, iron-based catalysts are often desirable in the place of precious metals as iron is Earth-abundant, biocompatible, and inexpensive.



In this contribution, we report the use of an iron complex bearing mesoionic carbene ligands to efficiently catalyse the hydrosilylation of ketones and aldehydes to alcohols. Mesoionic carbene ligands and their highly sigma donating nature have found versatile use in catalysis.<sup>2</sup> Using remarkably low catalyst loadings (0.05 mol% or less) and polymethylhydrosiloxane- a waste product from the silicon industry- as the reducing agent, this system quantitatively converts a variety of substrates on a gram scale - rivalling the state of the art for iron systems.<sup>3</sup>

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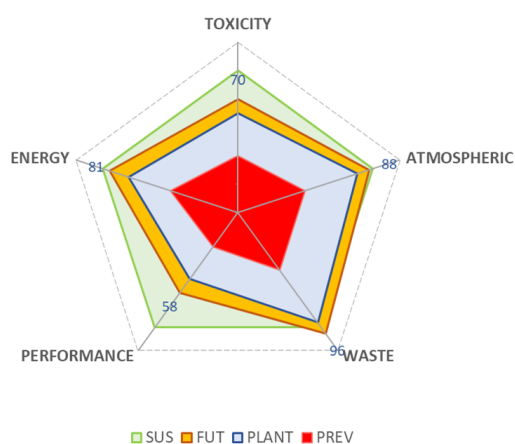


## Sustainability at the center of novel technologies development

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As developer of industrial technologies, Casale SA have the sustainability as a mission to reduce the footprint of plants and optimizing the resource utilization. Indeed, in 1986, when sustainability concepts were still very far from the scientific community, Casale SA was already strongly committed in plants revamping [1], which can be shortly described as a way of giving a second and more efficient life to an existing plant. The devotion towards sustainability has accompanied the research and development of new recent technologies; green and blue ammonia [2] are just two examples where the development of the catalysts is followed by the optimization of the reaction conditions. Within time, also the needed to measure and calculate the sustainability of plants and catalysts has caught the commitment of the company, bringing the consciousness of sustainability to higher level also inside the R&D. Through the use of a dedicated methodology, it is possible to calculate the impact in terms of sustainability footprint of a given process plant or section, still from its development. Sustainability Key performance indicators (SKPIs) value are the outcome of the calculation, but their obtainment passes through different stages. First, is the selection of the dimension that will be taken into account: environmental, economic and social are the most common one and are typically defined as the three pillars of sustainability. Secondly, it is necessary to select the category in which include the SKPIs: energy, catalysts, water consumption, toxicity, wastes etc. Process values (e.g flowrate, energy utilization, chemical composition of a stream etc.) are fundamental to calculate the value of the SKPIs, which are selected among hundreds of possibilities. Finally, the values are added in a comparison scale and are represented in a graphical mode, to make the sustainability level evaluation simpler and faster (Fig. 1).



This methodology allows to set the actual benchmark of an existing technology, identifying all its strengths but most importantly its weaknesses. This calculation allows the optimization of the process already at the stage of R&D, thanks to the continuous iteration of the calculation with the process simulation parameters. As outcome, Casale SA is therefore capable of continuously overcome the sustainability limits that have been evidenced and continuously improving the existing technologies, bringing the sustainability the core of the changes.

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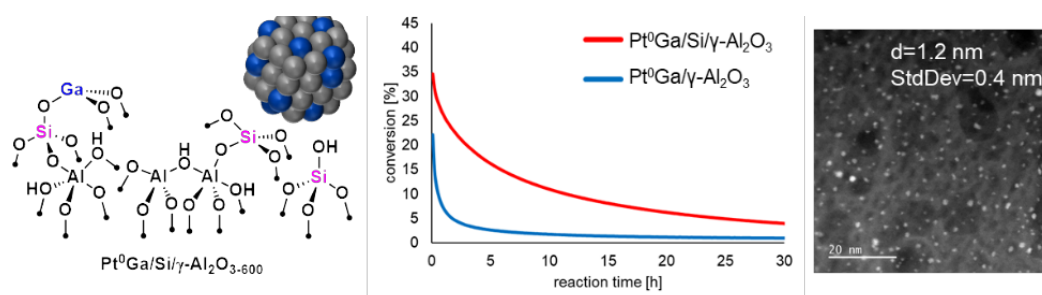
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## Investigation of Alumina-based Pt-Ga Systems for Non-Oxidative Propane Dehydrogenation Reaction

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Large scale exploitation of shale gas stimulates the developments of on-purpose propane dehydrogenation (PDH) technologies.<sup>1-3</sup> Both principal processes, based on Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> (Lummus Catofin process) and Pt-Sn/Al<sub>2</sub>O<sub>3</sub> (UOP Oleflex process), are applied in industry, whereas constant and rapid regeneration are necessary to maintain high productivity. In the case of Pt-based industrial systems, metal promoters and/or additional dopants play important roles to enhance the catalytic properties and stability. In order to understand actual effects of promoters/additives, preparation of tailored systems through SOMC/TMP approach is a powerful methodology since it enables to evaluate surface active structure by using physicochemical and spectroscopic techniques. Silica-based PDH catalysts *via* SOMC/TMP approach have been reported,<sup>4-6</sup> whereas application of SOMC/TMP to alumina-based materials, which are more commonly used in industry, has not been addressed. Herein, we prepared Pt-Ga systems supported on alumina and Si doped alumina *via* SOMC technique, and Si doped Pt-Ga systems showed higher catalytic activity stability to PDH reaction. Considering from STEM-EDX and XAS results, Pt-Ga systems on Si doped alumina included well-dispersed and uniformly alloyed nanoparticles, leading enhanced catalytic properties.



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**Covalent Functionalization of Transition Metal Phosphide Catalysts with Aryl Groups**Y. Shen<sup>1</sup>, V. Wyss<sup>1</sup>, M. F. Delley<sup>1\*</sup><sup>1</sup>Department of Chemistry, University of Basel, St. Johannis-Ring 19, 4056 Basel, Switzerland

Transition metal phosphides have gained considerable interest as catalysts due to their excellent catalytic properties in the hydrogen evolution reaction (HER) and in the hydrotreating process.<sup>[1-3]</sup> Covalent surface functionalization of transition metal phosphides offers a promising avenue to modulate catalytic performance and stability by tuning their electronic and structural properties.<sup>[4-5]</sup> However, covalent surface functionalizations of transition metal phosphides have been barely explored and the relationship between surface ligands and catalytic activity is still not well understood. The development of novel functionalization approaches and fundamental insight into surface ligand effect in catalysis are hence needed to enable rational catalyst design.

Herein, we present a strategy for synthesizing covalently functionalized cobalt phosphide using aryl organohalide and other reagents. The successful surface modification was shown by the characterization of the prepared materials by X-ray photoelectron spectroscopy (XPS). We investigated the catalytic properties of the modified cobalt phosphide in the hydrogenation of an  $\alpha$ ,  $\beta$ -unsaturated aldehydes as a function of surface ligands with varying electronic properties. This result provides insight into the relationship between catalytic selectivity and the surface chemistry of cobalt phosphide. Our research expands the range of functionalization methods for transition metal phosphide materials and shows that it can serve as a practical approach towards tuning their catalytic properties.

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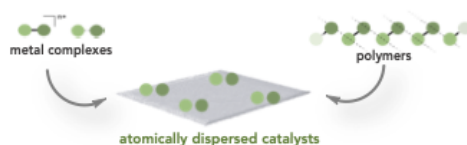
## Defined precursors for atomically dispersed catalysts

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Atomically dispersed single, double, and cluster catalysts are a class of catalyst that merges the separability of heterogeneous catalysts with the single-site nature and tunability of homogeneous catalysts.<sup>[1],[2]</sup> However, the synthesis of atomically dispersed catalysts can be challenging, especially when attempting to control the formation of heterobimetallic or mixed-metal sites.<sup>[3]</sup>

Here, heterogeneous catalyst design and synthesis is linked with techniques from coordination chemistry to develop routes to install dispersed metal atom sites on support materials.



Mixed palladium-platinum complexes were synthesised and a range of techniques investigated to disperse the PdPt sites across support materials. This resulted in mixed clusters and discrete double atom sites. These features were investigated by high resolution STEM. The catalysts were assessed in Csp<sup>2</sup>-O and Csp<sup>2</sup>-F hydrogenolysis, and electrochemical reactions.

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## Flow Synthesis of L-Pipecolic Acid using a Lysine Cyclodeaminase

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L-Pipecolic acid (L-PA) is a non-proteinogenic amino acid widely used as a building block for the synthesis of various bioactive molecules such as anesthetics, immunosuppressants and antibiotics. Typically, L-PA synthesis has been performed using chemical methods that involve harsh conditions and hazardous reagents, mainly due to the difficulty to obtain optically pure L-PA<sup>[1]</sup>. Alternatively, biocatalytic approaches have been employed to synthesize L-PA in a more sustainable manner. Several examples showed the selective deamination and reduction of L-lysine to obtain L-PA by using whole cells<sup>[2,3]</sup> or by a bi-enzymatic cascade in the purified form<sup>[4]</sup>. Herein, we present the application of a purified lysine cyclodeaminase (LCD) for the synthesis of L-PA in only one step and with catalytic amounts of cofactor. Biotransformations in batch reached full conversion at 50 mM L-lysine in 24 hours using 0.5% w/v LCD. To enable the biocatalyst reusability, LCD was immobilized on microbeads with a retained activity of about 25%. To further intensify the synthetic process, the immobilized biocatalyst was integrated into a packed-flow reactor achieving full conversion at 10 mM scale with 90 min of residence time.

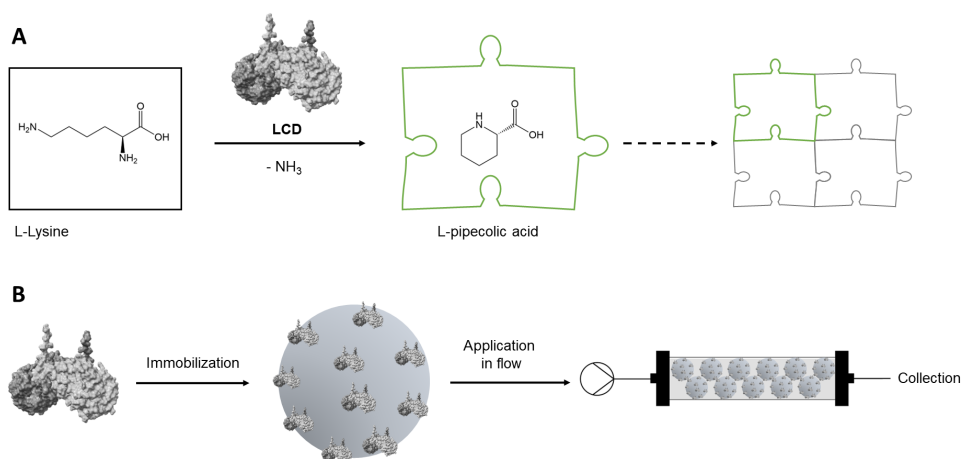


Figure 1. Synthesis of L-pipecolic acid (L-PA) from L-lysine using a Lysine Cyclodeaminase (LCD) (A). The enzyme was immobilized on microbeads for the application in continuous flow to optimize the reusability of the biocatalyst and the obtained yield (B).

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## **A Novel Electrochemical Approach to Sustainable NO<sub>x</sub> Reduction from Diluted Gas Streams**

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NO<sub>x</sub>, as key contributor to air pollution originating from fossil fuel combustion, pose severe implications for global warming and air quality. Their conversion has been implemented in transportation and in many industrial processes, but typically requires stoichiometric amounts of ammonia or urea to proceed. In the current work, we propose to transform these into a useful product, ammonia, using an innovative electrocatalytic process. This offers an environmentally-friendly alternative to the energy-intensive and carbon dioxide-producing Haber-Bosch method for ammonia generation, while contributing to a flue gas waste removal process. Traditional issues with electrochemical NO<sub>x</sub> reduction, primarily the low concentration in gas streams, have been here overcome by employing a membrane-electrode-assembly-electrolyzer, enabling us to perform the reaction directly in a diluted NO<sub>x</sub> gas stream. The applied catalyst demonstrated a promising yield rate of 0.45 mmol/h\*cm<sup>2</sup>, successfully converting up to 83% of NO<sub>x</sub> in the gas stream to ammonia.

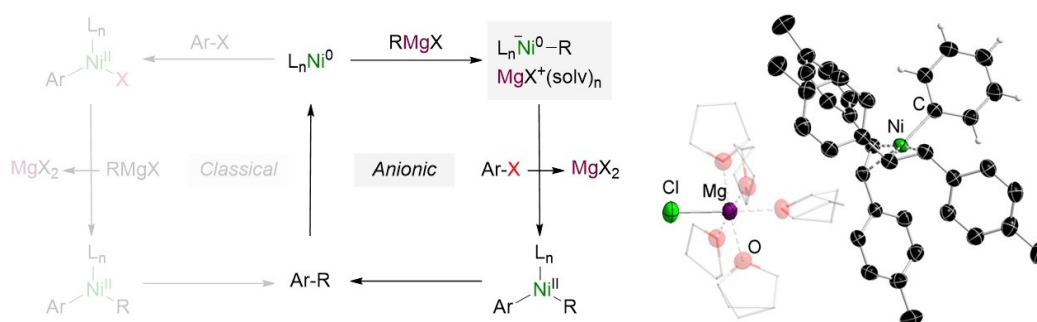
## Mechanistic Investigations of “Ligand-Free” Kumada-Tamao-Corriu Cross-Coupling Reactions

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The Kumada-Tamao-Corriu (KTC) cross-coupling reaction was first reported in 1972 and is a powerful synthetic tool to form C-C bonds from Grignard reagents and C(sp<sup>2</sup>)-halides using nickel catalysts.<sup>1</sup> Only a few years later, in 1979, Wenkert reported the use of aryl ethers as electrophilic coupling partners in KTC reactions.<sup>2</sup> Since then, the reaction has been further developed and efforts have been directed towards mechanistic understanding.<sup>3</sup> The majority of this research however involves the use of bespoke electron-donating ligands, such as NHCs and phosphines.

In this work, we will focus on mechanistic investigations of the KTC reaction using simple Ni(0)-olefin or Ni(II) catalysts, without the use of auxiliary ligands. Under these “ligand-free” conditions, the reaction instead relies on the formation of electron-rich anionic nickelates,<sup>4</sup> several of which have been isolated and characterised by solution and solid-state techniques. Furthermore, evidence that points towards the importance of bimetallic cooperativity in the Ni-catalysed cross-coupling of aryl ethers will be discussed.<sup>5</sup>



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## Electrocatalytic generation of metal hydrides promoted by concerted proton electron transfer mediators for the transformation of small molecules

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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 system to industrial processes. As such, M-H are involved in the electrochemical or thermochemical reduction of CO<sub>2</sub> to formic acid<sup>[1]</sup>, the reversible interconversion of H<sup>+</sup>/H<sub>2</sub><sup>[2]</sup> and in a wide number of hydrogenation reactions<sup>[3]</sup>. In this context, the facile electrocatalytic generation of M-H species presents one of the main limitations for the catalytic transformation of small molecules by utilizing renewable energy sources. Particularly, in the reduction of CO<sub>2</sub> to formic acid one of the main activation pathways involves the insertion of CO<sub>2</sub> into M-H bonds.<sup>[1]</sup> 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 a 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.

We have recently identified a novel strategy for the electrocatalytic generation of M-H species via a proton coupled electron transfer mechanism utilizing bioinspired CPET mediators to promote the formation of a manganese hydride species.<sup>[4]</sup> 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<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) was investigated to understand the product selectivity and a variety of spectroscopic techniques were employed to develop a mechanistic understanding of the reaction.

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## Protection of Methanol Synthesized From Methane via The Formation of Asymmetric Ethers

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Methane is a potent greenhouse gas with a 100 year global warming potential (GWP) 28-34 times greater than that of carbon dioxide.<sup>[1]</sup> Due to there not being a small- to medium-scale process for the conversion of methane to a more transportable value-added product, the extraction of oil at remote and decentralized locations often necessitates the flaring of methane, where it emerges as an associated gas.<sup>[2]</sup> A process which may selectively convert methane into a more easily transportable product is based on both the necessity to address the environmental impact of flaring, as well as the economic loss created by it.<sup>[3]</sup>

An unfavorable conversion-selectivity limit is imposed on the selective partial oxidation of methane to methanol.<sup>[4]</sup> This is caused by the weaker C-H bond of methanol in comparison to methane, causing it to be more readily oxidized under the conditions necessary to activate methane.<sup>[5]</sup> This necessitates a strategy to protect methanol from subsequent oxidation.

A tandem reaction, wherein methane is initially converted into methanol, with a consecutive conversion into a more oxidation resistant asymmetric ether would present such a pathway. Such a process would not only be a viable protection strategy for methanol from subsequent oxidation, but could also present a new pathway toward the synthesis of asymmetric ethers.

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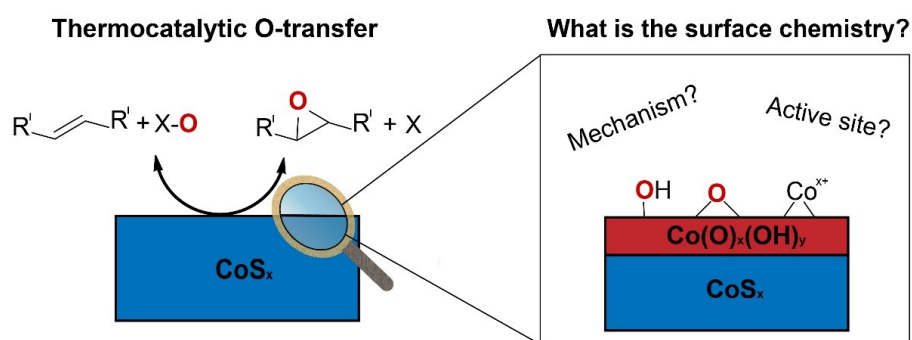
## The Surface Chemistry of Cobalt Sulfide in Thermo-Catalytic Oxygen Transfer Reactivity

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New advances in heterogeneous catalysis have often been achieved by applying known principles from related fields of molecular or enzymatic catalysis.<sup>1</sup> Here we get inspired by well-known principles from electrocatalysis of earth-abundant materials for the discovery of new thermo-catalytic reactions by these materials. Specifically, cobalt sulfide materials ( $\text{CoS}_x$ ) have shown high activity for the electro-catalytic oxygen evolution reaction (OER)<sup>2-3</sup>, and we hypothesized that these materials might also be active catalysts for thermal oxygen transfers.

We show that  $\text{CoS}_x$  can indeed catalyze thermal epoxidations and epoxide deoxygenations and outperform as-synthesized cobalt -oxide, -hydroxide, and -oxyhydroxide. This is curious as the  $\text{CoS}_x$  oxidize during epoxidation reactions, similarly to OER where the sulfides oxidize under the highly oxidative conditions.<sup>2-4</sup> Under the milder epoxide deoxygenations conditions, on the other hand, bare  $\text{CoS}_x$  remains exposed, suggesting an intrinsic oxygen transfer activity of the sulfides. In this poster we discuss parallels between the electro- and thermo-catalytic oxygen transfers by  $\text{CoS}_x$  in terms of surface chemistry, active species, and mechanism based on preliminary spectroscopic and mechanistic investigations. This work provides new insight into more insight into key structure-reactivity relationships on  $\text{CoS}_x$  surfaces and shows the utility of taking inspiration from different fields to make new discoveries in catalysis.



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## Cobalt-Based CO<sub>2</sub> Hydrogenation: Link Between Particle Size, Oxidation State and Product Selectivity

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**Introduction.** The effect of particle size on the reactivity of cobalt nanoparticles in Fischer-Tropsch chemistry is well established, but less is known about the impact on cobalt-based CO<sub>2</sub> hydrogenation.<sup>[1]</sup> To study this, we used Surface Organometallic Chemistry (SOMC) to synthesize well-defined cobalt nanoparticles (Co-NPs) on SiO<sub>2</sub>, varying particle size by adjusting treatment temperature.<sup>[2]</sup> This contribution advances the understanding of particle size effects in cobalt-based CO<sub>2</sub> hydrogenation.

**Experimental/methodology.** An SOMC-based protocol was established to synthesize supported Co-NPs using Co(Alkyl)<sub>2</sub>tmeda as precursor, yielding highly dispersed Co-NPs on SiO<sub>2</sub>. Characterization of the SOMC-derived materials was carried out using microscopy and spectroscopy to assess surface cleanliness and particle formation. The catalytic behavior of the materials was studied in CO<sub>2</sub> hydrogenation and found to change with particle size. This change was investigated using in situ XAS under CO<sub>2</sub> hydrogenation conditions.

**Results and discussion.** The SOMC-based protocol was established and used to synthesize supported Co-NPs with Co(Alkyl)<sub>2</sub>tmeda as molecular precursor, yielding highly dispersed Co-NPs on SiO<sub>2</sub>. Characterization revealed particle formation (Fig. 1a) and complete removal of organic moieties. In CO<sub>2</sub> hydrogenation, the catalytic behaviour was found to change with particle size (Fig. 1c), which was further studied using in situ XAS under CO<sub>2</sub> hydrogenation conditions (Fig. 1b). Results link particle size, oxidation state, and reactivity in cobalt-based CO<sub>2</sub> hydrogenation.

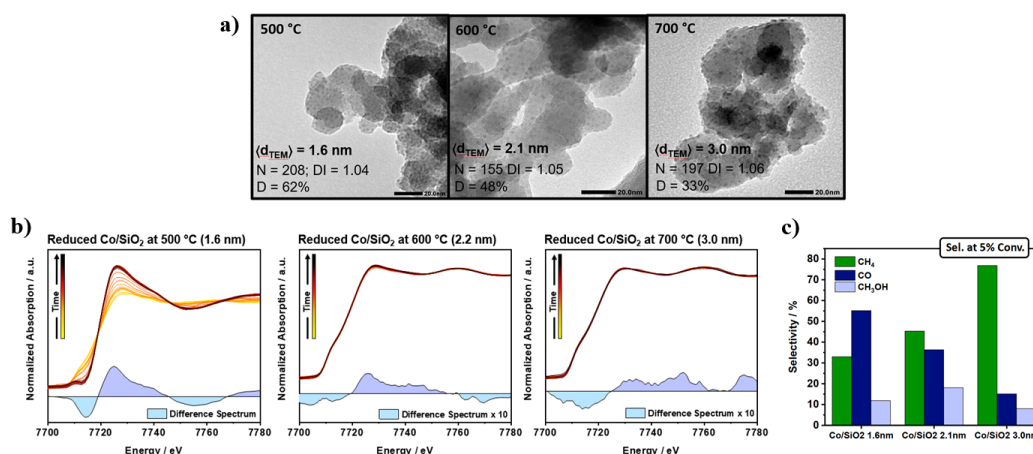


Figure 1: a) Bright-field transmission electron micrographs, b) in situ XANES and c) product selectivities in CO<sub>2</sub> hydrogenation at 5% conversion of SOMC-derived Co/SiO<sub>2</sub> at 1.6 nm, 2.0 nm and 3.0 nm.

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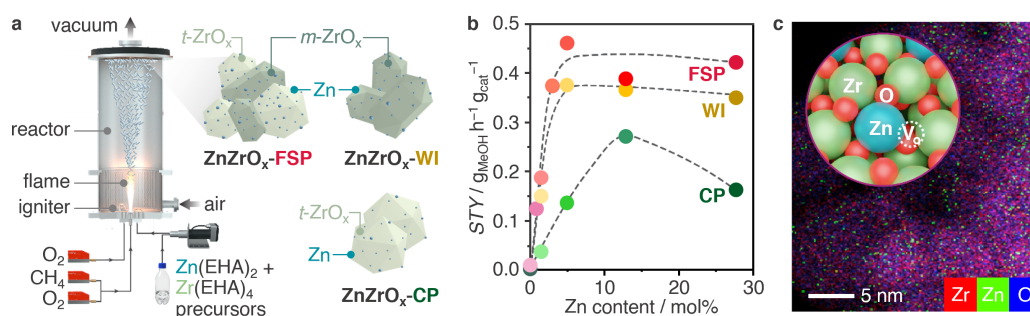
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## Design of selective, stable, and scalable ZnZrO<sub>x</sub> catalysts for sustainable methanol synthesis from CO<sub>2</sub>

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<sup>1</sup>ETH Zurich, <sup>2</sup>Institute of Chemical Research of Catalonia

Mixed zinc-zirconium oxides (ZnZrO<sub>x</sub>) are highly selective and stable catalysts for methanol production via catalytic carbon dioxide hydrogenation, a more sustainable route to produce this vital energy carrier and commodity. However, a lack of in-depth understanding of descriptors governing reactivity and stability of ZnZrO<sub>x</sub> catalysts hinder the performance improvements required for effective industrial implementation. The coprecipitation (CP) method typically employed in preparing ZnZrO<sub>x</sub> systems is also constrained by Zn incorporation into the bulk of ZrO<sub>2</sub>, leading to catalysts with low surface area and suboptimal CO<sub>2</sub> adsorption capacity.<sup>[1]</sup> Here, we conduct a systematic comparison of ZnZrO<sub>x</sub> catalysts synthesized by flame spray pyrolysis (FSP, **Fig. 1a**) and wet impregnation (WI) to coprecipitated analogues, to establish detailed synthesis-structure-performance relationships. FSP and WI systems display up-to 3-fold higher methanol productivities than their CP counterparts (**Fig. 1b**) with stable performance in both pure CO<sub>2</sub> and hybrid CO-CO<sub>2</sub> feeds, by maximizing surface area as well as the formation of atomically dispersed Zn<sup>2+</sup> sites incorporated in lattice positions within the ZrO<sub>2</sub> surface, as revealed by electron microscopy (**Fig. 1c**) and confirmed by operando X-ray absorption spectroscopy (XAS). In situ electron paramagnetic resonance (EPR) spectroscopy demonstrates that the catalyst architectures resulting from FSP and WI markedly foster the generation of oxygen vacancies (V<sub>O</sub>).<sup>[2]</sup> Kinetic and computational modelling show that these vacancies create active ensembles with surrounding Zn and Zr-O atoms (**Fig. 1c** inset) that favor methanol production through the formate pathway while suppressing CO formation.<sup>[2]</sup> This work elucidates the nature of active sites, their correlation to experimental fingerprints and working mechanisms, and provides a scalable synthetic pathway and design guidelines for this cost-effective and earth-abundant catalyst family in sustainable methanol synthesis.



**Fig. 1a** Scheme of the FSP setup for ZnZrO<sub>x</sub> catalysts and the resultant ZrO<sub>2</sub> polymorphs of FSP, WI, and CP catalysts. **b** Methanol space-time yield (STY) during CO<sub>2</sub> hydrogenation over ZnZrO<sub>x</sub> catalysts prepared by different methods with varying Zn content, at 593 K, 5 MPa, H<sub>2</sub>/CO<sub>2</sub> = 4, and GHSV = 24,000 cm<sup>3</sup><sub>STP</sub> h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>. **c** Energy dispersive X-ray (EDX) maps of the used FSP-made ZnZrO<sub>x</sub> catalyst with 5 mol% Zn, with a representative model of the most active m-ZnZrO<sub>x</sub> catalytic ensemble shown in the inset.

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