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Minimalistic Models of Oxotransferases as Catalysts for Site and Enantioselective Oxidation of Strong C-H Bonds

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Nature is a source of inspiration for the development of chemical transformations that stand as unsolved problems in contemporary synthetic chemistry and for creating sustainable alternatives to methods that are becoming increasingly prohibitive. Reaction mechanisms and reagents operating in metalloenzymes can be the starting point guiding the design of small molecule catalysts based in well-defined coordination compounds that retain the main chemical reactivity features of the enzyme while avoiding the size and complexity inherent of the protein scaffold.¹ Coordination complexes that reproduce fundamental aspects of the chemistry of oxygenases can be powerful oxidation catalysts; upon reaction with hydrogen peroxide, high valent metal-oxo species are formed that can engage in C-H oxidation reactions proceeding via short lived radical intermediates. Control of the first and the second coordination sphere of the catalysts can be used to shape the place where the metal-oxo reactive center attacks the C-H bond, and this translates into site and stereoselective C-H oxidation reactions. Recent strategies pursued for the design of biologically inspired catalysts based on the manipulation of electronic and steric properties of the catalysts, their application in the site and enantioselective oxidation of strong C-H bonds and mechanistic investigations will be discussed.²⁻⁴

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Development of a self-optimizing platform for flow-based peptide synthesis**B. Tamás¹, P. L. Willi¹, H. Bürgisser¹, N. Hartrampf^{1*}**¹University of Zurich, Winterthurerstrasse 190, 8057, Zürich, Switzerland

Despite improvements in data analysis techniques, data- and ML-based optimization is not yet widespread in chemistry due to the need to collect data of adequate quality and quantity. Automated fast-flow peptide synthesis (AFPS),¹ with its rapid reaction rates and already integrated analytical tools (in line UV-Vis), would be well suited to explore this toolbox.² Although reaction conditions for solid-phase peptide synthesis (SPPS) were optimized over decades, SPPS is sequence-dependent, and events such as often-observed aggregation can lead to a decreased synthesis outcome. The occurrence of aggregation is thus a major remaining challenge in batch- and flow-SPPS, and the impact of various parameters, such as protecting groups, the sequence itself, and linkers, needs to be better understood. We therefore developed improved data-based methods to exploit the generated in-line UV data in multiple ways to reduce aggregation: We developed a new approach to identify aggregation from UV data, which enables the recovery of lost or low-quality data while simplifying the prediction for future machine learning applications.³ Furthermore, we developed a real-time feedback loop in flow allowing quick intervention upon aggregation detection. These two methods serve as the initial steps in creating a more complex machine learning-based system that aims to eliminate sequence dependence in SPPS.

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Tracking Active Site Formation in Cu-Exchanged Zeolites for Partial CH₄ OxidationA. Brenig^{1,2}, J. W. Fischer³, D. Klose³, G. Jeschke³, J. A. van Bokhoven^{1,2*}, V. L. Sushkevich^{2*}¹Institute for Chemical and Bioengineering, ETH Zurich, ²Laboratory for Catalysis and Sustainable Chemistry, Paul Scherrer Institute, ³Institute for Molecular Physical Science, ETH Zurich

Introduction: Cu-exchanged zeolites are capable of oxidizing CH₄ into CH₃OH via a stoichiometric procedure involving Cu(II)/Cu(I) redox pairs.^[1] Material treatment by an oxidant results in the formation of Cu(II) active sites, which are reduced to Cu(I) during the subsequent reaction with CH₄. A multitude of framework- and composition-dependent Cu(II) centers with varying nuclearity and number of extra-framework O-ligands has been identified, which exhibit different redox/kinetic properties in partial CH₄ oxidation.^[1,2] In spite of the progress in understanding the behavior of these Cu(II) species upon interaction with CH₄, the processes occurring during the material activation by O₂ remain elusive. However, insight into the requirements for active site generation, their formation mechanism, and the nature of involved intermediates is a prerequisite for the selective creation of Cu(II) centers. This is of pivotal importance since a more controllable generation of active species represents a key opportunity for the rational design of materials with precisely tailored features. Therefore, the present study intends to establish an in-depth understanding of the pathways for Cu(II) site generation.

Materials and Methods: Three Cu-zeolites exhibiting different topologies (MOR, MFI, and CHA) but similar Cu-loading and Si/Al ratio have been synthesized by ion exchange. The characteristic geometric constraints and Al distributions of the selected frameworks enable the stabilization of different Cu(II) centers in specific relative fractions.^[1] The temperature effect on the evolution of Cu(II) species as well as the number and nature of active site precursors has been investigated by in situ electron paramagnetic resonance (EPR), ultraviolet-visible (UV-Vis), and X-ray absorption (XAS) spectroscopy via O₂ temperature-programmed oxidation (O₂-TPO). Operando EPR and UV-Vis spectra recorded during isothermal oxidative treatment at varying temperatures permit evaluating the formation rates of individual Cu(II) centers and their apparent activation energies. The spectroscopically determined site-specific kinetic properties are further correlated to the ones of the bulk material by simultaneously measuring the O₂ consumption. The redox behavior of the bulk is further established by determining the Cu(I) oxidation rates measured by in situ XAS during isothermal sample activation.

Results and Discussion: In situ XAS, EPR, and UV-Vis spectroscopy during O₂-TPO reveal that Cu-zeolite oxidation is an extremely facile process, which already occurs at temperatures as low as 183 K. Moreover, they indicate that material activation proceeds via at least one intermediate, which rapidly forms at low temperatures and is gradually transformed into the final Cu(II) state upon increasing the temperature. This is further highlighted by in situ XAS during isothermal treatment in O₂, which suggests the presence of two kinetic regimes corresponding to precursor formation and its subsequent transformation. A near temperature-independence of the intermediate's formation rate is reflected by the similar time spans required to reach 50% of total O₂ conversion during isothermal material activation experiments at different reaction temperatures by operando EPR and UV-Vis.

Significance: The present work aims at bridging the knowledge gap between the extensive amount of research dedicated to the reduction of Cu(II) active species by CH₄ and their preceding creation during oxidative treatment. Additionally, this proves beneficial for the study of other transition metal-exchanged zeolites (e.g., Fe) in different redox reactions such as the selective catalytic reduction of NO_x by NH₃ and benzene hydroxylation.

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CO₂ electroreduction to long-chain hydrocarbons on cobalt catalystsP. Preikschas¹, J. Zhang², R. R. Seemakurthi³, Z. Lian³, A. J. Martín¹, S. Xi⁴, N. López³, B. Yeo², J. Pérez-Ramírez^{1*}¹ETH Zurich, ²NUS, ³ICIQ, ⁴A*STAR

Renewable-powered electrocatalytic CO₂ conversion to long-chain hydrocarbons represents a sustainable path to chemicals and fuels. However, recently discovered systems still show insufficient efficiencies and, more importantly, lack C-C coupling capabilities required to yield longer, more valuable carbon chains.^[1-3] Herein, we present catalysts derived from oxygen-containing cobalt compounds for the selective conversion of CO₂ to C₁-C₇ hydrocarbons with the highest C-C coupling ability in electrocatalysis. Among different catalysts investigated, a Co₃O₄-derived catalyst demonstrated the highest partial current densities to C₂₊ hydrocarbons (**Fig. 1a**). The products formed follow closely an Anderson-Schulz-Flory (ASF) distribution with a chain growth probability (α) of 0.54 (**Fig. 1c**),^[4] surpassing nickel-based and other known electrocatalysts (0.2-0.4).^[1-3] Furthermore, this result sets electrocatalytic hydrocarbon formation within reach of thermocatalytic Fischer-Tropsch synthesis, with α values usually obtained in the range of 0.6 to 0.9.

A detailed analysis by *in situ* X-ray absorption and *in situ* Raman spectroscopies evidenced the partial reduction of Co₃O₄ under reaction conditions (**Fig. 1b**). Metallic and oxidic phases coexist during reaction in nearly equimolar amounts (**Fig. 1d**). Guided by experiments in hybrid CO/CO₂ feeds, density functional theory simulations revealed the formation of Co-Co₃O₄ interfaces as pivotal for the enhanced chain growth (**Fig. 1e**) and CO as the primary coupling component. All considered coupling mechanisms are significantly favored on interfacial sites compared to metallic cobalt. In the case of the most preferred mechanism (CO*+CH₂*), the coupling barrier is lowered by almost 0.97 eV (**Fig. 1f**). To prevent overreduction that causes the deactivation of the interfacial sites, intermittent reoxidation cycles were applied to regain the catalyst's ability to form hydrocarbons, which further highlighted the importance of a partially oxidized cobalt phase. Overall, our study opens new frontiers in the one-step conversion of CO₂ into hydrocarbons of significant chain lengths and suggests the exploration of metal-metal oxide interfaces as a promising strategy for further progress.

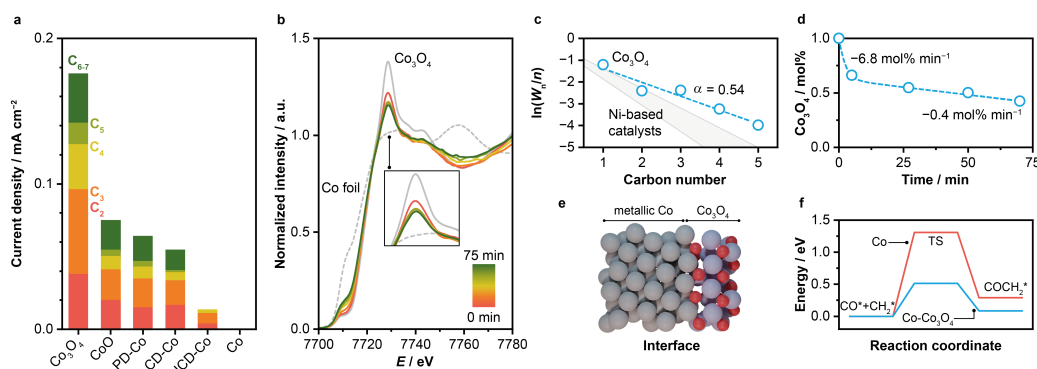


Fig. 1 **a** Partial current densities of C₂₊ hydrocarbons. PD-Co, CD-Co, and HCD-Co abbreviate cobalt phosphate, carbonate, and bicarbonate, respectively. **b** *In situ* Co K-edge XANES spectra of the Co-Co₃O₄ catalyst in comparison with Co and Co₃O₄. **c** ASF distribution of Co₃O₄-derived catalyst (blue) in comparison with range of Ni-based catalysts (gray). **d** Temporal evolution of Co₃O₄ fraction obtained from XAS. **e** Schematic representation of the Co-Co₃O₄ interface. **f** Energy profile of preferred C-C coupling mechanism.

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Decoding the Promotional Effect of Iron in Bimetallic Pt-Fe-Nanoparticles for the Low Temperature Reverse Water-Gas Shift Reaction

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The mitigation of anthropogenic CO₂ emissions and the concomitant development of a circular carbon-economy in recent years has seen the conversion of CO₂ to Syngas as a potential alternative for producing value-added chemicals.^[1] Pt based catalysts have previously been shown to effectively promote the reverse water-gas shift reaction (RWGS), especially when combined with promoter elements, but their active state is poorly understood.^[2] Various mechanisms for the activation of CO₂ and the formation of CO have been discussed, and a large research effort has been put towards the elucidation of the mechanistic pathways involved in RWGS.^[3]

In this work we show that the intimate incorporation of an iron-promoter into Pt-based nanoparticles supported on metal oxides can increase their activity and selectivity for the low temperature reverse water-gas shift (LT-RWGS) substantially and drastically outperform unpromoted Pt-based materials. Specifically, the study explores the promotional effect of iron in Pt-Fe bimetallic systems supported on silica (Pt_xFe_y@SiO₂) prepared by surface organometallic chemistry (SOMC).^[4,5] In-situ diffuse reflectance FT-IR spectroscopy (DRIFTS) and X-ray absorption spectroscopy (XAS) indicate a dynamic process at the catalyst surface caused by changes in reaction gas composition, revealing distinct reaction pathways for the monometallic Pt@SiO₂ and bimetallic Pt_xFe_y@SiO₂ systems and highlighting the enhanced catalytic performance in the latter.

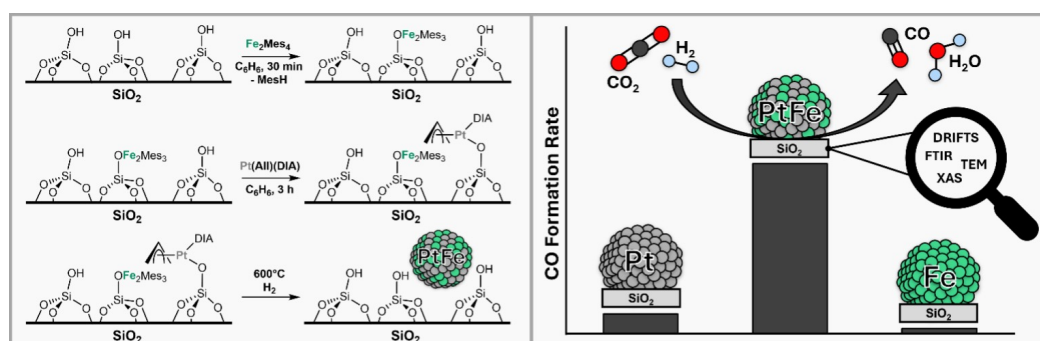


Figure 1. [Left] Synthetic method for the preparation of PtFe@SiO₂ systems by surface organometallic chemistry (SOMC). [Right] CO formation rate during LT-RWGS compared between monometallic Pt@SiO₂ and Fe@SiO₂ and bimetallic PtFe@SiO₂.

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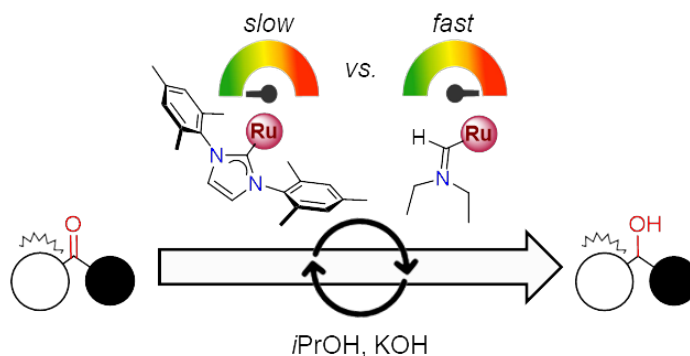
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Accelerating transfer hydrogenation of sterically hindered ketones with a novel mono-substituted aminocarbene (MAC) ruthenium complex

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Metal-assisted transfer hydrogenation (TH) is an attractive alternative to direct hydrogenation of organic molecules, since explosive pressurized H₂ gas is replaced by inexpensive and non-hazardous organic hydrogen surrogates.^[1] In this field, ruthenium-NHC complexes are among the most efficient catalysts.^[2] However, in most cases large steric hindrance around the unsaturated functionality of the substrate slows down or even completely blocks the hydrogen transfer reaction.^[3] Here, we used a mono-substituted aminocarbene (MAC)^[4] to synthesize a ruthenium complex that is electronically similar to a Ru-NHC complex but with a much reduced buried volume around the metal center. These features increased the initial activity of the ruthenium center in the transfer hydrogenation of ketones with respect to the Ru-IMes analogue, especially for sterically hindered substrates. Moreover, we will discuss a model that quantitatively correlates the steric properties of the substrate with the catalytic acceleration observed upon replacing the IMes ligand with the MAC ligand.



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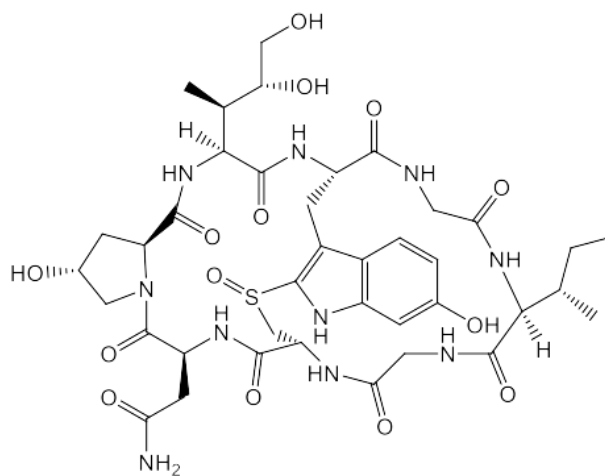
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First Industrial (Total) Synthesis of Amanitin Derivatives

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A short presentation about the implementation of the first industrial synthesis of Amanitin derivatives [1] entering phase I & II clinical studies. The unique properties and structural challenges of the molecule will be presented. A detailed synthetic analysis of the approach and chemistry will be presented. This project was a successful collaboration with our customer [2] as well as a contribution of different sites within our organization.



The use of the compound(s) as a payload in Antibody Drug Conjugates (ADC) will also be presents. A concise outlook to the perspective new linker generation at CARBOGEN AMCIS related to this class of compounds will also be discussed.

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Operando XAS-XRD Reveals Structural Dynamics in CoPt Nanoparticles under Dry Reforming of Methane Conditions

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Gaining insight into how the geometric and electronic structure of (mono)metallic nanoparticles is modified through the addition of a second metal (bimetallic nanoparticles) and how such structural changes affect in turn their catalytic properties^[1] is crucial for the rational advancement of catalysts. Further, as the structure of a catalyst is often dynamic^[2] ex-situ characterization methods may be insufficient to describe the active phases of a catalyst. Therefore, operando studies are key to correlate a catalyst's structure to its performance while relying at the same time on well-defined model systems.

The dry reforming of methane (DRM) is a reaction that converts CH₄ and CO₂ into a synthesis gas at 600-1000 °C and is typically catalyzed by transition metals such as Ni, Co, or Pt. In this study, we investigate SiO₂-supported, bimetallic CoPt nanoparticles and their monometallic counterparts (CoPt/SiO₂, Co/SiO₂, and Pt/SiO₂) for the DRM. Prior to the catalytic DRM tests, all catalysts were activated in-situ in a H₂/N₂ mixture (1-2 h). The bimetallic CoPt/SiO₂ catalyst shows superior activity and stability under DRM conditions at 800 °C in comparison to its monometallic counterparts (Fig. 1a).

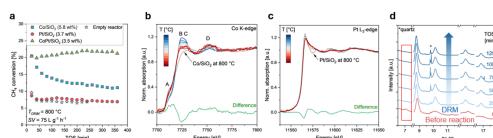


Figure 1: a) CH₄ conversion over Co/SiO₂, Pt/SiO₂, and CoPt/SiO₂ under DRM conditions (75 L g⁻¹ h⁻¹, 800 °C). b)-c) In-situ Co K-edge and Pt L₃-edge X-ray absorption near-edge structures (XANES) during H₂ activation of CoPt/SiO₂ from 50-800 °C in comparison to monometallic Co/SiO₂ and Pt/SiO₂. d) XRD during DRM (800 °C), λ = 0.338591 Å.

To elucidate the structure of the active phase in CoPt/SiO₂ under DRM conditions, and to probe structural dynamics, we conducted operando experiments using combined synchrotron X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) experiments. XAS analysis during in-situ H₂ activation of CoPt/SiO₂ at 800 °C showed differences in its features at the Co K-edge and Pt L₃-edge when compared to Co/SiO₂ or Pt/SiO₂, which could be attributed to a charge transfer between Co and Pt and an orbital hybridization in the CoPt alloy (Fig. 1b-c).^[3] Rietveld refinement of the XRD data after in-situ activation at 800 °C indicates the formation of two types of CoPt alloys: an ordered (intermetallic) CoPt (52%) and a random CoPt alloy (48%). Interestingly, upon switching to DRM conditions at 800 °C, XRD analysis revealed an instantaneous transformation of the intermetallic phase into a random alloy. This bulk transformation did not change the electronic structure/oxidation state of Co as evidenced by the Co K-edge XANES that remained invariant prior to and during DRM. In contrast, under DRM conditions, Co/SiO₂ underwent a partial oxidation showcasing the stabilization of the metallic state of Co when alloyed with Pt. This stabilization, combined with changes in the electronic/local structure and site isolation that very likely suppresses coking on Pt, contribute to the superior activity of CoPt/SiO₂ compared to Co/SiO₂ and Pt/SiO₂. Finally, we observed a phase transition from a random to intermetallic alloy during the cooling down to room temperature of the reacted catalyst, underscoring the significance of operando characterization in capturing dynamic changes and identifying the catalytically active phase.

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Engineering a Dual-Functionalized PolyHIPE Resin for Photobiocatalytic Flow Chemistry

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Photobiocatalysis is a relatively new field that combines the principles of photocatalysis and biocatalysis to drive chemical reactions using light and biological catalysts, such as enzymes. The vast majority recent photobiocatalytic systems work by using homogeneous photocatalysts and free enzymes in batch conditions [1]. One common application of this approach utilizes the photocatalyst for the in-situ production of reactive oxygen species (ROS) that can subsequently be used by enzymes such as halogenases to access the corresponding halogenated substrates [2,3]. In the realm of sustainable chemistry, the integration of photocatalysis with biocatalysis in a single material system represents a big step towards environmentally friendly chemical processes. Our recent work [4], describes the engineering of a novel polymeric high internal phase emulsion (polyHIPE) resin that houses both a photocatalyst and an enzyme, facilitating efficient photobiocatalytic reactions in a flow chemistry setup. The research involved a systematic exploration of different organic photosensitizers (orgPS), based on 4,4-Difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) and benzo[*c*]-1,2,5-thiadiazole (BTZ) scaffolds. Moreover, their ability to generate hydrogen peroxide (H₂O₂), and their compatibility with chloroperoxidase from *Curvularia inaequalis* (CiVCPO) were probed. Subsequently, the best performing orgPS was incorporated in the polyHIPE resin matrix which was further modified to be equipped with a carboxylic acid handle that enabled the covalent immobilization of CiVCPO. Our research addresses several challenges in the field, including the effective immobilization of photocatalysts and enzymes, maintaining their respective activity, and ensuring adequate light penetration. In addition, this approach enables the efficient bromination of aromatic substrates, including the natural flavonol Rutin, under mild conditions (air, blue light, room temperature) and continuous flow. Finally, this methodology not only demonstrates technical feasibility but also marks a significant advancement in environmental sustainability and potential industrial applicability which is enabled by flow processes.

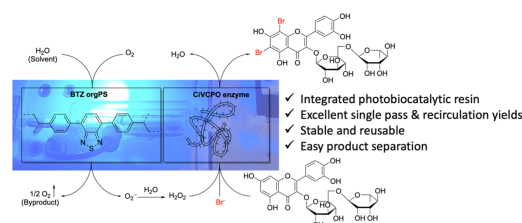


Figure 1. Photobiocatalytic mechanism leading to the bromination of starting material Rutin under flow conditions

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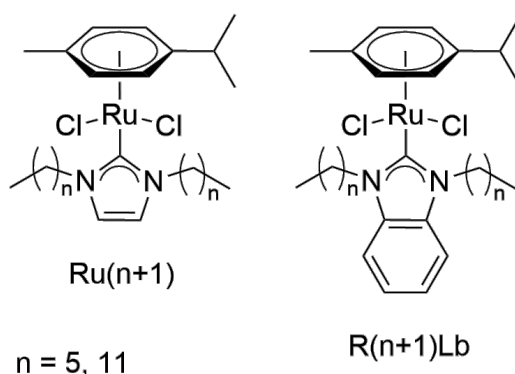
Ruthenium-NHC complexes as precursors for highly active lignin hydrogenolysis catalysts

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Core-shell nanoparticles (CSNPs) show excellent stability and selectivity for catalysis due to the presence of a protective shell encapsulating the active nanoparticle surface.¹ The increased stability and selectivity have proven beneficial for biomass conversion to value-added chemicals² – an important topic for a more sustainable future. However, current strategies for the synthesis of CSNPs are not generalised for metal core-carbon shell structured particles. Herein, we propose a strategy for the synthesis of CSNPs by employing *N*-heterocyclic carbene (NHC) ligands, which have been widely used as nanoparticle stabilisers,³ where pyrolysis of the coated nanoparticles may generate CSNPs. Studying the relationships between CSNP physical properties and chemical properties with the nature of the organometallic precursor used allows us to identify key features that may indicate greater stability and higher activity in C-O bond hydrogenolysis.

A series of ruthenium complexes featuring NHC ligands were prepared and used to generate NPs. NHC ligands featuring alkyl side chains (Fig. 1) were chosen to emulate the carbon chains of many other surfactants previously used to generate stabilised NPs.⁴ After sequential reduction of the organometallic precursors, supporting step, and pyrolysis, the low-Ru-loading catalysts were tested for C-O bond hydrogenolysis of diphenyl ether under mild conditions (140 °C and 15 bar H₂). Catalysts derived from one of the precursor complexes, Ru12b, supported on carbon black and MCM-41-structured aluminosilicate were determined to be highly active for this transformation (turnover number > 2500 and 1500, respectively) and selective for monocyclic products (87% and 70%, respectively). The catalysts were characterised by scanning transmission electron microscopy (STEM) to reveal ultra-small Ru nanoparticles (< 5 nm).



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Multi-origin and topology-dependent selectivity in the methanol-to-olefins process from transient operando DRIFTS-GC

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The methanol-to-olefins (MTO) process has gained attention over the years as sustainable synthetic route due to the central role of methanol as direct link between renewable feedstocks, as CO₂, and commodity chemicals and fuels. We report the evidence of a strong deuterium isotope effect when applying CH₃OH/CD₃OD switch experiments on ZSM-5 (MFI) zeolite indicating a multi-origin olefin selectivity. The products distribution in the CH₃OH/CD₃OD switch experiments demonstrated a dependence of specific classes of products on the presence or absence of the C-D bond. In the case of ZSM-5 (Figure 1) in the first CH₃OH phase of 5 cycles, the concentrations of all products increased determining a curve that was expected to grow over the subsequent cycles. In the subsequent CD₃OD pulsing phase, ethene (C₂⁼) concentrations were instead lower than the expected behavior drawn following the initial course of the CH₃OH phase. Propane (C₃⁻) concentrations did not undergo an abrupt change, although the concentrations seemed to point under the predicting curve. The behavior of C₃₊ hydrocarbons concentrations opposed that of C₂⁼ and C₃⁻, and the values increased in the CD₃OD phase. This implies an interconnection between the two subclasses of products. The concentrations returned to the expected ones in the subsequent CH₃OH switches. Therefore, the formation of the hydrocarbon pool over the cycles continued in the CD₃OD phase, but CD₃OD impacted products selectivity differently from CH₃OH. Looking at the catalyst surface, the signals of polymethylbenzenium ions and alkylated-cyclopentenyl cations observed by DRIFTS redshifted and intensified in the CD₃OD phase, thus confirming deuteration and increased concentrations of hydrocarbons in the zeolite. This behavior is possibly linked to the different reactivity of the adsorbed species upon deuteration. The same methodology applied onto other zeolite topology provide other kind of dependencies revealing a multi-origin and topology-dependent olefin selectivity.

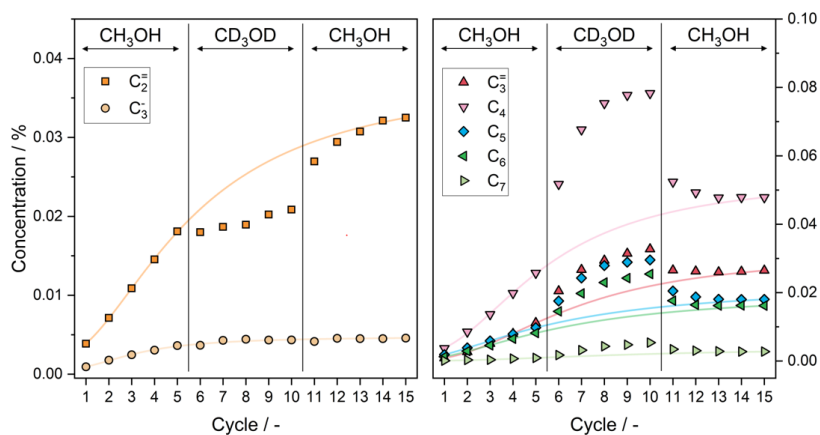


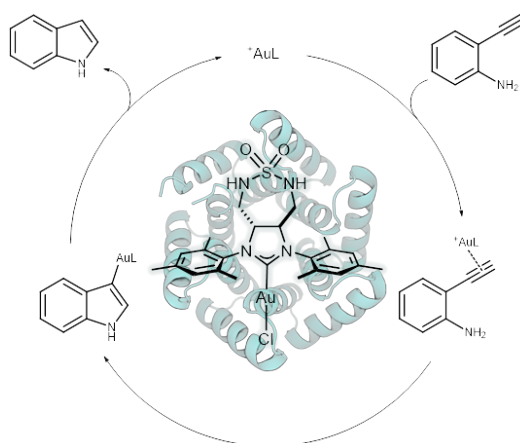
Figure 1. Concentration of products during the CH₃OH/CD₃OD switch experiment in ZSM- 5: (orange square) ethene, C₂⁼; (pale orange circle) propane, C₃⁻; (red triangle up) propene, C₃⁼; (pale red triangle down) C₄ fraction; (blue diamond) C₅ fraction; (green triangle left) C₆ fraction; (pale green triangle right) C₇ fraction.

Design and Characterisation of a de novo Gold Artificial MetalloenzymeE. Morris¹, J. Uhrhan¹, B. Lozhkin¹, S. Basler¹, I. Kalvet², T. R. Ward^{1*}, D. Baker^{2*}

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The ability to design and produce enzymes from scratch would endow Chemists with a vastly superior biocatalytic toolbox than is currently accessible. Such an ability would allow for the creation of an 'ideal' enzyme for a given transformation, which could be expressed in high yield and with high (thermal) stability. The field of enzyme design has, however, lagged behind that of protein design in recent years, owing principally to the more significant computational challenges involved, as well as the many unknowns we still face with respect to how an enzyme's structure relates to its function [1].

Combining designed protein scaffolds with transition metal catalysts to create *de novo* artificial metalloenzymes adds another rlayer of complexity but with it, a host of advantages. Herein, we showcase a thermostable *de novo* tandem repeat hydroaminase [2], designed to bind to an NHC-Au cofactor. We demonstrate strong binding affinity between the cofactor and the protein using crystallography and other biophysical methods. Furthermore, several rounds of directed evolution improved the enzyme's activity for the desired hydroamination reaction, resulting in significantly higher turnover numbers (TONs) and observed rates compared to the free cofactor.



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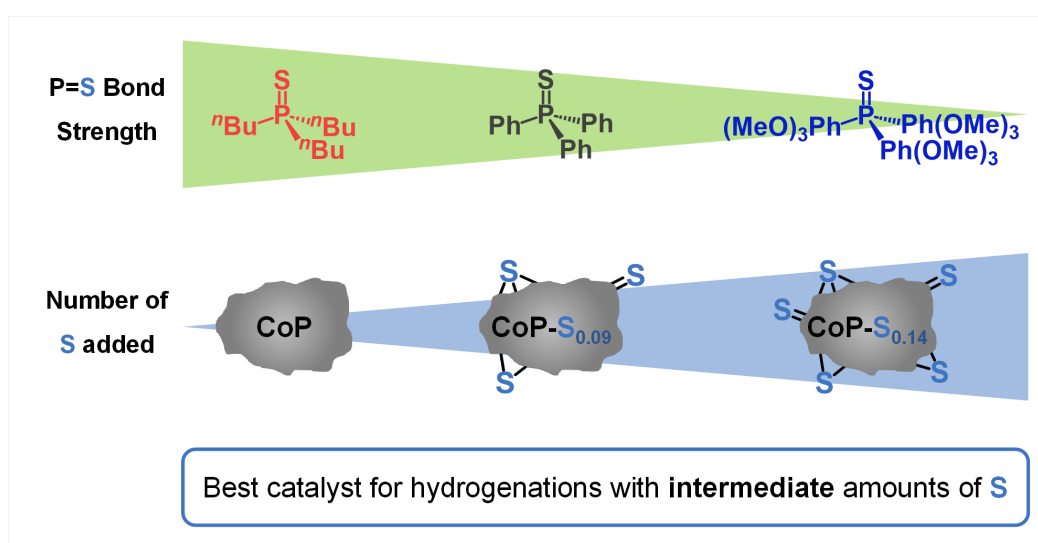
Controlled Sulfur-Doping of Transition Metal Phosphides Enhances their Catalytic Properties

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Transition metal phosphides have shown high catalytic ability for hydrotreating reactions and water splitting.¹⁻² Further improvement of the catalytic performance of phosphides in these applications can be obtained when a small amount of sulfur is incorporated into the material.³⁻⁵ However, the reason behind this observed sulfur effect is unclear due to the structural complexity of sulfur-modified metal phosphides prepared by conventional doping or mixing methods. For instance, it is challenging to distinguish between effects on catalysis from sulfur inside or at the surface of the metal phosphide.⁴⁻⁵

We have recently developed a more controlled method to dope transition metal phosphides with sulfur where sulfur is exclusively introduced at the surface.⁶ We used different phosphine sulfide reagents to transfer sulfur to the surface of cobalt phosphide (CoP). Variation of the P=S bond strength of the phosphine sulfides added different amounts of sulfur and showed that there is a distribution of different sulfur binding sites on CoP binding with strengths between 69 and 84 kcal/mol. We then tested a series of CoP-S_x materials having different number and types of sulfur at the surface for the catalytic hydrogenation of α,β -unsaturated aldehydes. This revealed a dual role of sulfur in catalysis as both promoter and poison. CoP with an intermediate amount of sulfur at the surface – neither too much nor too little – proved to balance these effects the best. Our approach gives fundamental information on the surface chemistry of metal phosphides and opens new avenues for catalyst design.



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Insight into structure-activity relationships of SiO₂-supported bimetallic Pd-Fe catalysts for CO₂ hydrogenation to methanol

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The direct hydrogenation of CO₂ to methanol is a sustainable alternative to the current industrial production of methanol from synthesis gas (CO and H₂). The industrial catalyst for methanol synthesis from synthesis gas (Cu/Zn/Al₂O₃) shows rapid deactivation, both under CO and CO₂ hydrogenation conditions, due to steam-induced sintering of the Cu and ZnO phases. [1] Pd-based catalysts are currently being investigated as an alternative to Cu-based CO₂ hydrogenation catalysts due to Pd's higher sintering resistance.[2] Although supported Pd nanoparticles show modest methanol productivity, incorporating a second metal such as Ga or In has shown to considerably enhance methanol yield.[3] However, other lower-cost metal promoters such as Fe remain unexplored for this reaction. This study investigates the effect of Fe addition to Pd-based catalysts on the catalyst's structure and catalytic performance. Three catalysts containing the same quantity of palladium, but varying Pd:Fe ratios (i.e. 2, 1 and 0.5), were synthesized using charge enhanced dry impregnation (CEDI). CEDI synthesis, followed by activation, yielded small nanoparticles (NPs) with an average size of ca. 2 nm that are highly dispersed on the SiO₂ support, as observed by TEM.

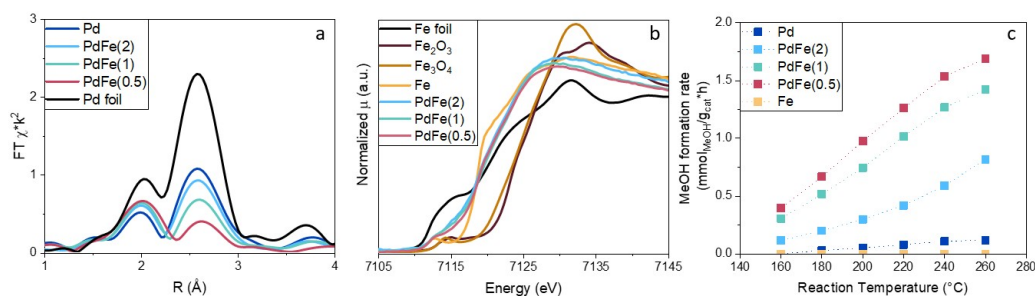


Figure 1: a) Pd K-edge EXAFS; b) Fe K-edge XANES; c) Methanol formation rate for Pd/SiO₂, PdFe(2)/SiO₂, PdFe(1)/SiO₂, PdFe(0.5)/SiO₂, and Fe/SiO₂ together with Pd and Fe references.

Fig 1a shows the Fourier transform of Pd K-edge EXAFS data of the activated catalysts. The analysis of the Pd K-edge EXAFS data revealed the formation of Pd-Fe alloys in all of the three bimetallic catalysts, as evidenced by the presence of Pd-Pd and Pd-Fe coordination shells. As the Fe content increased, the interatomic distance between Pd-Pd and Pd-Fe and the coordination number (N) N_{Pd-Pd} decreased, while N_{Pd-Fe} increased, in line with the formation of Fe-richer alloys with increasing Fe content. However, Fe K-edge XANES (fig. 1b) showed the presence of both alloyed Fe (with Pd) and FeO_x species in a ca. 50:50 ratio (independent of the Fe content) in all of the Fe-containing catalysts. The catalytic tests (fig. 1c) revealed that Pd/SiO₂ and Fe/SiO₂ are largely inactive, whereas the bimetallic catalysts showed an increasing methanol formation rate with increasing Fe content. In particular, PdFe(0.5)/SiO₂ was 18 times more active than monometallic Pd/SiO₂. Hence, this study suggests that the high catalytic activity of Pd-Fe based catalysts is associated with the presence of both alloyed Pd-Fe (in the form of NPs) and FeO_x species.

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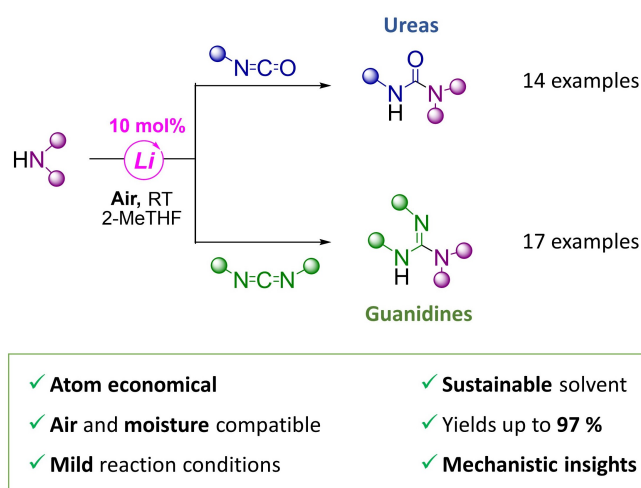
Air Compatible Alkali Metal Amide Catalysed Hydroamination of Heterocumulenes

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While the high reactivity of alkali metal amides has led to their widespread utilization in synthetic chemistry, it also imposes some major drawbacks: reactions have to be carried out under strictly inert conditions, employing toxic organic solvents.[1] Breaking down the barrier between organometallic and aerobic chemistry, our group has recently reported the stoichiometric applications of lithium amides for ester amidation[2] and hydroamination of styrenes[3] under air, at room temperature using biorenewable 2-methyl THF as solvent.

Upgrading stoichiometric reactions to catalytic regimes, we herein present the first lithium amide catalysed hydroamination of isocyanates and carbodiimides being compatible with air and moisture. A broad range of ureas and guanidines were synthesized using an operationally simple one pot approach, employing n-BuLi as a pre-catalyst. In an effort to understand the catalytic cycle, key intermediates were isolated and characterized in solution and solid state. The methodology was successfully expanded to sodium and potassium amides, thus unveiling the potential of alkali metal amides in aerobic chemistry.



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Mechanochemically derived iron atoms on defective boron nitride for stable propylene production

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¹ETH Zurich, ²EMPA, ³Leibniz-Institut für Katalyse

Single-atom catalysts (SACs), possessing a uniform metal site structure, are a promising class of materials for selective oxidations of hydrocarbons.^[1] However, their design for targeted applications requires careful choice of metal-host combinations and suitable synthetic techniques.^[2] Here, we report the iron atoms stabilized on defective hexagonal boron nitride (h-BN) *via* mechanochemical activation in a ball mill as the first catalyst in N₂O-mediated oxidative dehydrogenation of propane (N₂O-ODHP) that combines high propylene selectivity (up to 95%) and remarkable stability. This one-pot, solvent-free synthesis allows simultaneous carrier exfoliation and surface defect generation, creating anchoring sites for catalytically active iron atoms. The incorporation of a small metal quantity (0.5 wt%) predominantly generates atomically dispersed Fe²⁺ species, as confirmed by combining advanced microscopy and electron paramagnetic, UV-vis and X-ray photoelectron spectroscopy analyses. Single-atom nature of iron is found to favor selective propylene formation, while metal nanoparticles yield large quantities of CO_x and cracking byproducts. The lack of acidic sites, hindering coke formation, and defect-stabilized Fe atoms, preventing metal sintering, ensured stable operation over 18 h on stream. These results uncover ball milling as facile and efficient method for preparation of h-BN-supported transition metal SACs, and reaffirm N₂O-ODHP as a promising propylene production technology.

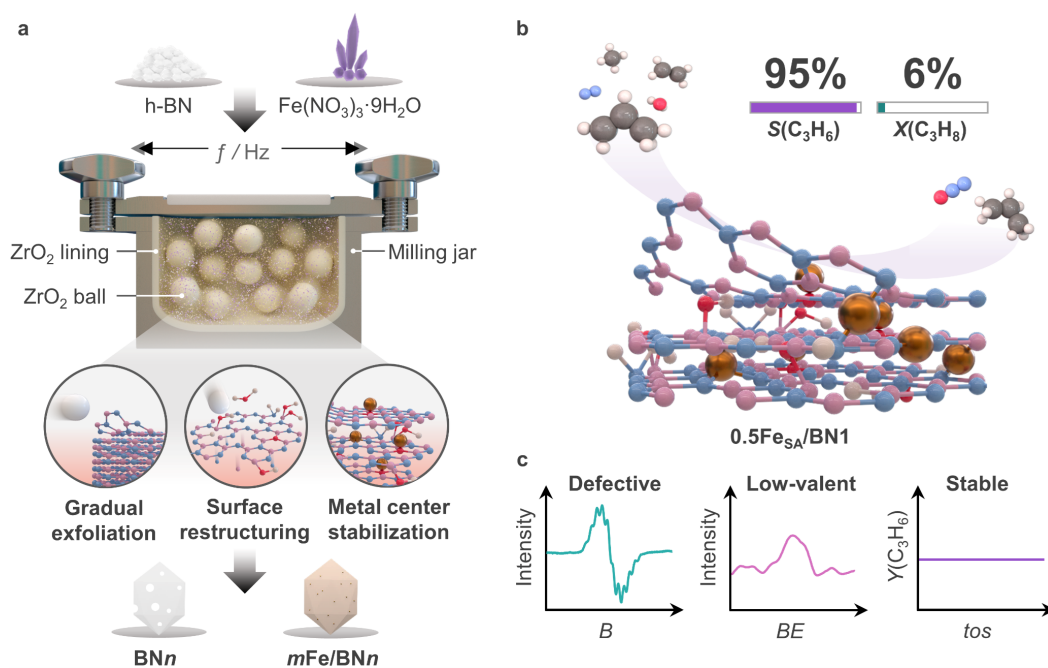


Fig. 1. **a** Preparation of $m\text{Fe}/\text{BN}_n$ catalysts (m = metal content in wt% and n = milling time in h) and associated physiochemical processes occurring during the synthesis. **b** N₂O-ODHP performance of $0.5\text{Fe}_{\text{SA}}/\text{BN}1$. Conditions $m_{\text{cat}} = 1$ g; $F_{\text{T}} = 20$ cm³ min⁻¹; Feed = 8, 8, and 84 vol% C₃H₈, N₂O and He; $T = 723$ K; $P = 1$ bar. **c** Summary of the key electronic and catalytic properties of $0.5\text{Fe}_{\text{SA}}/\text{BN}1$.

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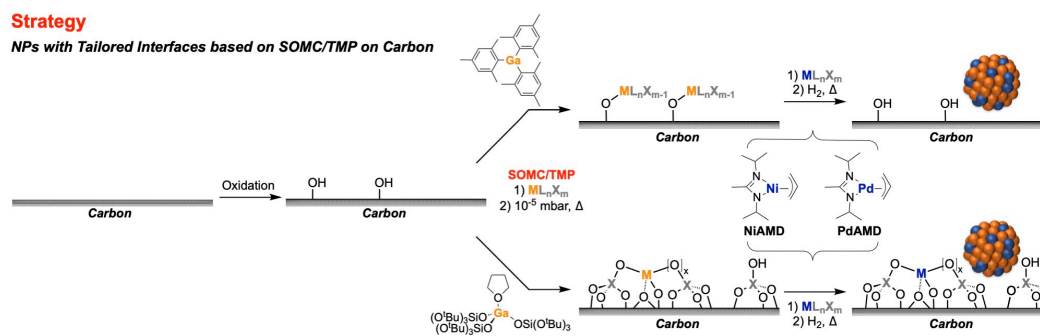
Hydrogenation of CO₂ over Carbon-Supported NiGa and PdGa Catalysts: Influence of Ga-Precursor Choice on Catalytic Performance

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The hydrogenation of CO₂ to methanol has gained a lot of attention in the recent decades, as it has been foreseen to be one of the keysteps to enable the valorisation of CO₂ and thus allowing to enable a sustainable production of this widely used platform chemical. In recent years, silica-supported, alloyed Group10 M_nGa nanoparticles have been shown to be promising catalysts for this transformation^[1-3]. In the case of PtGa it was additionally shown, that changing the support from silica to carbon increased the activity of the catalyst while not affecting the product selectivity, likely due to a facilitated desorption of the products as a result of the absence of lewis-acidic Ga^{III} interfacial sites^[3].

Therefore, in this work we aim at expanding the understanding of interfacial effects towards supported NiGa, as well as PdGa nanoparticles. We thus prepared purely carbon-supported NiGa and PdGa nanoparticles, as well as nanoparticles exhibiting a silica interface, by using a recently reported approach relying on surface organometallic chemistry on carbon, combined with the use of tailored molecular Ga precursors^[4].



Regarding the NiGa/C system, the absence of a silica interface resulted in a catalyst with product selectivities as well as activities, comparable to the previously reported NiGa/SiO₂ system, despite the bigger particle size which was obtained on carbon^[2]. On the other hand, the use of a Ga-silicate precursor during synthesis, resulted in a reversed product selectivity and a suppression of the catalyst's activity. Transmission electron microscopy measurements revealed, that this change in selectivity, can be linked to the difference in Ga-speciation in the absence of a silica interface, as observed by differences in alloy composition, as well as the presence/absence of Ga₂O₃ domains – both factors which were reported to influence the catalytic performance of NiGa/SiO₂. In the case of PdGa/C, no differences in Ga-speciation were observed. However, a suppression of the catalyst's activity in the absence of a silica interface was found, alongside a lower activity compared to the PdGa/SiO₂ counterpart. The increased activity in the presence of a silica interface, is thus likely a result of increased dynamics, such as facilitated alloying/dealloying processes, as known to occur on the highly dynamic silica-supported counterpart.

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The new Debye beamline at SLS2.0: a versatile platform for operando X-ray chemical and structural analysis with multimodal X-ray absorption spectroscopy and scattering

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The newly constructed Debye beamline at the Swiss Light Source (SLS), available after the SLS upgrade mid-2025, is positioned to provide multimodal X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) analysis to investigate the chemical, geometrical and electronic structure of functional materials under operating conditions. Equipped with a 5 T superbend magnet source and utilizing an in-house engineered quick scanning channel-cut monochromator (Si111, Si311), the Debye beamline offers an accessible energy range from 4.5 keV to 60 keV. A cutting-edge motion control system provides a diverse range of control options, facilitating Quick-scanning XAS through sinusoidal motion and custom trajectories as well as precise step-scanning measurements, all seamlessly executed with the same direct-drive motor. Precise motion position triggered XRD pattern collection at stationary points in the monochromator oscillation or through automated energy switching allows to realise quasi-simultaneous XAS and XRD analyses. Further enhancement of the Debye beamline will be achieved by extending measurement capabilities to include time-resolved X-ray total scattering.

The modular designed experimental end-station allows for rapid changes between experiment types affording the full flexibility demanded by the chemistry and material science communities. Development of integrated experimental controls, data acquisition, data handling and analysis pipelines lay the foundations for a streamlined user interface allowing rapid results visualization and experiment automation. By offering standard reaction environments for electrochemical, battery, catalysis and materials science research together with potentiostat, micro gas chromatograph, mass spectrometer and gas delivery infrastructure (up to 60 bar), the Debye beamline is designed for _ research.

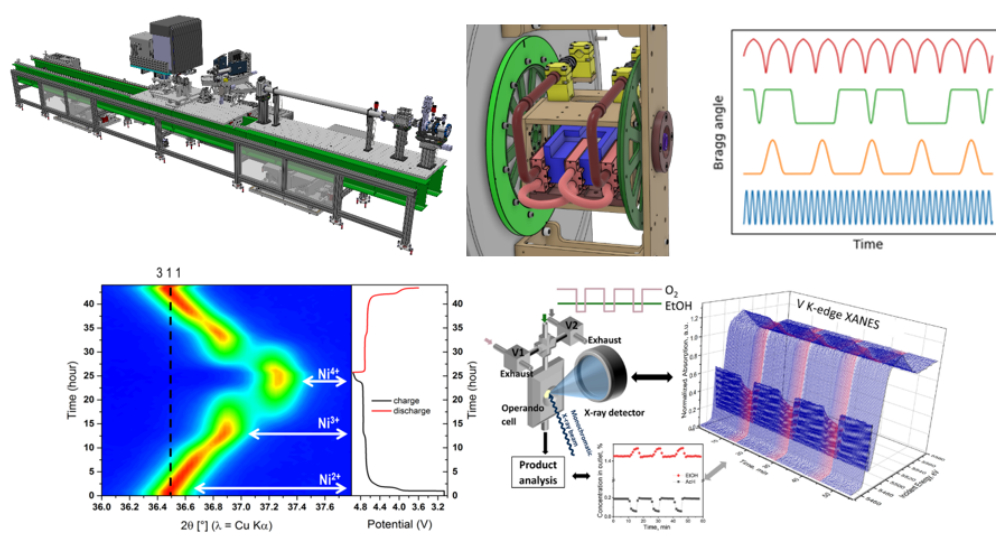


Figure 1. Design of the Debye end-station experimental table, monochromator, motion patterns and experimental capabilities for operando XAS and XRD analyses.

A scalable dynamic flow reactor for challenging continuous processes

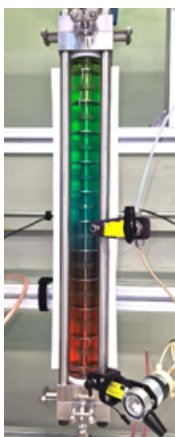
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Continuous reactions are routinely carried out using various types of flow reactors, often relying on static mixers or small channels to thoroughly mix the reacting partners. However, such approaches are usually not well suited for processes requiring long residence times, stoichiometric amounts of solid reagents or that are prone to fouling [1].

We herein present our work on the development, characterization (residence time distribution, heat transfer and gas-liquid mass transfer) and application tests of a flow reactor equipped with a dynamic mixer (DCR - Dynamic Contiplant Reactor), which was designed for continuous processes that requires handling of solids/fouling as well as reactions demanding long residence times. This reactor allows for an easy transfer from batch reactions to flow and can be used to carry out a large diversity of challenging chemical reactions.

Application tests will be discussed, as well as the implementation of PAT tools such as online FTIR, UV-Vis or pH sensors on the reactor.

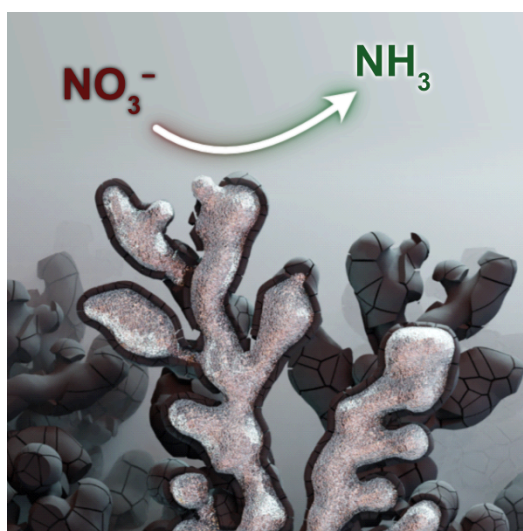


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Electrochemical nitrate to ammonia reduction with a dendritic MoO_x catalystR. N. Dürr¹, Y. Xu¹, D. F. Abbott¹, T. N. Huan², V. Mougel^{1*}

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Due to the poor nitrogen uptake capability of agricultural plants, approximately 50% of the globally used nitrogen-based fertilizers is lost in the environment among others in the form of nitrate.^[1] This does not only lead to significantly surpass the planetary boundary of the nitrogen biogeochemical flow and endangerment of natural ecosystems,^[2] but especially nitrate-contaminated water presents a serious health risk for humans, which consumption is known to cause Methemoglobinemia (Blue Baby Syndrome).^[3] Hence, the electrocatalytic reduction of nitrate has received increased attention as promising strategy to convert a toxic pollutant into benign or even value added products, such as ammonia. In this work a highly active and stable dendritic reduced molybdenum oxide (MoO_x) catalyst is presented, which is synthesized *via* a two-step electrodeposition process. In addition to converting nitrate to ammonia with a faradaic efficiency of up to 99%, this catalyst shows a high ammonia yield rate reaching > 4 mmol h⁻¹ cm⁻² and an outstanding stability during a continuous operation test for more than 4 months at elevated current densities.^[4]



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Convergent active site evolution of platinum single-atom catalysts for acetylene hydrochlorination and implication for toxicity minimization

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¹ETH Zürich, ²ICIQ-CERCA, ³Johnson Matthey

Platinum single atoms supported on carbon have demonstrated stable synthesis of vinyl chloride (VCM) via acetylene hydrochlorination,^[1] emerging as potential replacements for toxic mercury catalysts to produce this key monomer. Compared to gold-based alternatives,^[2] fundamental studies aimed at designing platinum catalysts with industrial potential are in early stages. To date, chloroplatinic acid has been mostly used as the metal precursor in catalyst synthesis, leaving significant opportunities to explore other platinum complexes and their impact on catalyst reactivity and other aspects related to their sustainability.

Herein we synthesize platinum single-atom catalysts (Pt SACs, 0.2-0.8 wt% Pt) with eight customized metal precursors featuring ammine, hydroxyl, nitrate, and chloride ligands. Our standardized, scalable impregnation protocol on carbon extrudates enhances practical scope. Catalytic tests show a strong initial activity dependence on precursor, with tetraammine-derived Pt SACs displaying a 2-fold higher VCM yield than chlorinated counterparts (**Fig. 1a**). Dynamic active site restructuring causes their activity to gradually converge, resulting in outstanding precursor-independent stability during 150 hours on stream. This is rationalized through reaction-induced evolution of distinct metal-ligand architectures into a common, active, and stable Pt-Cl_x (x = 2-3) species (**Fig. 1b**), as uncovered by *operando* X-ray absorption spectroscopy (XAS, **Fig. 1c**) aided by density functional theory. The robustness of Pt SACs, regardless of the employed metal precursor, allows us to minimize the toxicity of the catalyst based on a multi-parameter assessment, favoring halide-free Pt complexes (**Fig. 1d**). This study brings us a step closer to the application of safe-by-design catalysts for VCM synthesis and demonstrates the importance of toxicity analyses in catalyst design programs.

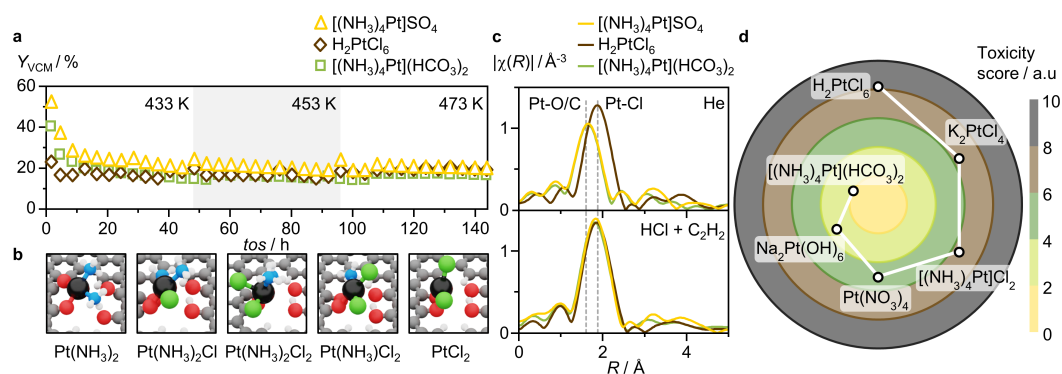


Fig. 1a Time on stream (*tos*) performance, expressed as VCM yield (Y_{VCM}), of selected Pt SACs. **b** Schematic representation of the progressive ammonia-chloride ligand exchange that the tetraammine-derived Pt SACs undergo, as uncovered by **c** *operando* Pt L_3 edge XAS analysis. **d** Toxicity assessment of Pt precursors.

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Doped NiO yields ultra-low overpotential electrocatalysts in alkaline media – towards practical anion exchange membrane electrolyzers

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The development of efficient hydrogen evolution reaction (HER) catalysts is crucial for green hydrogen production and sustainable energy. We introduce a highly tunable, robust electrocatalyst made of doped NiO grown on Ni-foam, synthesized through the ultrafast combustion technique. This catalyst exhibits remarkable HER performance, with overpotentials up to less than 70 mV at 25°C and 30 mV at 70°C at 100 mA cm⁻² in 1 M KOH. Additionally, by fine-tuning the fuel/metal ratio during the synthesis, the doped NiO on Ni-foam demonstrated outstanding oxygen evolution reaction (OER) activity as well, achieving a new benchmark overpotential c.a. 80 mV at 10 mA cm⁻² in 1 M KOH at 25°C. Stability and performance were tested in a zero-gap flow cell electrolyzer with different membranes with combustion-derived doped NiO grown on Ni-foam as water-splitting catalysts, showing sustained activity over prolonged periods and accelerated degradation tests. Comprehensive physicochemical characterizations (electrochemical, XRD, SEM, FIB, TEM, EDX, AFM, ICP-OES, TGA, DSC, and XPS) are presented to support this study.

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Precursors of Ethylene Oxide and CO_x in Ethylene Epoxidation: In-Situ AP-XPS Study Revealing Absence of OMC Species on Ag foil

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Ethylene oxide (EO) holds a crucial role in the chemical industry as a foundational building block, with its production via ethylene epoxidation (EPO) being a pivotal process in the chemical sector. Silver-based catalysts currently represent the sole commercially viable EPO catalyst, owing to their high selectivity toward EO. Extensive efforts have been dedicated to elucidate the underlying mechanism in the past 20 years, with the oxametallacycle (OMC) mechanism widely accepted as the dominant pathway. The OMC mechanism proposes that ethylene (C₂H₄) reacts with adsorbed oxygen on the silver surface to form a stable OMC species, which serves as the common intermediate for ethylene oxide and acetaldehyde (AA), with AA rapidly transforming into CO_x. However, experimental evidence investigating the intermediates on Ag surface including OMC species under EPO conditions has remained elusive. In this study, we used synchrotron-based ambient pressure X-ray photoelectron spectroscopy (AP-XPS) to investigate a series of C 1s spectra under in-situ EPO and ethylene oxide decomposition conditions. Combined with DFT calculations, our results indicate that CO is present on the Ag surface as the precursor of CO_x, while OMC intermediates are absent under either in-situ EPO or EO decomposition conditions. This finding has important implications for the further understanding of EPO reaction mechanisms.

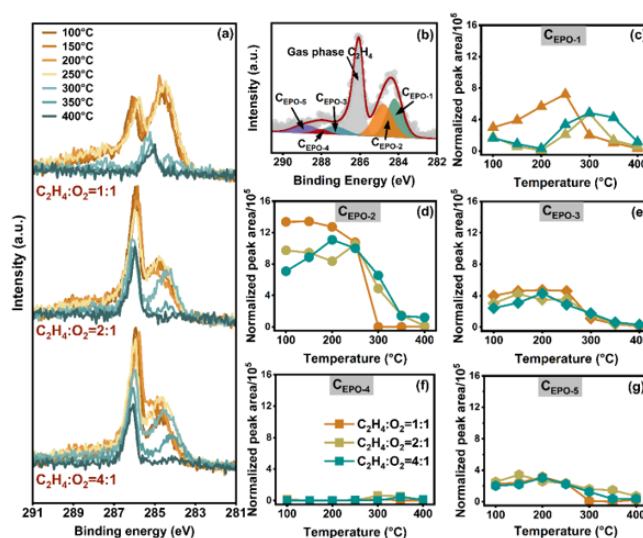


Figure 1. (a) C 1s spectra acquired in different reaction environments with increasing temperature (KE=200 eV). (b) Example of C 1s deconvolution. (c-g) Normalized peak area of C₁₁, C₁₂, C₁₃, C₁₄ and C₁₅ in different reaction environment as a function of temperature.

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Graphitic carbon nitride (g-C₃N₄) modified by ionic liquids for an improved water-splitting performance

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Graphitic carbon nitride (g-C₃N₄) is a stacked organic semiconductor with tri-s-triazine repeating units forming a graphitic p-conjugated structure.[1] Its sufficiently large band gap and visible light response makes g-C₃N₄ an excellent photocatalyst for the water-splitting reaction.[2]

However, to achieve an optimal performance, g-C₃N₄ needs modification through morphological adjustments and heteroatom incorporations. This study explores the use of ionic liquids (ILs) to achieve these modifications, serving both as soft-templating agents and doping agents for heteroatom incorporation.

Various ILs were tested to evaluate their impact on the morphology and on the water-splitting performance of g-C₃N₄. The findings indicate that different ILs lead to distinct morphologies and varying OER performances. This confirms that ILs can effectively function as all-in-one agents, enhancing both the structure and catalytic efficiency of g-C₃N₄ for water-splitting applications.

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Formation and Stability of μ_2 -Peroxo on Titanosilicates, Anatase, and Rutile: Implications for Zeotype Catalysts

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Extra-framework TiO₂ in titanosilicate oxidation catalysts has traditionally been associated with diminished selectivity, prompting significant efforts towards devising synthetic methodologies yielding extra-framework -free materials. In this study, employing ¹⁷O solid-state NMR spectroscopy, we explore the formation and stability of μ_2 -peroxo entities on titanosilicates with or without extra-framework TiO₂, alongside TiO₂ polymorphs (anatase and rutile). Relative to TiO₂ nanoparticle benchmarks, we infer that H₂O₂ activation, specifically peroxo formation, and subsequent decay correlate with the presence of rutile-like extra-framework TiO₂. Notably, μ_2 -peroxo moieties exhibit resilience on anatase, while their decay is rapid on rutile. Through DFT computations, we attribute the enhanced stability of μ_2 -peroxo surface species on anatase to the unique configuration of μ_2 -oxo groups on the (101) facet, facilitating the stabilization of crucial intermediates via hydrogen bonding. Noteworthy is the differentiation of μ_2 -peroxo species formed on titanosilicates and anatase, as they manifest distinctive ¹⁷O NMR spectroscopic profiles, directly reflecting the Ti-coordination environments, thereby enabling their discernment.

J. Phys. Chem. C, 2024, 128, 13, 5553–5558

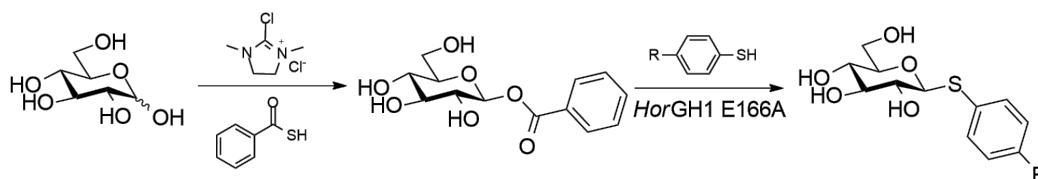
Glycosyl Benzoates as Novel Donors for GlycosynthasesD. Lim¹, S. de Lorenzo¹, L. Pillet¹, F. Paradisi^{1*}¹Department of Chemistry, Biochemistry, and Pharmaceutical Sciences, University of Bern

Mimetics of carbohydrates that are resistant towards enzymatic hydrolysis have found value as therapeutics. However, the chemical synthesis of glycoconjugates often still requires the use of multi-step protecting group strategies to introduce the desired linkages.

Alternatively, biocatalytic methods are becoming increasingly attractive due to their excellent regio/stereoselectivity and their high efficiency while requiring much milder conditions. In particular, the use of mutant glycosidases, aptly termed glycosynthases, has allowed the stereoselective formation of glycosidic linkages under aqueous conditions in high yields and nearly without competitive hydrolysis, the latter of which is problematic in the use of natural glycosidases.

Here, we highlight the development of a procedure for the one-pot synthesis of glycosyl benzoates directly from unprotected sugars in aqueous media. We found that these glycosyl donors were excellent substrates for wild-type and mutant glycosidases.

Furthermore, using a series of arene nucleophiles, we also demonstrated good to excellent conversions (up to 94%) of β -glucosyl benzoate to the corresponding *p*-nitrophenyl- and thioglycosides. The use of this methodology potentially allows for the selective and sustainable synthesis of stable glycosidic analogues of glycosides present in many commercial products and pharmaceuticals.



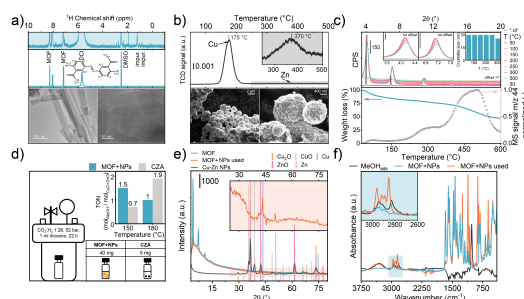
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Metal-Organic Framework-based catalysts for CO₂-to-methanol process

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The presented study is crucial to resolving the important issue of CO₂ capture and hydrogenation: the development of a highly selective catalyst toward valuable methanol. We aim to establish the structure-activity relationships of the metal-organic catalysts modified with the metal nanoparticles in CO₂-to-methanol reaction. We synthesized the Mg-IRMOF-74-II (MOF) catalyst following the procedure^[1] (Fig. 1a) and prepared Cu-Zn nanoparticles via the chemical reduction method (Cu:Zn 1:1 mol, NPs)^[2] to install them in the MOF using incipient wetness impregnation (Fig. 1b). We were able to observe the characteristic features of the Mg-IRMOF-74-II linkers^[1] (Fig. 1a,e) by ¹H liquid state NMR and ATR-IR spectroscopies. We observe that the MOF possesses high crystallinity and stability in the range of temperatures relevant for the methanol synthesis (Fig. 1c) by in situ lab XRD and TGA-MS in H₂-containing atmosphere. We tested the MOF-NPs catalyst (CuO:ZnO:MOF 1:1:12 mol) in a batch system^[3] at 52 bar and low CO₂:H₂ ratio and compared it with the existing industrial analog, CZA (CuO:ZnO:Al₂O₃:MgO 8:3:1:0.3 mol). The MOF-NPs catalyst performed better at lower temperatures (Fig. 1d). Reduction of the Cu already took place at 150 °C after the catalytic test (Fig. 1e). ATR-IR of the used catalyst demonstrated the appearance of the new bands in 2800 – 3000 cm⁻¹ region over the used MOF-NPs catalyst, which can be assigned to the adsorbed methoxy groups and methanol^[4]. This underlines the role of the MOF as efficient environment for the synthesis of methanol in the presence of Cu-Zn nanoparticles. In conclusion, the synthesized MOF-NPs materials are active in the CO₂-to-methanol process. These results significantly contribute to the catalysis and MOF chemistry community, providing new fundamental insights into a promising but poorly understood catalytic system.



Physical and chemical properties of the MOF-NPs system. a) ¹H NMR of the Mg-IRMOF-74-II (MOF, top) and its HRTEM images, interplanar spacing distances estimated ~21 Å (bottom); b) H₂-TPR of the Cu-Zn nanoparticles (NPs, top) and their SEM images (bottom); c) in situ lab XRD (top) and TGA-MS (bottom) of the MOF in a H₂-containing atmosphere. Particle size of the MOF were calculated using Scherrer equation (insert). MS signal m/z 44 corresponds to CO₂. Conditions: XRD in situ 40 mL/min N₂ + 1.5 mL/min H₂, 50 – 500 °C, 1 bar; TGA-MS 19 mL/min He + 1 mL/min H₂, 50 – 600 °C, 1 bar. d) Catalytic tests of the MOF+NP catalyst and industrial CZA catalyst. The TON are calculated per mol of CuO+ZnO. Conditions: 150 and 180 °C, 52 bar, CO₂:H₂ 1:26, 420 mL autoclave, 40 mg of the MOF-NPs or 5 mg of the CZA in 1 mL dioxane, 22 h test; e) synchrotron XRD of the Cu-Zn NPs, MOF, and MOF+NP catalyst after the reaction at 150 °C. Conditions: 64 keV, q 0.2 – 5.2 Å⁻¹, glass capillary, ID15a, ESRF; f) ATR-IR of the MOF+NP catalyst before and after the reaction at 150 °C, the reference spectra of methanol adsorbed on the MOF is provided. The spectra were taken at RT, in air atmosphere.

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Enhancing catalyst effectiveness in chemical polyolefin recycling

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The influence of reaction engineering is often underestimated in chemical recycling of plastics versus areas such as catalyst design,^[1] despite being a three-phase reaction including fluids whose viscosity is six orders of magnitude larger than water, making it not trivial to ensure effective catalyst-plastic-H₂ contact. The absence of quantitative criteria to guide catalyst evaluation may result in suboptimal catalyst effectiveness, hindering accurate benchmarking.^[2] In this work, we demonstrate that suboptimal stirring can lead to 85% and 40% differences in catalyst effectiveness and selectivity, respectively, and develop a criterion to guide hydrogenolysis of commercial grade high density polyethylene and polypropylene. Comparison of reaction and diffusion rates disclosed that the reaction develops near the H₂-melt interface (**Fig. 1a**). Multiphase computational fluid dynamics (volume-of-fluid analysis) could link stirrer geometries to H₂-melt interface (**Fig. 1b**), which was quantified through the fractional hydrogen occupancy in a control volume. Particle trajectories could also be predicted after coupling a discrete phase model (VOF-DPM), as illustrated in **Fig. 1c**, revealing stark differences in the ability of different geometries to place particles in H₂-rich zones. Upon comparison with experimentally obtained catalytic performance, these observations could be translated into a quantitative criterion applicable under any commonly reported reaction conditions to maximize catalyst effectiveness based on operating in optimal power number (N_p) ranges (green area in **Fig. 1d**). Forward-looking investigations toward expanded models analyzed the validity of this approach throughout the reaction and forecasted a quick rise in the relevance of temperature gradients when scaling up reactors. This work highlights the importance of early engineering considerations in chemical plastic recycling.

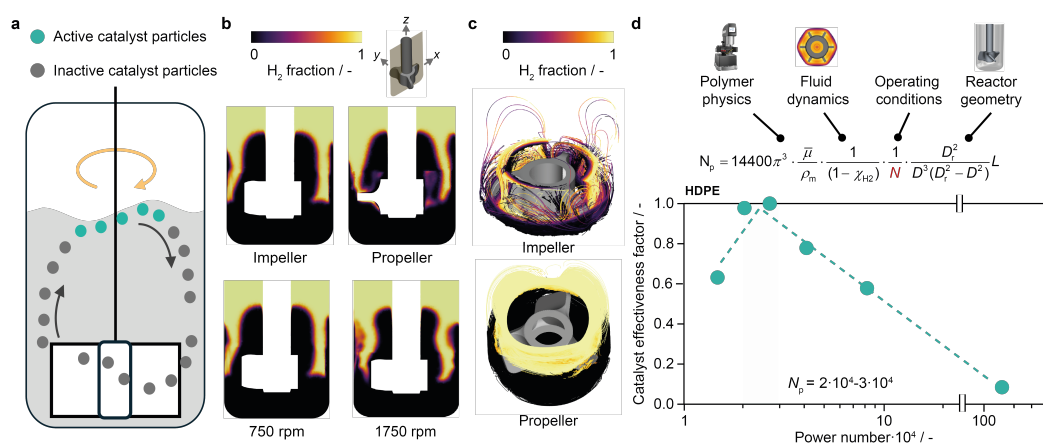


Fig. 1. **a** Representation of the reactive zone within the reactor. **b** Simulated H₂ fractions across the zx -plane for impeller and propeller geometries. Simulation parameters: $T = 498$ K, $p = 20$ bar, stirring rate = 750 rpm, HDPE ($M_w = 200$ kDa). **c** Particle trajectory distributions, colored according to the H₂ fraction in the vicinity. **d** Power number (N_p) formula with design variables (top), and dependence of catalyst effectiveness with N_p (bottom) and recommended range. ρ_m = polymer density; μ = average polymer viscosity, χ_{H_2} = fractional hydrogen occupancy, N = stirring rate, L = stirrer blade height, D = stirrer blade diameter, D_r = diameter of the reactor.

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Ligand-replaced asymmetric inorganic-organic hybrids for highly active biomass assisted electrocatalytic water splitting

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Through the ligand replacement strategy, this study successfully synthesized NiClOH-Pm_xPz_{1-x} nanorod inorganic-organic hybrid materials to improve the performance of urea-assisted water oxidation reaction. Ligand replacement not only introduces significant surface defects on NiClOH-Pm nanorods, but also promotes the stress on Ni sites, thereby significantly improving the electrocatalytic performance. In particular, the composite material exhibits excellent performance in the urea oxidation reaction, such as low surface charge transfer resistance, smaller Tafel slope, and current densities of 1.37 at 10 mA cm⁻² and 100 mA cm⁻², respectively. V and an overpotential of 1.53 V. In addition, the optimized ligand ratio also enhances π - π interactions, thereby improving electronic conduction and catalytic efficiency. This study demonstrates a new electrocatalyst design approach to improve the electrochemical performance and efficiency of hybrid inorganic-organic materials through ligand substitution.

Structure - catalytic performance relationship of modified SAPO-34 for methanol-to-olefins (MTO) reaction

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For shifting production of chemicals towards more sustainable routes and accelerating climate neutrality, a much in-depth understanding of catalyst stability and selectivity is needed. One of the interesting sustainable route to obtain valuable chemicals is the conversion of methanol, obtained from recycled or biogenic CO₂, into hydrocarbons (MTH). MTH reaction was discovered in 1970s as an answer to oil crisis and has gained a lot of attention from both scientists and industry in the last decades [1]. Based on the product distribution, this reaction can be divided into MTP (methanol – to propylene), MTG (methanol-to-gasoline), MTA (methanol-to-aromatics) and MTO (methanol-to-olefins). MTO reaction is catalyzed by acid zeolites which allow to activate hydrocarbon substrates by a transfer of proton. Based on reaction mechanism – dual-cycle mechanism, two different cycles (alkene and aromatic) are running in parallel inside zeolite structure and favoring different product distribution. The most common catalysts for MTO reaction are ZSM-5 and SAPO-34 [2]. Nowadays, it can be observed renewed interests toward the MTO reaction, as it is becoming an important intermediate step in the development of sustainable carbon-based fuels and chemicals. In our research we would like to establish structure - catalytic performance relationship for SAPO-34 modified by different cations.

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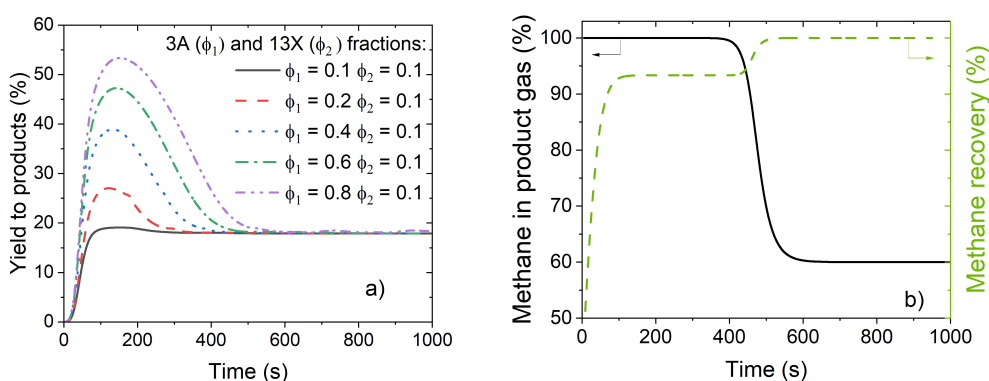
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Flexibilisation of methanol synthesis from CO₂ by alternating carbon capture and utilizationE. MOIOLI^{1,2}, A. Pappagallo¹, H. Petremand¹¹Paul Scherrer Institute, ²Politecnico di Milano

The electrification of chemical processes poses important challenges to the development of new reactive systems that can adapt to the seasonal variation in feedstock availability. As CO₂ converting reactions require large amount of electrolytical H₂, the economic performance of these reactions is sustainable only in the limited times where electricity is cheap. For this reason, the abatement of point source CO₂ emissions via carbon utilization is a difficult pathway in the current market conditions. To avoid this challenge, it would be convenient to design process units that flexibly treat the CO₂ emission source, alternatively removing or converting CO₂. In this way, the point emission could be completely mitigated, yielding a chemical product when the market conditions are favorable or simply separating CO₂ when electricity is expensive. This system could operate during the entire year, extending the amortization of CAPEX over a larger number of operating hours.

In the current market conditions (no clear CO₂ trade market), the best performance could be achieved when CO₂ should be separated from streams containing other valuable products. This is the case of biogas. Biogas upgrading through adsorption-based methods is a commercially available technology. A relevant adsorbent to this scope is the zeolite 13X, which is employed in this work. The presence of an adsorbent can be exploited also in the carbon utilization mode, to perform a sorption-enhanced synthesis. In this work, the chosen carbon utilization mode is the methanol synthesis, enhanced by the presence of zeolite 3A, which selectively adsorbs water at the methanol synthesis conditions.

In the fixed bed reactor, both sorbents are present in the reactor. Thanks to the higher capacity of zeolite 13X, the amount of this latter in the reactor can be 5 times less than the water adsorption zeolite (3A). The system is operated with 4 reactors in parallel, to form a temperature swing adsorption unit. The system is optimized to have similar time-on-stream in both operation modes. The calculated profiles are shown in figure 1. The economic analysis showed that both configurations can outperform the standard CO₂ utilization approaches, by realizing a continuous CO₂ abatement in a simple plant configuration.



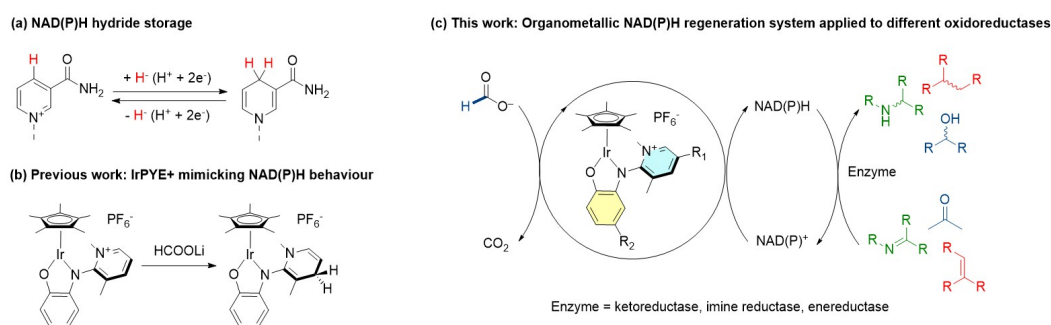
The path to a versatile and biocompatible organometallic NAD(P)H regeneration system using an Ir⁺PYE⁺ complex

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NADH is a crucial cofactor in many oxidoreduction enzymatic processes due to its ability to reversibly store hydrides on the nicotinamide moiety (Fig. 1a). Despite its importance, the use of NADH is limited by high cost, low stability, and stoichiometric utilization.^[1] To overcome these limitations, several research groups have explored various cofactor regeneration systems aimed at reducing the costs associated with NADH-dependent reactions.^[2,3] Among these, NAD(P)H regeneration using organometallic complexes has been extensively studied over the past decades, providing numerous metal-based catalysts. Nevertheless, integrating these catalysts into enzymatic biocatalytic systems presents significant challenges, primarily due to mutual inhibition between the enzyme and the metal catalyst and the difficulty of identifying biocompatible reaction conditions.^[4]

We recently developed an iridium complex bearing a pyridylidene-amine (PYE) ligand that exhibits unique functional ligand-type reactivity, storing the hydride on the heterocycle ring and mimicking NADH-type reactivity (Fig. 1b). This complex also catalyzes NAD(P)H reduction.^[5] Building on this work, in the present study, we focused on the application of our optimized ligand for efficient NAD(P)H regeneration under biocompatible conditions, exploring its use with various classes of enzymes (Fig. 1c) and investigating solutions to prevent mutual inhibition, such as compartmentalization of the two systems.



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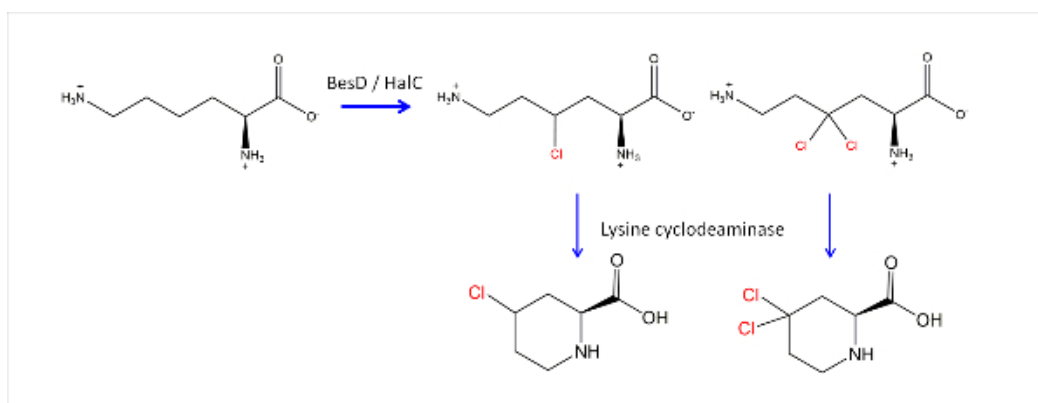
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Optimizing Enzymatic Cascades for Halogenated L-Pipecolic Acid Production

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L-Pipecolic acid is a natural non-proteinogenic α -amino acid found as an active ingredient in various antibiotics (such as rapamycin and Virginiamycin S1) and anesthetic drugs (including Mepivacaine and Ropivacaine).[1] Derivatives of pipecolic acid are valuable in medicinal chemistry as antimicrobial agents, anti-inflammatory drugs, and neurotransmitter modulators, as well as in organic synthesis and material science. Halogenating L-pipecolic acid can enhance its lipophilicity, thereby improving cellular absorption and bioavailability, as well as stability of the drug.[2] However, chemical synthesis of halogenated pipecolic acid is cost-prohibitive, adding to the already high cost of pipecolic acid. Enzymatic synthesis offers a green and cost-effective alternative for producing pipecolic acid derivatives. One such method involves a cascade of halogenase and lysine cyclodeaminase enzymes using L-lysine as the substrate. [3] In this study, we utilize two enzymes, BesD and HalC, to perform chlorination at the 4th carbon of L-lysine, resulting in mono- and di-chlorinated L-lysine, respectively. After complete chlorination, lysine cyclodeaminase is employed to convert the chlorinated lysine into cyclic chloro-pipecolic acid. We characterize the final mono- or di-chlorinated pipecolic acid product using mass spectrometry and present optimized reaction conditions for the halogenation to form stable chloro-lysine. To scale up the production of mono-/di-chlorinated lysine via halogenases, we compare different enzyme immobilization strategies, including covalent and ionic bonding on various supports, as well as cross-linking enzyme aggregates.



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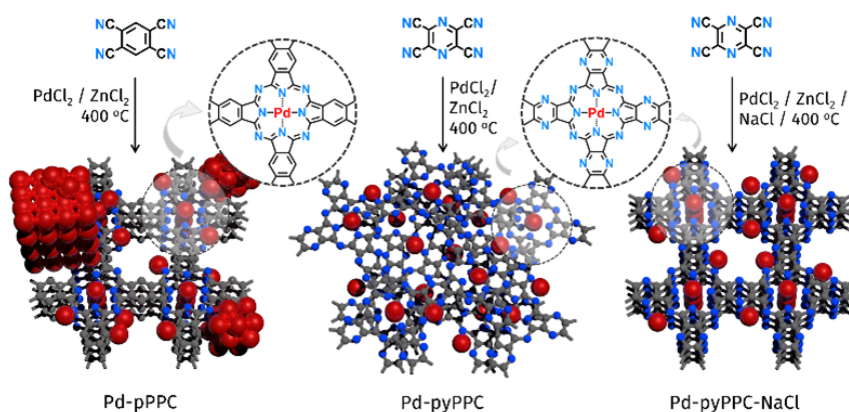
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High-Loading Pd-Phthalocyanine Covalent Organic Framework based SACs for Cross-Coupling Reactions

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Heterogeneous single-atom catalysts (SACs) have garnered attention for their effectiveness, attributed to their high atom efficiency, improved catalytic activity, selectivity, and stability. This is due to their dispersed atomic structure, which allows them to bridge the gap with homogeneous catalysts.^[1] Despite their promise, a significant challenge lies in achieving high metal loadings while maintaining stability and catalytic activity. The potential of organic supports such as g-C₃N₄ and N-doped carbons in achieving high metal loadings underscores their significance. However, the limited number of available options highlights the need for new supports and synthetic methods. Covalent organic frameworks (COFs) offer promising features such as tunability, precise control over structure for metal integration, uniform distribution of catalytic sites, and large surface areas, addressing the demand for novel supports and synthetic approaches.^[2]



This study focussed on developing ultra-high metal-loading single-atom catalysts (SACs) utilizing porous palladium polyphthalocyanines (Pd-PPCs). By employing ionothermal conditions and starting materials like tetracyanobenzene and tetracyanopyrazine, along with mixtures of PdCl₂/ZnCl₂ or PdCl₂/ZnCl₂/NaCl metal salts, we successfully synthesized Pd-pPPC and Pd-pyPPC, achieving remarkable metal loadings of up to approximately 17wt% as presented in the Figure. This innovative synthesis approach integrates the formation of polymeric support with metal impregnation seamlessly, eliminating the need for additional processing steps. The resulting catalysts demonstrated encouraging performance in the Suzuki-Miyaura cross-coupling reaction, both in batch and continuous flow setups.

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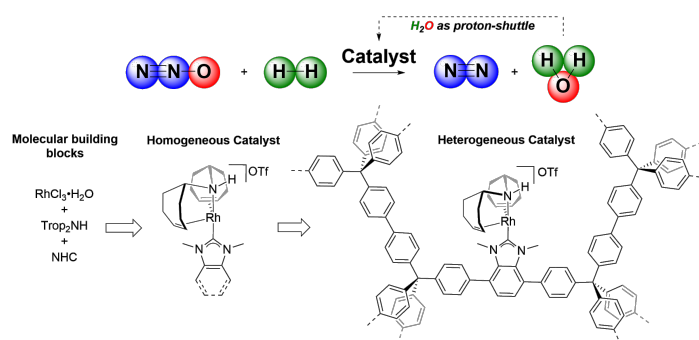
Highly Efficient Homogeneous Catalyst For N₂O Hydrogenation and the Key Role of Water: Proton shuttling and H₃O₂⁻ structures

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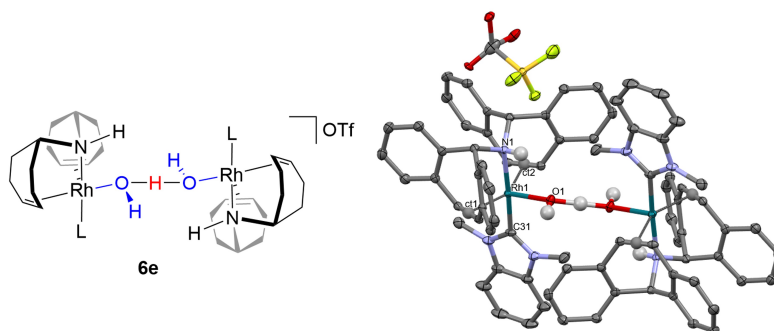
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Laughing gas, nitrous oxide (N₂O), is the isoelectronic and isostructural ‘nitrogen analogue’ of carbon dioxide (CO₂). Despite its name, N₂O is no laughing matter due to its significance as an atmospheric pollutant. In recent times, N₂O has been identified as the most ozone depleting agent of the 21st century and a potent greenhouse gas [1]. Therefore, solutions are urgently needed to mitigate its release and incorporate N₂O into the value chain of product chemicals. More knowledge is required to achieve these solutions.

We choose to study the N₂O hydrogenation reaction with homogeneous catalysts, as it is a ‘simple on paper’ reaction and it allows for investigation of intermediates and kinetics of the reaction under relatively mild conditions. Additionally, we deployed these molecular catalyst onto heterogeneous support systems, enabling a ‘direct’ comparison of the activity between the homogeneous and the heterogeneous phase catalyst.



We can now report the discovery of a homogeneous catalyst that is 400 times more efficient than those previously reported in the literature [2]. It shows unprecedented activity (ca. 230,000 TONs) in the hydrogenation of N₂O under mild conditions (3 bars, 65 C). The exceptional activity can be attributed to two factors: catalyst design optimization and the dual roles of water. We demonstrate how water, as a product of the reaction, interacts with intermediates, facilitating the reaction to proceed with lower energies through unique H₃O₂⁻ dimeric ‘trapped proton’ structures and through proton-shuttling mechanisms. We suggest that this dimerization is the key reason for the observed differences in reactivity between the homogeneous and heterogeneous realms.



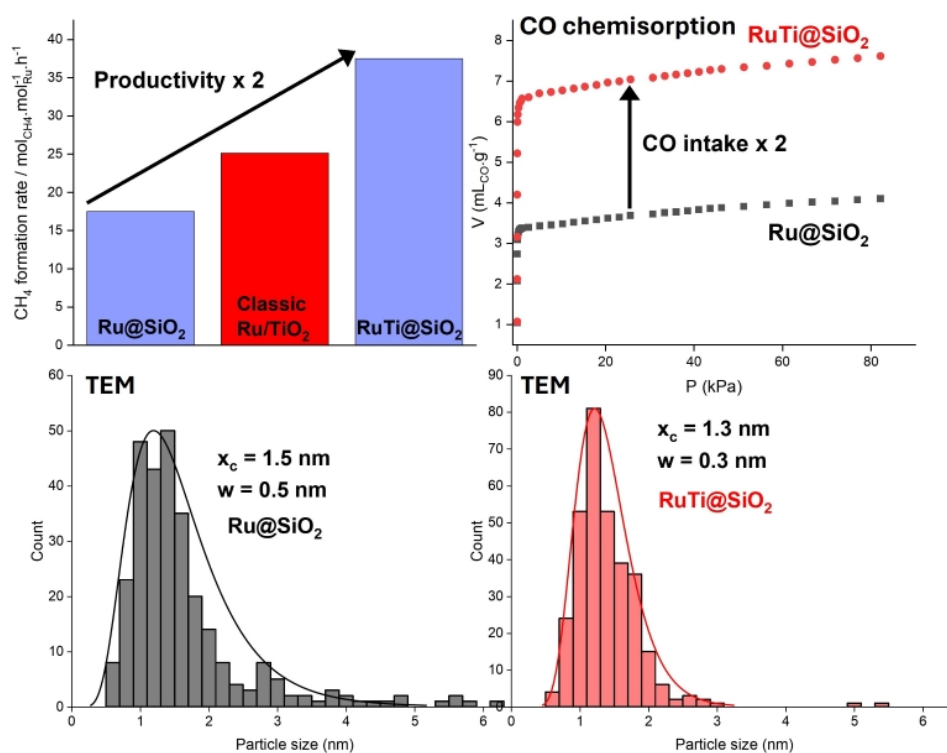
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Ti-doping in silica-supported Ru methanation catalysts

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Supported metal nanoparticles on oxide support are one of the main axes of research to convert CO₂ to methane. Among various catalysts, Ru/TiO₂ has been reported to show outstanding performances in terms of methanation activity, selectivity, and stability.¹ The catalyst suffers from poor molecular understanding nonetheless, in particular the role of the support species at the interface with the Ru nanoparticles during methanation conditions is still not established. Therefore, the project deals with the understanding of the catalyst at a molecular level and in particular the role of Ti(IV) and Ti(III) species in proximity with the Ru nanoparticles. To attain this goal, the Surface Organometallic Chemistry (SOMC) has been used to design the model catalysts with tailored interfaces Ti(IV)/Ru on silica-based supports.² Catalytic data have shown that such interface promote methanation reaction by increasing with a factor 2 the methane productivity, surpassing both silica and classical TiO₂-supported Ru nanoparticles. A battery of characterization as Transmission Electron Microscopy (TEM), X-Ray Absorption Spectroscopy (XAS) and H₂/CO Chemisorption show that Ti species on the silica surface increase the dispersion of the ruthenium on the support compared to plain silica. Yet, the sole dispersion effect can not explain the increased productivity entirely. Our leading hypothesis is the existence of charge transfer between Ti and Ru leading to a CO intake multiplied by two in presence of Ti. Similar interaction has been reported earlier between Ti and Pt.³ EPR study is being carried out to unveil the fundamental origins of the promotion effect.

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SiO₂-Supported Co_xPt_{1-x} Nanoalloys for the Dry Reforming of Methane

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The dry reforming of methane (DRM) allows converting two major greenhouse gases, CH₄ and CO₂, to produce H₂ and CO, by using noble or some transition metals such as Ni or Co supported on metal oxides as catalysts. The DRM requires high temperatures (600 – 1000 °C) to achieve high conversions. Under these conditions, many catalysts for DRM suffer from deactivation due to carbon deposition, particle growth, and oxidation. Bimetallic nanoparticles offer a versatile strategy to overcome the limitations of monometallic systems as they allow the tuning of a catalyst's electronic and/or geometric structure.^[1]

Here, we investigate SiO₂-supported Co_xPt_{1-x} nanoparticles aiming to understand the effect of the Co:Pt ratio on the catalyst's structure and catalytic performance. The catalysts with varying Co:Pt ratios were synthesized by strong electrostatic adsorption (SEA).^[2] After reduction in H₂/N₂ the nanoparticles showed a high dispersion on the SiO₂ support and had an average particle size of $d_{(S)TEM} = 1.7 - 3$ nm (Fig. 1a) with a total metal loading between 1.5 – 4 wt% (elemental analysis). XRD measurements of the as-reduced catalysts (performed in air-tight capillaries) evidenced nanocrystalline face center cubic (fcc) phases in all materials, with crystallite sizes in the range of ca. 1-3 nm.

In-situ X-ray absorption near-edge structure (XANES) experiments of Co_{0.5}Pt_{0.5}/SiO₂ and Co/SiO₂ after the reduction in H₂/N₂ revealed differences in the Co K-edge XANES features in the bimetallic Co_{0.5}Pt_{0.5}/SiO₂ when comparing with the monometallic Co/SiO₂ catalyst (Fig. 1b, data collected at 50 °C). These differences in the Co K-edge XANES features between Co_{0.5}Pt_{0.5}/SiO₂ and Co/SiO₂ have been ascribed previously to changes in the electronic (and local geometric) structure due to charge transfer and orbital hybridization in Pt and Co.^[3]

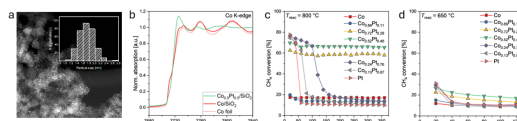


Figure 1: a) STEM image of an air exposed Co_{0.5}Pt_{0.5}/SiO₂ catalyst (pre-reduced at 800 °C in 10 % H₂/N₂ for 1 h), $d_{(S)TEM} = 1.7 \pm 0.3$ nm, b) Co K-edge XANES of Co/SiO₂, Co_{0.5}Pt_{0.5}/SiO₂ (data collected at 50 °C after in-situ H₂-TPR at 800 °C for 1 h and Co foil c-d) CH₄ conversion of a series of Co_xPt_{1-x}/SiO₂ catalysts under DRM conditions (75 L g_{cat}⁻¹ h⁻¹, 800 °C and 650 °C).

The Co:Pt ratio in the catalyst significantly impacted the catalytic performance (CH₄ and CO₂ conversions) and stability at 800 °C (Fig. 1c). Pt/SiO₂ deactivated rapidly within 60 min time on stream (TOS), while Co/SiO₂ displayed low activities and H₂:CO ratios of about 0.2. In contrast, the bimetallic Co_xPt_{1-x}/SiO₂ catalysts demonstrated enhanced stabilities and CH₄ conversions, whereby the best catalytic performances were observed for Co:Pt ratios close to 1:1. Based on our XAS data we attribute the enhanced performance of Co_{0.5}Pt_{0.5}/SiO₂ to the alloying between Pt and Co at the nanoscale and the resulting modification of the metals' electronic structure.

At 650 °C (Fig. 1d), however, we observe a deactivation of all catalysts, including Co_{0.5}Pt_{0.5}/SiO₂, yet Co_{0.5}Pt_{0.5}/SiO₂ deactivates at a lower rate than Pt richer catalysts. Our operando Co K-edge XANES under DRM conditions at 650 °C and ex-situ Raman spectroscopy of the spent catalyst elucidate an important finding: Co that in Co_{0.5}Pt_{0.5}/SiO₂ is initially alloyed with Pt, partially oxidizes with TOS. This oxidation results in a partial dealloying, forming CoO_x and Pt-rich nanoparticles. This process likely triggers additional coke formation on the Pt-rich sites, resulting in turn in deactivation.

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Controllable production of single-walled and multi-walled carbon nanotubes in CH₄ catalytic pyrolysis using Fe-Mo/MgO

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Carbon nanotubes (CNTs) has been on the radar for the last decades among researchers and industries owing to its unique advantages in electrical conductivity, mechanical strengthen, specific surface area (SSA), chemical and thermal stability.^{1,2} To synthesize CNTs, the common precursors include ethylene, propylene, acetylene, methanol, ethanol, benzene and so on.³ In recent years, more and more attention has been attracted on CH₄ catalytic pyrolysis^{4,5} as it produces not only CNTs but also CO₂-free H₂, which is a feasible technique for CO₂ net-zero-emission.

In CH₄ catalytic pyrolysis, common catalysts, such as Fe, Ni, and Co supported on SiO₂, Al₂O₃ and MgO respectively, are applied for CNT synthesis.⁶ In addition, a second metal, such as Mo, is usually introduced to improve the CNT production. In this contribution, Fe-Mo/MgO is used as catalysts for CNT synthesis. By adjusting the Mo loading, CNTs with different diameter are successfully synthesized, including single-walled and multi-walled CNTs. Moreover, the carbon productivity is improved by the Mo introduction and Fe-1Mo/MgO reaches five-fold carbon productivity compared with Fe/MgO.

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Unraveling the Promoting Effect of Diamine-Modified Metal-Organic Frameworks on the Ruthenium-Catalyzed CO₂ Hydrogenation to Methanol

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Homogeneous catalytic systems for CO₂ hydrogenation to methanol have been extensively researched as promising low-temperature alternatives to commercial processes.^[1] The amine-assisted pathway, in particular, shows significant potential for integrating carbon capture with methanol production.^[2] In addition to traditional liquid-phase amine systems, solid-supported amines (SSAs) have emerged as effective capture agents in assisting the hydrogenation reaction.^[3] This study showcases the efficacy of incorporating highly porous SSAs in the form of diamine-functionalized metal-organic frameworks (MOFs) to enhance CO₂ conversion to methanol at a low partial pressure of 2 bar.

Utilizing the ruthenium PNP-pincer complex Ru-Macho-BH (RuH(BH₄)(CO)(Ph₂PCH₂CH₂NHCH₂CH₂PPh₂)) as the catalyst, the introduction of MOF Mg₂(olz) (olz⁴⁻ = (*E*)-5,5'-(diazene-1,2-diyl)bis(2-oxidobenzoate)) functionalized with *N,N'*-diethylethylenediamine resulted in a sixfold increase in methanol production compared to its homogeneous counterpart. Through a series of spectroscopic investigations and time-resolved experiments, we aimed to elucidate the multifunctional role of the MOF that impacts both the CO₂ capture and the catalytic conversion processes.

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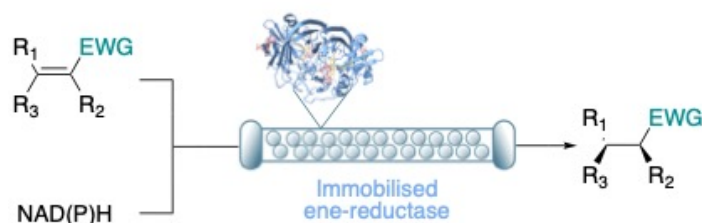
Insights into reduction of activated double bonds in flow using ene-reductases

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The increasing demand for enantiopure molecules in the fine-chemical and pharmaceutical industry requires well-characterised, efficient and stable catalysts. One of the most widely used industrial reaction to access chiral compounds is the asymmetric reduction of alkenes. While this field is still dominated by transition metal catalysis,^[1] biocatalytic hydrogenation catalysed by ene-reductases (ER) can offer a more sustainable alternative. These flavin-dependent enzymes are indeed able to catalyse the stereoselective reduction of activated C=C bonds at the expense of a nicotinamide cofactor.^[2]

Although ER have been intensively studied and significant progress have been made over the past few decades,^[2] examples of immobilisation of these enzymes and their applications in flow biocatalysis are scarce.^[3-5] In an attempt to intensify ene-reductases catalysed processes, we rationally immobilised three different enzymes on solid supports with good to excellent yields (67-100 %) and various recovered activities (from 20% up to 106 %). Moreover, we reported an increase in thermal stability up to 30x, which can be desirable to enhance the solubility of organic compounds. These encouraging results triggered the ongoing substrate scope investigations of biocatalytic reductions in flow. Herein, we therefore present a systematic study of ene-reductase catalysed flow bioprocess as a versatile tool for improved process productivity and sustainability, which can be of great utility for the sustainable production of valuable building blocks,^[2] fragrances,^[6] and pharmaceuticals.^[7]



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Phosphine activity descriptors for palladium single-atom heterogeneous catalysts in cross-couplings

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Single-atom heterogeneous catalysts (SACs) have gained increasing interest over the past years, due to their great potential to render the production of fine chemicals more sustainable and allow for exclusive insights into surface-catalyzed transformations.^[1] Precisely designed active sites enabled SACs to exhibit activities rivaling homogeneous catalysts.^[2] However, while much effort is spent on active site tailoring during catalyst synthesis, possibilities for in-situ manipulations by adding suitable compounds have yet to be explored. Here, we investigate the effect of organophosphorus(III) compounds on the performance of a palladium SAC in a prototypical example of the Sonogashira-Hagihara (SH) cross-coupling (Figure 1a). By monitoring product formation in the presence of a pre-selected set, representative of the chemical space of phosphines, we identify a complex combination of multiple properties affecting SAC activity. While strongly governed by steric features (Figure 1b), electronic properties lead to a rift between different phosphine classes (Figure 1c). Demonstrated in the SH coupling, our results underscore the opportunities these materials hold for fine chemical synthesis and will aid future work regarding SACs in cross-coupling reactions in general.

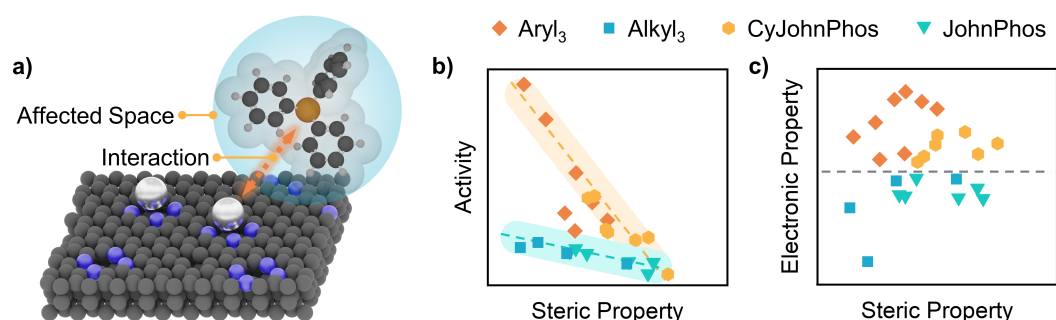


Figure 1 a) 3D visualization of a phosphine interacting with a spatially isolated palladium single-atom on the surface of a nitrogen-doped carbon carrier (Pd₁@NC), affected by steric properties of the phosphine. b) Activity of the as-prepared Pd₁@NC in the presence of the phosphine classes investigated in this work and c) their respective electronic feature plotted against a steric property.

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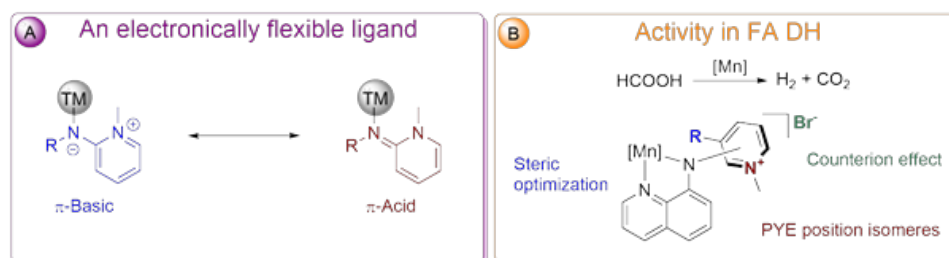
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Manganese complexes bearing bidentate PYE ligands for formic acid dehydrogenation

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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 remains challenging. 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. Our group recently reported a state-of-the-art iridium complex bearing a O-functionalized pyridylidene-amine (PYE). The PYE moiety features unique donor flexibility (Fig. 1A) known to impart high catalytic activity, *e.g.* in olefin oxidation. Given the growing interest in using more abundant transition metals, we sought to develop manganese complexes bearing a PYE moiety for catalysing FA dehydrogenation. Here we will present bidentate manganese(I) complexes containing a PYE moiety that are active in FA dehydrogenation catalysis (Fig 1B). We will discuss the role of the bidentate PYE ligand on catalytic performance, including electronic and steric effects, as well as mechanistic insights using both thermodynamic and kinetic investigations.



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Defects in Metal Oxides and their Effects on CatalysisA. M. Rösch¹, V. Wyss¹, M. F. Delley^{1*}¹University of Basel, Mattenstrasse 22, 4002 Basel

The presence of defects is often thought to enhance the activity of heterogeneous catalysts, for instance by serving as adsorption sites for substrates or by tuning the electronic structure of the catalyst.^[1-2] However, elucidating the role of defects in catalysis remains challenging. State-of-the-art methods for generating defects on the surface rely on harsh conditions such as elevated temperatures, argon plasma treatment or H₂-reductions.^[3,4] Such preparation methods introduce multiple types of defects that could exhibit different reactivity during catalysis. Furthermore, spectroscopic signatures that are put forward as evidence for defects in heterogeneous catalysts are often controversially discussed.^[5,6] Deriving quantitative relationships between the amount of defects and an improvement of catalytic activity is hence extremely difficult using conventional preparation methods and has only been achieved in specific cases, for instance with a Pd-In₂O₃-ZnO₂ catalyst.^[7] Thus, new methods for a more directed introduction of defects on heterogeneous catalysts need to be developed in order to understand and use defects in catalysis.

Here, we describe a mild chemical method to introduce defects into metal oxides in a more selective way. Spectroscopic analysis of the defective materials enabled tracking the defects in the materials. We then studied the effect of defects in metal oxides in epoxidation catalysis by comparing the catalytic performance of the materials with defects to the defect-free materials. Our work shows that the presence of defects clearly enhances epoxidation catalysis by metal oxides and opens new opportunities for quantitative structure-reactivity relationships with defects. This may accelerate the development of new highly active catalytic materials.

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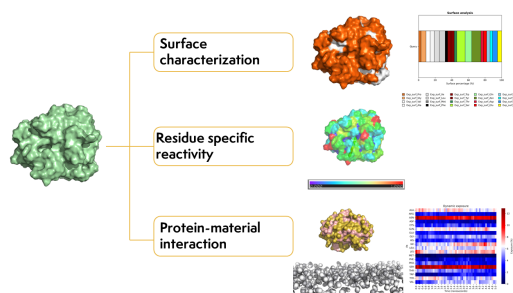
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Data-driven tools for enzyme immobilization - auxiliary enzymes are case studyD. Roura Padrosa¹, C. L. Fernández Regueiro¹, V. Marchini¹¹InSEIT AG, Freiestrasse 3, 3012 Bern (Switzerland)

Industrial biocatalysis continues to evolve with the integration of computational biology and *in silico* methods, which aid in the discovery and optimization of biocatalysts.¹ From the storing and deciphering of vast amounts of genetic data, to the design and study of macromolecules such as proteins, all fields have benefited from this revolution.² In the field of enzyme engineering, for example, continuous development of novel tools and better algorithms for the evolution of enzymes. However, there were no bioinformatic tools for enzyme immobilization. Here, we present a case-study on the use of novel bioinformatic tools for the design and optimization of immobilized biocatalysts. The bioinformatic tools allow the study of the surface, the reactivity, and the dynamics of the enzyme to be immobilized, identifying the desirable attachment points on the protein structure.³ Moreover, through basic analysis of the material used to immobilize we can match material and enzyme to ensure the maximum performance of the final immobilized biocatalyst.



We have applied these tools to a set of auxiliary enzymes for cofactor recycling, peroxide detoxification and protein/peptide degradation. With these set of enzymes and in combination with our bioinformatic tools, we can obtain up to 10x increase in activity compared to the previous literature and in most cases, the enzymes show increased stability and can be reused for more than 3 cycles with no apparent loss of activity.

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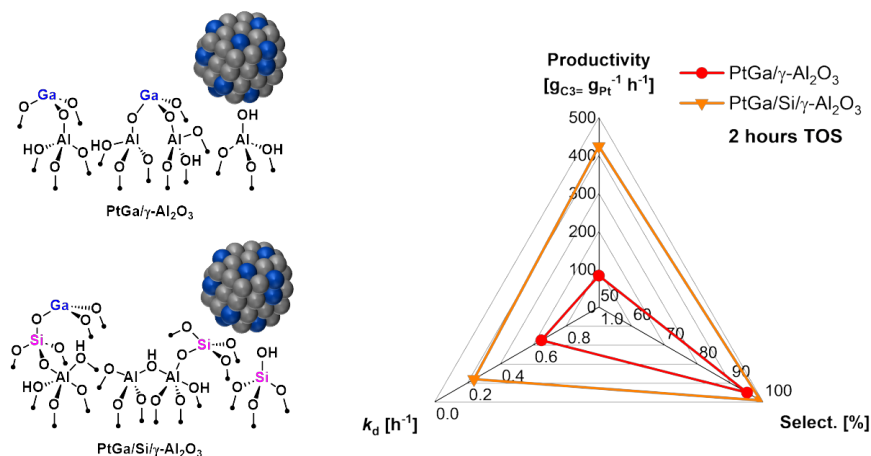
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Promotional Effects of Si Addition to Alumina-based Pt-Ga Systems on Catalyst Stability for Propane Dehydrogenation Reaction

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The further developments of propane dehydrogenation (PDH) catalysts with high productivity, selectivity and stability have been demanded due to large scale exploration of shale gas.¹⁻³ In industrial scale of propene production, two of major catalyst families, Cr₂O₃/Al₂O₃ (Lummus Catofin process) and Pt-Sn/Al₂O₃ (UOP Oleflex process), have been developed; both of them require constant regeneration in order to maintain high productivity. For Pt-based PDH catalysts, dopants (promoters), such as Sn and Ga, play an essential role to improve the catalyst stability and productivity. In order to understand the effects of dopants at a molecular level, the preparation of PDH catalysts with well-defined surface sites using surface organometallic chemistry (SOMC) is a powerful approach to develop structure-property relationships based on detailed characterization by spectroscopic and microscopic techniques.^{4,5} Considering the recent development of alumina-supported Pt-based industrial catalysts promoted by Ga and Si,² we have developed SOMC approach to obtain model catalytic systems. Herein, we have found in particular that Pt-Ga systems on Si doped alumina prepared *via* SOMC technique show indeed higher catalyst stability for PDH reaction than Pt-Ga systems on alumina. Although STEM-EDX and XAS results indicate that initial structures on both supports are similar, post analyses reveal that Si doping makes Pt-Ga systems much more stable under PDH reaction condition.



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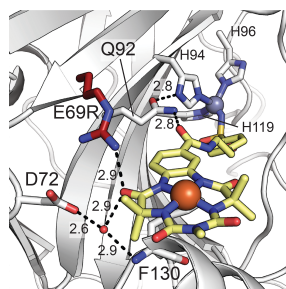
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Directed Evolution and Modification of an Artificial Hydroxylase Based on a Thermostable Human Carbonic Anhydrase

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The assembly of artificial metalloenzymes provides a second coordination sphere around a metal catalyst. Such a well-defined microenvironment can lead to enhancing the activities and selectivity of the catalyst. Herein, we present the development of artificial hydroxylase (ArHase) by embedding a Fe-TAML (TAML = Tetra Amide Macrocyclic Ligand) catalyst into a human carbonic anhydrase II (hCAII). Incorporation of the Fe-TAML catalyst ([BS-Fe-bTAML]⁻) within hCAII enhanced the Total TurnOver Number (TTON) for the hydroxylation of benzylic C–H bonds. After engineering a thermostable variant of hCAII (hCAII^{TS}), the resulting ArHase, [BS-Fe-bTAML]⁻ · hCAII^{TS}, was subjected to directed evolution using cell lysates in a 384-well format. Through three rounds of laboratory evolution, the best-performing variants exhibited 36-fold enhancement in the initial rate and 2.8-fold enhancement in the TTON for the hydroxylation of benzylic C–H bonds.



Frequently, flexible loop regions significantly affect the activity and selectivity of (metallo)enzymes. To mimic these, we introduced a set of rationally-designed motifs with a length of 22 to 51 amino acids inserted into the protein scaffold of hCAII^{TS}. Investigation of the catalytic activity of the modified ArHases revealed an up to 1.55 fold improvement of TTON while maintaining increased thermostability. This study highlights the potential of relying on a thermostable host protein to improve the catalytic performance of the hCAII-based ArMs and the introduction of additional structural motifs for further engineering efforts.

Organic Groups on a Transition Metal Phosphide Catalyst Tune Hydrogenation ReactionsY. Shen¹, M. F. Delley^{1*}¹University of Basel, Mattenstrasse 22, 4058 Basel

Hydrogenations are important reactions for the industrial production of fine chemicals. For these reactions typically rare and expensive noble-metal based catalysts are used. Transition metal phosphides (TMP) offer promising alternative hydrogenation catalysts as these materials are more earth-abundant and show high catalytic activity.^[1-2] Surface functionalization of heterogeneous catalysts has been shown to be an effective method to tune catalytic properties.^[3] However, for transition metal phosphides such surface modification approaches are mostly limited to heteroatom doping methods at this point, though a few isolated reports foreshadow the potential of organic functionalization for these materials.^[4-6] The range of possible organic surface functional groups on TMP is quite limited, though, which hinders a fundamental understanding of the operative effects on catalytic properties. Therefore, the development of novel functionalization strategies for TMP catalysts and fundamental insight into the impact of surface-bound functional groups on catalysis is required to render rational catalyst design for these more earth-abundant materials possible.

Herein, we discuss a versatile approach for functionalizing cobalt phosphide (CoP) with a range of organic modifiers. The successful modification of CoP was shown by combined X-ray photoelectron spectroscopy (XPS), elemental analysis, and thermogravimetric analysis (TGA). We then tested both the bare and modified materials as catalyst for the hydrogenation of α , β -unsaturated aldehydes and compared their performances. A systematic series of organic functional groups with varied steric and electronic properties enabled elucidating the relationship between catalytic performance and the surface chemistry of functionalized CoP. Our work provides a new method for the covalent modification of CoP with organic groups and provides a route to adjust catalytic properties by modulating surface functional groups.

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Atomically dispersed palladium-platinum catalysts from defined precursors

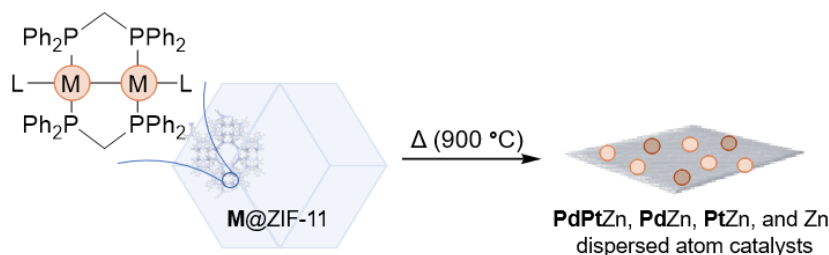
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Atomically dispersed single, double, and cluster catalysts combine the separability of heterogeneous catalysts with the tunability and single-site nature of homogeneous catalysts.^{[1],[2]} However, their synthesis can be challenging, and limited options exist for the controlled formation of mixed-metal sites.^[3]

In this work, PdPt complexes were investigated as precursors to single/double atom sites. A zinc-based zeolitic imidazolate framework (ZIF) approach was employed,^[4] and the precursors' increased solubilities over simple Pd and Pt salts, and ability to be directly incorporated into the ZIF framework, provided an effective route to isolated metal sites.

Catalyst testing was carried out, including high-throughput screening at the SwissCat+ platform at ETH Zurich to understand the influences of the Pd, Pt, and Zn atoms under different conditions.



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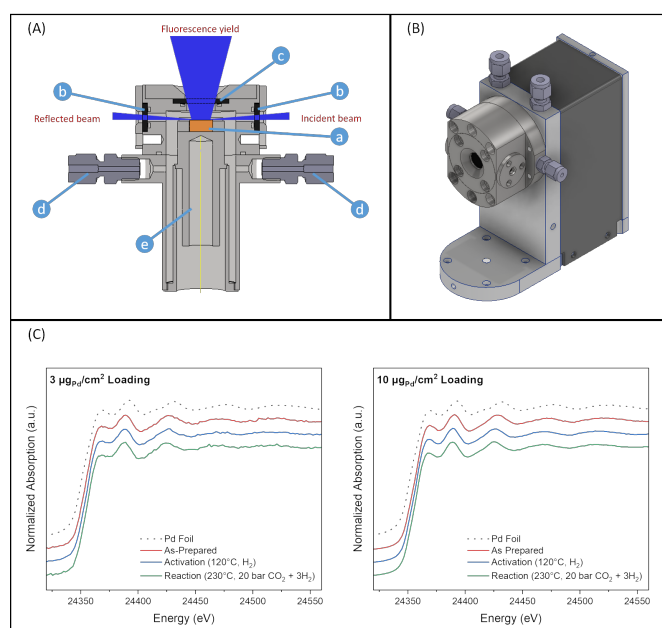
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High-Pressure Grazing Incidence Cell for In Situ XAS Characterization of Nanoparticles on Planar Substrates under CO₂ Hydrogenation Conditions

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Well-defined model catalysts studied under realistic CO₂-to-methanol hydrogenation conditions offer structure-activity insights, which enables a more profound understanding and a better design of methanol synthesis catalysts. In contrast to conventionally prepared catalysts, physical synthesis methods such as cluster beam deposition (CBD) can produce model nanoparticles of precise atomic structure and composition [1]. Depositing such nanoparticles on various planar substrates at very low metal loadings (0.1 – 10 μg/cm²) provides an opportunity to understand particle size's effects and the catalyst's support on the reactivity. However, such model catalysts also present a challenge for *in situ* structural characterization using bulk-sensitive methods, such as X-ray absorption spectroscopy (XAS), since they are optimized for studying catalysts with about three to four orders of magnitude higher metal loading [2]. To address this, we have developed a grazing incidence (GI) *in situ* XAS cell that enables the study of the structure of these model catalysts under CO₂-to-methanol hydrogenation conditions at relevant temperatures and pressures. We have successfully measured *in situ* XAS data for nanoparticles deposited on flat substrates using fluorescence detection. In particular, we obtained high-quality Pd K- and Au L₃-edge XAS data in 30-60 min for Pd and Ag_{0.7} Au_{0.3} nanoparticles with ca. 2.5 – 10 μg/cm² loading at 230°C temperature and 20 bar pressure of reactive gases (CO₂:3H₂:Ar). With this proof-of-concept, we now intend to investigate innovative bimetallic systems produced by gas-phase cluster deposition and contribute to a rational design of CO₂ hydrogenation catalysts.



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The role of metal nanostructure in ceria-supported catalysts for ammonia oxidation to nitrous oxide

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Nitrous oxide, N₂O, is a mono oxygen donor, offering an attractive solution to the challenge of selective oxidations and unlocking new paths towards more efficient manufacture of an array of bulk chemicals.^[1] Still, its high cost, resulting from the conventional production via ammonium nitrate decomposition, precludes industrial implementation. Ammonia, NH₃, oxidation to N₂O, a more facile and direct process, is a promising alternative, but necessitates the development of suitable catalysts. Recently our group has put forward an effective strategy for generating stable and selective catalysts using ceria, CeO₂, as a redox-active support. This led to the development of single-atom catalysts based on Mn and Cr, establishing the co-catalytic role of CeO₂ as a facilitator of oxygen supply, and setting new benchmarks of N₂O productivity.^[2,3] However, to derive robust and general guidelines for the design of NH₃ oxidation catalysts to N₂O, comprehensive studies into the effect of metal and support nanostructure on catalytic performance are required.

In this work we systematically assess the effect of changing the metal speciation (by varying metal content) and CeO₂ properties (by varying calcination temperature) on catalytic performance of supported Mn and Cr catalysts. The properties of CeO₂ influence the performance of all catalysts, reflected in a loss of N₂O selectivity and activity due to a decreased surface reducibility when the support is calcined at higher temperature prior to metal deposition (**Fig. 1a**). Conversely, we uncover a remarkable insensitivity of Mn-based systems to metal nanostructure, reaching identical N₂O selectivity with single-atom and nanoparticle-based systems (**Fig. 1b**). This contrasts strongly with Cr-based systems, which only attain high N₂O selectivity in atomically dispersed form, emphasizing the unique synergy that emerges when Mn and CeO₂ are in contact, regardless of metal content. This phenomenon is attributed to the highly reducible nature of MnO_x, which allows it to cooperate with CeO₂ and enable efficient transport of oxygen for the reaction proceeding via a Mars-van Krevelen mechanism (**Fig. 1c**).

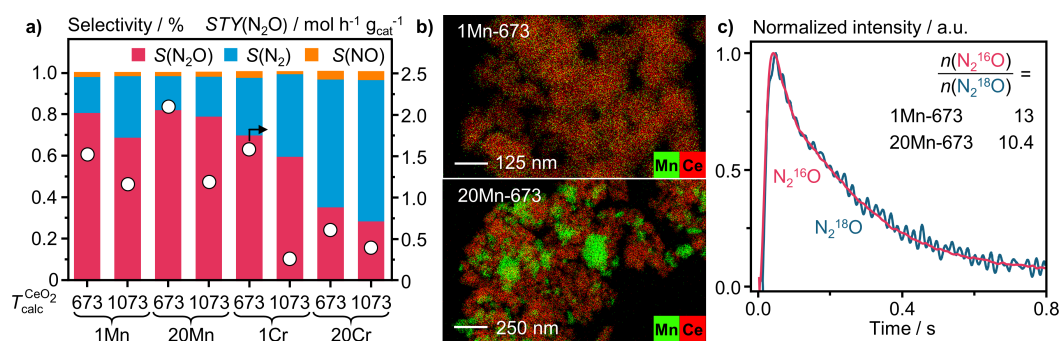


Fig. 1a Catalytic performance of selected CeO₂-supported Mn- and Cr-based systems. **b** Elemental mapping of selected Mn catalysts. **c** Transient responses upon pulsing an equimolar Ar, NH₃, ¹⁸O₂ reaction mixture over Mn catalysts in a temporal analysis of products (TAP) reactor.

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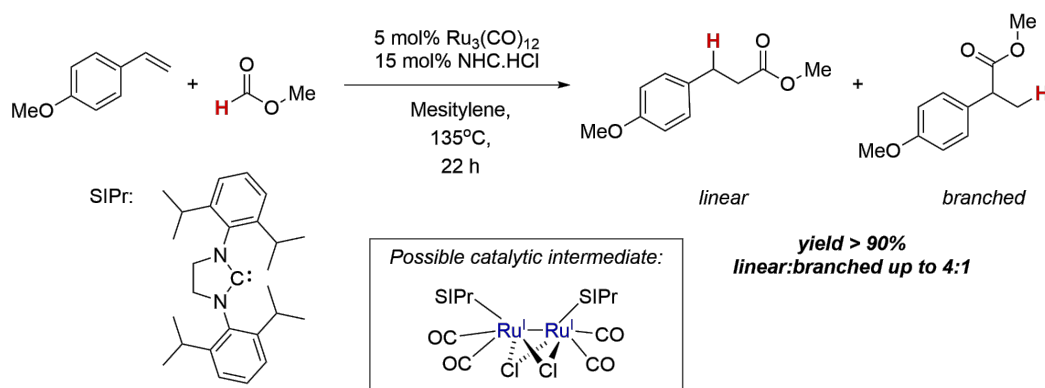
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Ru-NHC Complexes for the Hydroesterification of Alkenes

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Current industrial methods for the production of chemical feedstocks are dominated by petrochemicals. In particular, toxic CO gas is used in considerable number of C-C bond forming reactions. Methyl formate is a potential CO surrogate that can be obtained sustainably from CO₂, green hydrogen, and green methanol. Hydroesterification of alkenes using formate esters is an atom economic route to C-C bond formation, without the need for additional CO gas.^[1] In particular, the synthesis of adipic acid, one half of nylon-6,6, is a valuable chemical feedstock currently produced only from petrochemicals. The efficient synthesis of dimethyl adipate from methyl formate and 1,3-butadiene, would be of immense value.

We have investigated the use of N-heterocyclic carbene (NHC) ligands to improve activity of ruthenium carbonyl catalysts for the hydroesterification of alkenes, and the selectivity towards linear products. An initial screening of different NHCs identified saturated SIPr.HCl to be the most active and selective in the hydroesterification of 4-vinylanisole. Preliminary mechanistic studies suggest an NHC-Ru(I) dimer to be a possible catalytic intermediate, as the NHC-Ru(0)(CO)₄ catalysts result almost exclusively in hydrogenation of the alkene.^[2]



Further investigations into hydroesterification of other alkene substrates, including 1,3-butadiene, will be described, as we progress towards the sustainable and selective synthesis of C₂₊ products from atmospheric carbon.

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Understanding and controlling activity and selectivity patterns of Pd₁@C₃N₄-catalyzed Suzuki-Miyaura couplingsM. Usteri¹, G. Giannakakis¹, A. Bugaev², J. Pérez-Ramírez^{1*}, S. Mitchell^{1*}¹ETH Zürich, ²Paul Scherrer Institut

Single-atom heterogeneous catalysts (SACs) have been proposed as sustainable alternatives to molecular palladium complexes in cross-coupling applications due to their improved metal recoverability.^[1] Despite their potential, the surface-catalyzed mechanisms and reactivity patterns of SACs, especially in directing cross-coupling over homocoupling, remain poorly understood. Additionally, the role of phosphine ligands and the optimal properties of carriers for high yields are still fundamental questions. To advance property-performance relationships, here we report a kinetic and mechanistic study of the Suzuki-Miyaura coupling (SMC, **Fig. 1a**), a key reaction for constructing C-C bonds, over a Pd₁@C₃N₄, the first SAC with a well-defined coordination environment reported for this reaction.^[2] Our study reveals that optimizing the interplay between base strength, solubility, and surface wetting is crucial for mitigating mass transfer limitations in the triphasic reaction system (**Fig. 1b**). High selectivity is achieved by minimizing the competitive coordination of bases and ligands to the Pd centers (**Fig. 1c**), which influences reaction pathways for the formation of undesired products. In-situ X-ray absorption spectroscopy (XAS) evidences the electronic structures and coordination environments of Pd sites, uncovering the roles of base and ligand coordination in activating Pd sites. The insights enable us to design selective ligand-free reaction pathways by choosing solvents and bases that fulfill the ligand function (**Fig. 1d**). Our findings highlight the importance of mechanistic studies to distinguish specificities of SACs compared to other catalytic systems.

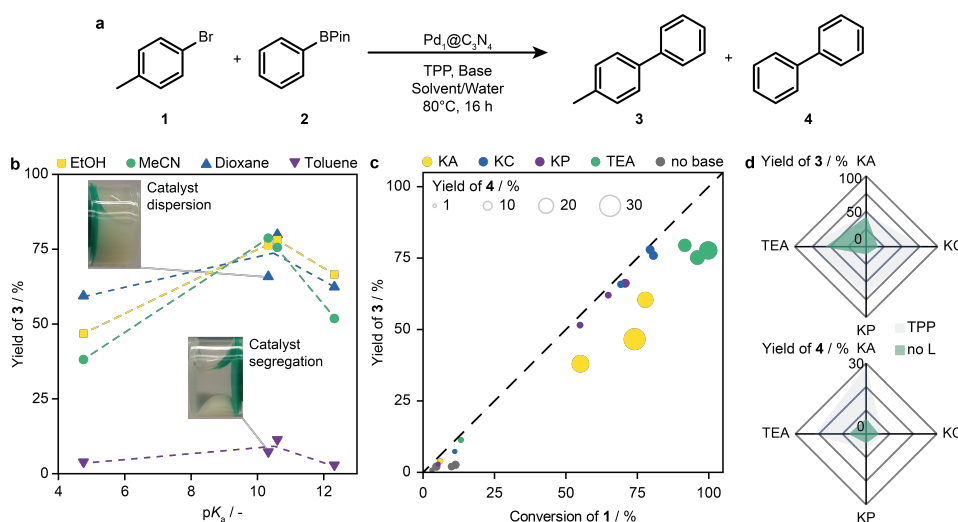


Fig. 1a SMC studied over Pd₁@C₃N₄. **b** Product 3 yield versus base pK_a in water for each solvent. Insets show the catalyst dispersion in K₂CO₃-containing solvent mixtures. **c** Conversion-yield map of the tested base-solvent combinations. **d** Effect of the absence of triphenyl phosphene (TPP) on product yields in ethanol.

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Epoxidation of Olefins by Cobalt Sulfide and its Parallels to Oxygen Evolution Reaction Electrocatalysis

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Electrocatalysis and thermal catalysis share many fundamental principles but exhibit large differences in their typical reaction conditions. This contrast makes it challenging to leverage knowledge across the two subfields in catalysis. However, the known electrocatalytic properties of earth-abundant materials may facilitate the search for new catalytic applications of these materials in thermal reactions. For example, cobalt sulfide (CoS_x) has shown high activity for the electrocatalysis of the oxygen evolution reaction (OER). We speculated that CoS_x may also catalyze the epoxidation of olefins since both OER and epoxidations involve an interfacial oxygen transfer. This poster describes our discovery of the thermal catalysis of CoS_x for the epoxidation of olefins. CoS_x has higher catalytic activity than other Co-based bulk materials showing a similar activity pattern as in OER electrocatalysis. Combined mechanistic studies and detailed spectroscopic analysis of the spent materials provided insight into the epoxidation mechanism on Co-based materials and showed interesting parallels to key surface intermediates on Co-based materials in electrocatalytic OER. We speculate that the easy formation of these key intermediates are responsible for the high catalytic ability of CoS_x for epoxidation catalysis and perhaps also for electrocatalytic OER. Our work underlines the use of taking inspiration across different fields of catalysis to identify the potential of earth-abundant materials for new catalytic applications.

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Directed dual charge pumping tunes the d-orbital configuration of Pt cluster boosting hydrogen evolution kineticZ. Zhang¹¹Department of Chemistry, University of Zurich, Winterthurerstrasse 190, Zurich, CH-8057 Switzerland

Achieving high catalytic activity with a minimum amount of platinum (Pt) is crucial for accelerating the cathodic hydrogen evolution reaction (HER) in proton exchange membrane (PEM) water electrolysis, yet it remains a significant challenge. Herein, a directed dual-charge pumping strategy to tune the d-orbital electronic distribution of Pt nanoclusters for efficient HER catalysis is proposed. Theoretical analysis reveals that the ligand effect and electronic metal-support interactions (EMSI) create an effective directional electron transfer channel for the d-orbital electrons of Pt, which in turn optimizes the binding strength to H*, thereby significantly enhancing HER efficiency of the Pt site. Experimentally, this directed dual-charge pumping strategy is validated by elaborating Sb-doped SnO₂ (ATO) supported Fe-doped PtSn heterostructure catalysts (Fe-PtSn/ATO). The synthesized 3%Fe-PtSn/ATO catalysts exhibit lower overpotential (requiring only 10.5 mV to reach a current density of 10 mA cm⁻²), higher mass activity (28.6 times higher than commercial 20 wt.% Pt/C), and stability in the HER process in acidic media. This innovative strategy presents a promising pathway for the development of highly efficient HER catalysts with low Pt loading.

Design of technical ZnO/ZrO₂ catalysts for green methanol synthesisT. Zou¹, T. P. Araújo¹, M. Agrachev¹, X. Jin¹, F. Krumeich¹, G. Jeschke¹, S. Mitchell¹, J. Pérez-Ramírez^{1*}¹ETH Zurich

Mixed zinc-zirconium oxides have recently emerged as promising catalysts with selectivity and stability advantages in CO₂ hydrogenation to methanol, as developmental efforts mainly rely on coprecipitation (CP) or flame spray pyrolysis (FSP) synthesis methods that commonly feature atomic zinc dispersion in optimal architectures.^[1] While impregnation methods are ubiquitous for dispersing active phases on carriers for numerous catalytic applications, reported efforts usually result in large and inactive ZnO nanoparticles or other poorly-defined architectures, leading to uncompetitive performance compared to CP- and FSP-made counterparts.^[2]

Herein, we revisit impregnation to produce ZnO/ZrO₂ catalysts in technical form by targeting maximal surface zinc dispersion with controlled speciation. By tuning the catalyst formulation, we identify 5 mol% Zn supported on a commercial monoclinic zirconia carrier (5ZnO/ZrO₂) with the highest surface area to maximize both zinc dispersion and methanol productivity. The ability of ZrO₂ to host isolated zinc species was governed by its surface area, a key performance descriptor (**Fig. 1a**). Operando XAS and in situ EPR spectroscopy studies demonstrated the retention of atomically dispersed Zn throughout the reaction with facile generation of nearby oxygen vacancies to form the active site under reaction conditions (**Fig. 1b**). The optimal catalyst architecture and performance were largely retained upon translation from powder to technical forms. Guided by kinetic modeling, a methanol space time yield (STY) of 0.73 g_{MeOH} h⁻¹ g_{cat}⁻¹ and selectivity of 75% was attained over the shaped 5ZnO/ZrO₂ technical catalyst with excellent stability (**Fig. 1c**). A uniform zinc distribution was detected throughout the mesoporous shaped body with no deterioration in Zn dispersion due to upscaling (**Fig. 1d**).^[2] These findings represent a crucial step towards industrial adoption of cost-effective, noble metal-free catalysts.

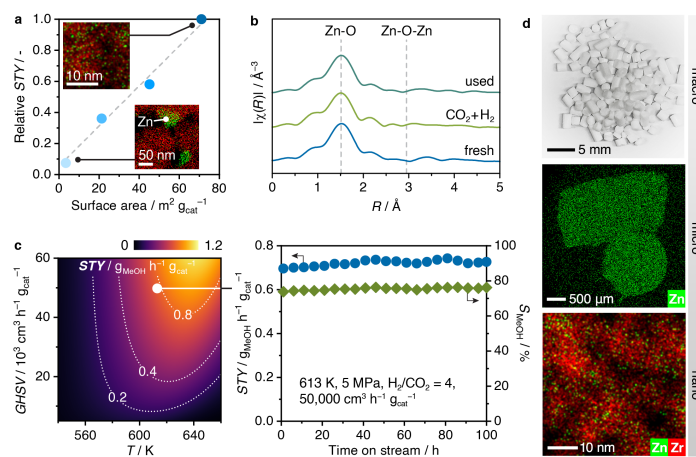


Fig. 1. **a** Effect of surface area on *STY* and zinc speciation of ZnO/ZrO₂ catalysts with 5 mol% Zn. **b** Operando Zn K edge EXAFS of the optimal 5ZnO/ZrO₂ catalyst. **c** Model-predicted *STY* for the technical 5ZnO/ZrO₂ catalyst and stability test at the indicated reaction condition. **d** Photograph and elemental maps of the technical catalyst at different length scales.

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Are Pt-based catalysts always necessary for hydrogen and oxygen recombination reactions?

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Hydrogen-oxygen recombination reaction, also known as catalytic hydrogen combustion (CHC), offers significant potential for efficient and safe power generation and a carbon-free energy cycle. However, conventional H₂ combustion in an open flame mode has drawbacks, such as the drastic risk of flashbacks and NO_x emission. In terms of safety, CHC is an efficient way to mitigate H₂ slip from H₂-involved industrial processes. However, little is known about the catalytic activity of non-precious transition metals (TMs) and their reaction kinetics for the CHC reaction. Our research targets the synthesis, selection, and kinetic analysis of well-dispersed nano-sized catalysts for non-precious metal catalysts for the CHC reaction. Using detailed electron microscopy and spectroscopy methods, we discuss the reason behind the diminished catalytic activity of non-precious metal catalysts. Moreover, the kinetically controlled region was determined using a new data acquisition approach to collect more data points. The activation energy and pre-exponential factor were compared between different catalysts based on the Arrhenius model. This knowledge is highly valuable and facilitates the design of supported catalysts and optimization of the CHC reaction for various applications with different requirements.

Elucidating the mechanism of Fe incorporation in in situ synthesized Co-Fe oxygen-evolving nanocatalysts

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Ni- and Co-based catalysts with Fe as a dopant demonstrate promising activity in the oxygen evolution reaction (OER) during alkaline water electrolysis, with the presence of Fe in a certain quantity being crucial for their enhanced performance¹⁻². The mode of incorporation, local placement, and structure of Fe ions in the host catalyst, as well as their direct/indirect contribution to enhancing the OER activity, remain under active investigation³. Herein, the mechanism of Fe incorporation into a Co-based host was investigated using an in-situ synthesized Co-Fe catalyst in an alkaline electrolyte containing Co^{2+} and Fe^{3+} . Fe was found to be uniformly incorporated as a dopant element rather than as a separate phase, which occurs solely after the anodic deposition of the Co host structure, and results in exceptional OER activity with an overpotential of 319 mV at 10 mA cm^{-2} and a Tafel slope of 28.3 mV dec^{-1} . Studies on lattice structure, chemical oxidation states, and mass changes indicated that Fe is doped into the Co host structure by replacing the Co^{3+} sites with Fe^{3+} from the electrolyte. Operando Raman measurements revealed that the presence of doped Fe in the Co host structure reduces the transition potential of the in-situ Co-Fe catalyst to the OER-active phase of CoO_2 . The findings of our facile synthesis of highly active and stable Co-Fe particle catalysts provide a comprehensive understanding of the role of Fe doping in Co-based electrocatalysts, covering aspects that include the incorporation mode, local structure, placement, and their mechanistic role in enhancing OER activity⁴.

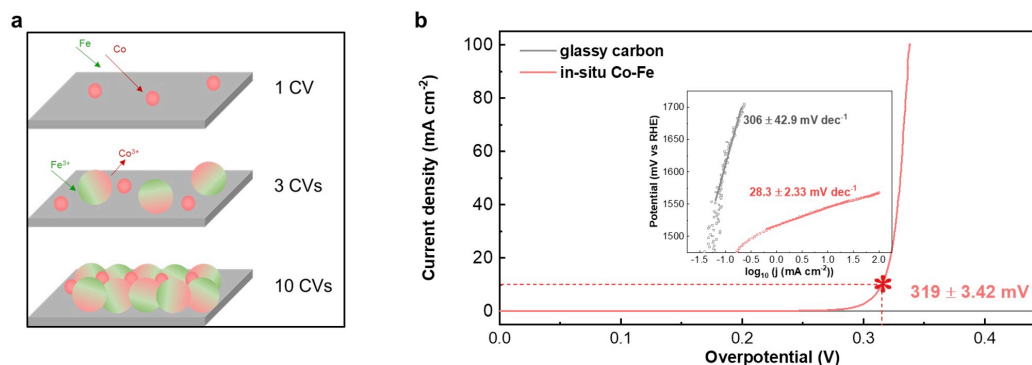


Fig.1 a) Schematic of the in-situ synthesis of Co oxides host-structure and Fe incorporation as anodic cyclic voltammetry was applied. b) Cyclic voltammetry (CV) curves of glassy carbon (GC) in Fe-free KOH and in KOH-CoFe after 10 cycles. Inset: Tafel slopes. The scan range of the CVs were 1.0 to 1.7 V vs RHE and the scan rate was 10 mV s^{-1} .

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