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Biocatalytic Reduction of Six-Membered Ring Heterocyclic Imines in Continuous Flow

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This short talk was included in the program on a short term basis. There is no abstract available.

Visit the website of the Paradisi Group to learn more about David's and the group's research activities:
<https://paradisiresearch.com>

Media-Programmed Electrochemical Divergence: Selective Access to Z-Allylic Alcohols or Allenes through Engineered Micellar Nanoreactors and Surface-Confined Acidic Microenvironments

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Electrochemistry offers new opportunities for sustainable synthesis,^[1] yet controlling divergent outcomes from a single substrate remains challenging.^{[2],[3],[4]} Here, we show that programmed reaction media can dictate electrochemical pathways, enabling propargyl alcohols to selectively form either Z-allylic alcohols or allenes under mild, transition-metal-free conditions.

In aqueous PS-750-M micellar media, electrosemitranshydrogenation delivers Z-allylic alcohols with 100% selectivity. The micellar nanoreactor acts as both a confined reaction environment and an extraction shuttle, suppressing over-reduction and eliminating the need for hydrogen gas, organic solvents, or toxic waste-generating reductants.

In contrast, switching to a non-micellar medium with a catalytic proton source in the bulk medium and proton film at the anode redirects the reaction toward allenes. Under anodic conditions, a surface-confined phosphate film forms to protect the anode from over-reduction, while functioning as a strong Brønsted acid pool that promotes C–O bond activation and selective dehydration–reduction.

These results establish media-programmed electrochemical reactivity as a general design principle, in which engineered microenvironments and electrode interfaces enable divergent synthesis from a common precursor, advancing sustainable and programmable organic synthesis.

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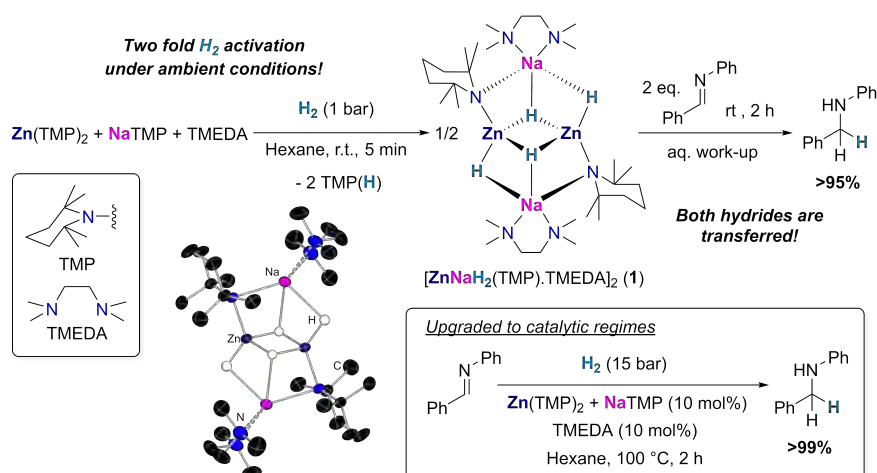
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Sodium Zincate Mediated Dihydrogen Activation and Catalytic Imine Hydrogenation

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The catalytic activation of dihydrogen (H_2) and subsequent hydrogenation of unsaturated substrates is a cornerstone transformation in synthetic chemistry. Once considered the exclusive domain of transition metals, this reactivity has more recently been extended to main group systems, including Frustrated Lewis Pairs² and Group 2 metal amide complexes,³ which have demonstrated the enormous potential of these systems in catalytic applications. By contrast, despite early reports that $nBuLi$ can activate H_2 , the application of Group 1 metal compounds in this field remains very limited, largely due to the formation of insoluble hydride salts $[MH]_{\infty}$.⁴



Breaking new ground in this area, we report the activation of H_2 by combining the highly basic amide NaTMP (TMP = 2,2,6,6 tetramethylpiperidide) with the sterically encumbered $Zn(TMP)_2$. By switching on bimetallic cooperativity, this system can heterolytically cleave H_2 under mild reaction conditions (1 bar, 25 °C, 5 min) to furnish the hydrocarbon-soluble $[NaZnH_2(TMP)TMEDA]_2$ catalyst (**1**). (TMEDA = N,N,N',N' tetramethylethylenediamine) (Figure 1). Furthermore, conducting the reaction in a one-pot fashion enables the reduction of a series of imines to the corresponding amines in high yields. Remarkably, this H_2 activation and hydrogenation reactivity has been upgraded to catalytic regimes, by working under relatively mild reaction conditions (15 bar, 100 °C, 2 h) compared to other zinc based systems.⁵ By combining spectroscopic studies with the isolation of key reaction intermediates and DFT calculations, mechanistic insights on how these transformations take place will be presented, advancing the understanding of this unique Na/Zn cooperation.

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Electrophile Selection: the Key for the Optimization of Tryptophan derivatives synthesisE. Sgroi¹, F. Paradisi^{1*}¹Department of Chemistry, Biochemistry and Pharmaceutical Sciences, University of Bern, Freiestrasse 3 3012 Bern, Switzerland

From drug scaffolds to chemical probes, L-tryptophan plays key roles in biological systems and is increasingly valued in pharmaceutical and synthetic biology applications [1,2]. While tryptophan synthase (TrpS) achieves near-stoichiometric indole : serine ratios, it often requires protein engineering to broaden its substrate scope to non-canonical substrates [3]. *E. coli* Tryptophanase (TnaA), known since the work of Snell (1964) to catalyze L-tryptophan synthesis from indole and serine, offers a wider substrate tolerance [4], but high excess of serine is required. However, L-serine is not the only option, and alternative nucleophiles may offer a better performance. Through a systematic study of the electrophilic component of the reaction, we have identified S-Benzyl-L-Cysteine (SBC) which reduces the required equivalents by 6 fold (to 1:2 ratio), accelerates the reaction rate and enables straightforward product isolation, by exploiting the low solubility of the benzylmercaptan byproduct in the buffer (Figure 1).

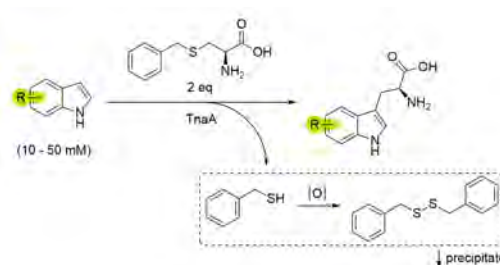


Figure 1. Biosynthesis of L-tryptophan from Indole and S-Benzyl-L-Cysteine.

Combined with an extensive nucleophilic substrate scope across indole derivatives and promising scalability, this work establishes TnaA as a versatile platform for the sustainable production of tryptophan-based pharmaceutical building blocks, offering a competitive alternative to canonical tryptophan synthase systems [5].

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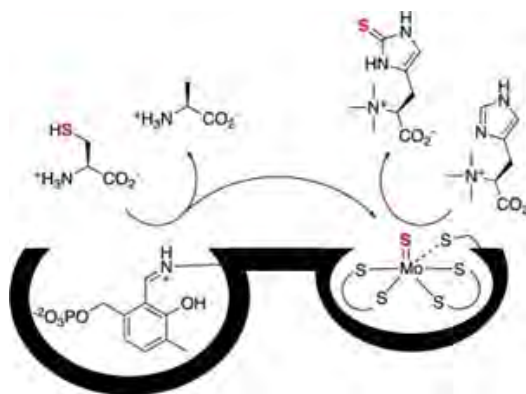
Molybdoenzyme Mediates Carbon-Sulfur Bond Making and Breaking in Ergothioneine Biosynthesis

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Molybdoenzymes are proteins of ancient origins with diverse biological functions, utilizing specific cofactors with molybdenum or tungsten at their centers, commonly referred to as molybdopterin (MPT). Most known molybdoenzymes catalyze stereoselective and regioselective oxidation, dehydroxylation, hydration, and the formation and cleavage of C-O and X-O bond through two-electron transfer mechanism, and have seen potential use in organic synthesis.^[1] We discovered MPT-dependent ergothioneine synthase (MES) as the first reported instance of molybdoenzyme catalyzing C-S bond formation, thereby adding it to the repertoire of enzymatic C-S bond formation.^[2,3] MES from *Caldithrix abyssi* composed of an N-terminal module related to tungsten-dependent acetylene hydratase and a C-terminal cysteine desulfurase. These two modules cooperate to transfer sulfur from cysteine onto trimethylhistidine. However, the complexity of producing molybdoenzyme constrained the preceding study to *in vivo* model.

Here, we present our latest efforts to understand the activity of this class of MPT-dependent enzymes *in vitro*. Our work encompasses production and purification, reconstruction of biocatalytic activity *in vitro*, and an initial look of the MES structure.



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The role of synthesis in tuning Fe speciation in Fe-ZSM-5 toward NO-assisted N₂O decomposition

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Iron-exchanged zeolites are redox-active materials able to activate N₂O, a potent greenhouse gas and environmental pollutant, making them highly relevant in environmental catalytic processes, such as N₂O decomposition [1] and NO-N₂O-SCR [2], and in direct chemical oxidations, such as methane to methanol [3]. The sites capable of N₂O activation in CHA and FER topologies have been identified as isolated iron ions stabilized by six-membered rings of the zeolite framework [1], [2]. However, controlling the iron speciation and distribution by synthesis has proven challenging, as isolated iron ions often coexist with oligomers and particle-like species.

In this work, we studied the influence of the preparation method, post-treatment, and the nature of the iron precursor on the iron speciation and distribution in ZSM-5. Standard characterization and catalytic testing were combined with in situ XAS and EPR spectroscopy to monitor the iron species during pulsed NO-assisted N₂O decomposition experiments.

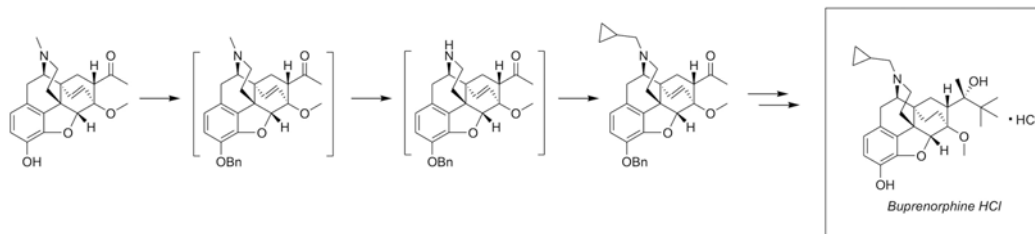
Iron-exchanged ZSM-5 samples were prepared by incipient wetness impregnation (IWI) with iron acetylacetonate (Fe(acac)₃), and by hydrothermal synthesis (HTS) using Fe(NO₃)₃ and Fe(acac)₃. All calcined materials were also exposed to high temperature treatment in Ar flow to promote the redispersion of clustered species into isolated iron ions [3]. This was confirmed by ex-situ DRUV spectroscopy, through a decrease of the oligomer-specific bands. Catalytic testing indicated higher activity of Ar-treated catalysts, with N₂O conversion of ca. 50% at 400 °C, compared to only ca. 23% N₂O conversion for the non-Ar-treated counterparts. This distinct behavior pointed to an increase in active site population for the Ar-treated materials.

Fe K-edge quick-XANES experiments indicated that only a minor fraction of Fe species can accomplish a complete redox cycle $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$. The reversible changes in the pre-edge and rising edge were revealed exclusively through pulsed experiments. EPR spectroscopy experiments further emphasized the differences in the Fe speciation across synthesis procedures and post-treatment. In particular, the IWI-synthesized and Ar-treated material exhibited a strong signal at $g' = 2$, which was previously assigned to contributions from isolated Fe in the α -exchange cationic position and clustered Fe species [4]. Our pulsed EPR experiments (N₂O in NO/Ar at 400 °C) showed the reversible change of the $g' = 2$ signal ($\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$), alongside the $g' = 6$ signal characteristic of isolated Fe sites in six-membered rings (β -exchange cationic position), suggesting that two distinct isolated Fe species interact reversibly with the N₂O/NO system [4]. The absence of the $g' = 2$ signal in the non-Ar-treated counterpart pointed to the role of the post-treatment in fixing the Fe ions in precise cationic positions in ZSM-5. The nature of the iron precursor affected the speciation similarly. By coupling catalytic testing with pulsed in situ spectroscopic experiments, we show that post-treatment and iron precursor type influence Fe speciation in Fe-ZSM-5. These findings contribute to the improved design of catalysts for NO-assisted N₂O-decomposition.

[1] D.C. Cano-Blanco, J.W.A. Fischer, F. Buttignol, I. Alxneit, G. Jeschke, O. Kröcher, D. Ferri, *ACS Catalysis*, **2025**, 15, 17.[2] F. Buttignol, A. Garbujo, P. Biasi, O. Kröcher, D. Ferri, *Journal of the American Chemical Society*, **2025**, 147, 10.[3] M.L. Bols, J. Devos, H.M. Rhoda, D. Plessers, E.I. Solomon, R.A. Schoonheydt, B.F. Sels, M. Dusselier, *Journal of the American Chemical Society*, **2025**, 143, 1624.[4] E. Berrier, O. Ovsitser, E.V. Kondratenko, M. Schwidder, W. Grünert, A. Brückner, *Journal of Catalysis*, **2007**, 249, 67.

Sustainability by Process Design – Development of a 3-Step Domino-Sequence en route to buprenorphineT. Debnar¹, D. Petzold¹¹Siegfried AG, Untere Brühlstrasse 4, 4800 Zofingen, Switzerland, E-Mail: thomas.debnar@siegfried.ch

Buprenorphine, a semisynthetic opioid, is widely used for both pain management and opioid dependence due to its unique pharmacological profile. Acting as a partial agonist at μ -opioid receptors and an antagonist at κ -opioid receptors, it offers a safer alternative to traditional opioids, with reduced risks such as respiratory depression and longer-lasting effects.



A new, second-generation (2G) synthetic process for producing buprenorphine has been developed, significantly improving upon the first-generation (1G)¹ method. This optimized process incorporates an efficient three-step domino sequence, resulting in a higher overall yield (42% vs. 24%), fewer synthetic steps (10 vs. 17), and substantial reductions in raw material use, energy consumption, and waste generation (50% less waste). These advancements enhance both economic and environmental sustainability in buprenorphine production.

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Simultaneous contactless operando conductivity and operando EPR measurements in catalysis

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Heterogeneous catalysts supported on semiconducting oxide materials play a decisive role in governing catalytic performance in reactions such as CO₂ hydrogenation and ammonia oxidation [1,2]. It is widely recognized that oxygen vacancies (Vo) are key active sites, either facilitating reactant activation or enabling oxygen release in Mars-van Krevelen type mechanisms. By using contactless operando conductivity measurements and operando electron paramagnetic resonance (EPR) spectroscopy, we are able to monitor oxygen vacancies in real time under reaction conditions. Operando EPR provides direct insight into the presence of isolated Vo as well as exchange-coupled vacancy-bound polarons during catalysis [3], whereas contactless conductivity measurements reveal relative changes in electronic transport that can be correlated with vacancy dynamics and reaction kinetics [4]. From a catalysis perspective, the simultaneous application of these complementary techniques is highly desirable. However, this approach poses intrinsic challenges: highly conductive samples are typically unsuitable for EPR measurements, while poorly conductive materials do not exhibit measurable changes in conductivity.

In this contribution, I will present our approach to contactless operando conductivity measurements [4], emphasizing the potential of this emerging technique for a broad catalysis audience. I will further discuss selected catalytic model systems that exhibit strong performance in either contactless operando conductivity or operando EPR measurements, thereby demonstrating the complementary strengths of both methods. Building on these examples, I will illustrate how such operando techniques provide valuable insights into heterogeneous catalysis. Finally, I will address the challenge of combining contactless operando conductivity with operando EPR measurements, outlining the inherent limitations, potential strategies to overcome them, and their broader significance for advancing mechanistic understanding in the field.

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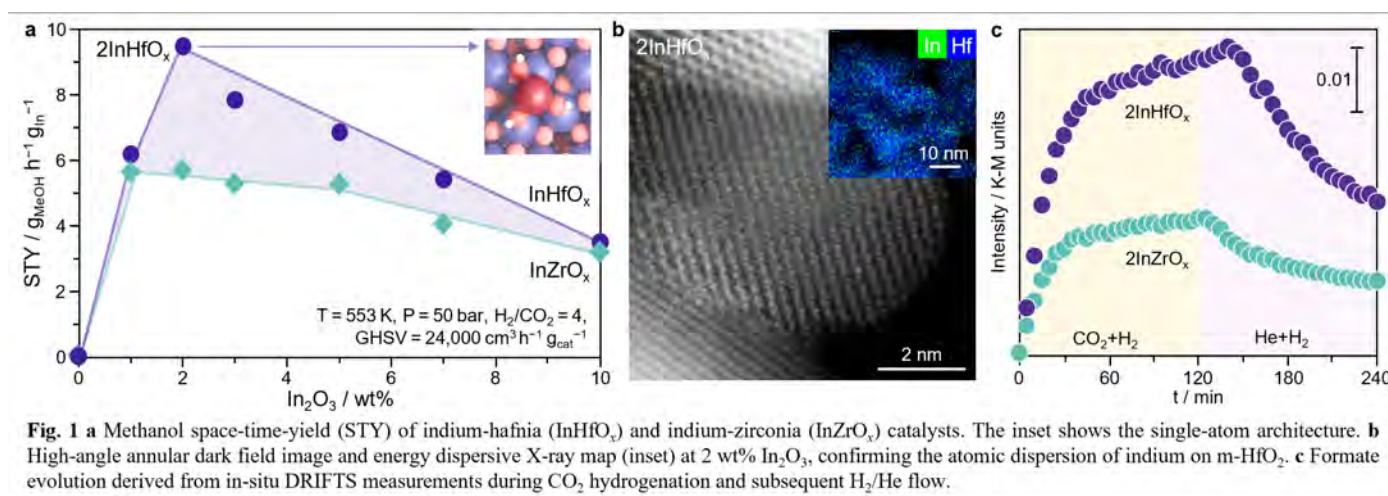
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Single atoms of indium on hafnia enable superior CO₂-based methanol synthesis

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Green methanol synthesis via CO₂ hydrogenation is a promising route to reduce the footprint of chemical and fuel production. While traditional copper-based catalytic systems are highly active, they often suffer from low selectivity and poor stability under CO₂-rich conditions. Since the discovery of indium oxide (In₂O₃) as a highly selective and stable alternative, its combination with monoclinic zirconia (m-ZrO₂) support has stood out as a benchmark system, and no other oxide carrier has matched its promotional effect.^[1] Detailed mechanistic studies suggested that distinct interfacial geometric and electronic interactions govern the exceptional performance and outstanding stability.^[1,2]



Here, we show that monoclinic hafnia (m-HfO₂), a wide-bandgap dielectrics underexplored in heterogeneous catalysis, can surpass this benchmark. Nanostructured indium-hafnia (InHfO_x) systems achieve up to 70% higher indium-specific methanol productivity than indium-zirconia (InZrO_x) analogues (**Fig. 1a**), with the largest gains observed at low In₂O₃ contents (i.e. 2 wt%), where isolated indium sites dominate (**Fig. 1b**).^[3] High-resolution electron microscopy, kinetic analysis, in-situ X-ray absorption and electron paramagnetic resonance spectroscopy, and density functional theory collectively identify single-atom indium sites as the predominant active species. Crucially, m-HfO₂ provides enhanced surface structural stability and mediates redox potential of indium single atoms, enabling a cooperative surface hydride-proton reservoir that promotes CO₂ activation and formate hydrogenation through its wide bandgap (**Fig. 1c**). Extending beyond In₂O₃, we show the promotional effect of m-HfO₂ could be translated into gallium- and zinc oxides via a dual-site mechanism, where the metal centres and support activate H₂ and CO₂, respectively. Our findings establish m-HfO₂ as a powerful support for advancing CO₂-based methanol synthesis, broadening design principles by coupling single-atom catalysis and wide bandgap dielectrics engineering.

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[3] Y.-T. Chiang et al., *Nat. Nanotechnol.*, **2026**, 21, 588.

Pressure-Invariant Formate Intermediacy in CO₂ Hydrogenation over Cu/ZnO/Al₂O₃

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In light of the current environmental crisis, the selective hydrogenation of CO₂ to methanol has been intensively studied to reduce greenhouse gas emissions. The benchmark catalyst for this process, Cu/ZnO/Al₂O₃ (CZA), has received considerable attention from the research community for its dynamic behavior under catalytic conditions (50–100 bar and 200–300 °C), and the mechanistic pathway remains a matter of debate. Previous studies have identified three possible reaction mechanisms: (i) the formate pathway, in which adsorbed and activated CO₂ binds a hydrogen atom *via* the carbon, (ii) the formyl pathway, in which CO₂ is first converted to CO, which in turn is hydrogenated, and (iii) the *trans*-COOH pathway, whereby the hydrogen atom is bound to the oxygen in CO₂. Out of these three proposed mechanisms, the latter is based on theoretical calculations and has yet to be confirmed with experimental evidence.^[1,2]

In this work, we investigate the effect of pressure on the reaction mechanism of CO₂ hydrogenation over the industrial CZA catalyst using combined steady-state isotopic transient kinetic analysis-Fourier-transform infrared (SSITKA-FTIR) methodology. The reactions are performed at five different pressures and the changes are monitored *via* mass spectroscopy (MS, Fig. a), which reveals the quick and irreversible conversion of CO₂. This is supported by the lack of any carbonate species in the FTIR spectra. Formate is identified as the key intermediate across all pressures (Fig. b), confirming the formation of methanol *via* the above-mentioned formate pathway. No characteristic vibrational bands for any of the other proposed intermediates, responding to the isotopic switch from ¹²CO₂ to ¹³CO₂, could be observed. Even below 0.15 bar, where methanol can no longer be detected in the product stream, formate remains present on the surface of the catalyst and responsive to the isotopic switches. The calculated residence times of CO and formate reveal that, at low pressures, the CO₂ to CO conversion cannot follow through a formate intermediate, due to the noticeably shorter residence times of CO. At higher pressures, the similar retention times of CO and formate render it difficult to distinguish between parallel and consecutive pathways (Fig. c). The results of this mechanistic study bring us closer to the intentional design of optimized catalysts for the CO₂ to methanol conversion.

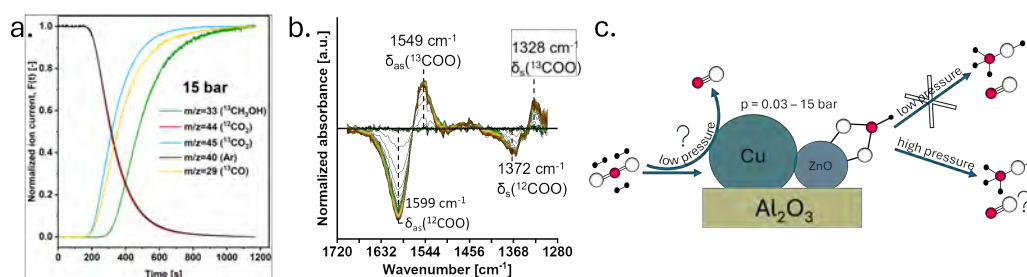


Figure: **a.** Normalized MS response and **b.** difference FTIR spectra acquired at 15 bar during the switch to labelled gas, focused on the formate region; **c.** schematic representation of the mechanistic findings.

[] M. Zabitskiy, V. L. Sushkevich, D. Palagin, M. A. Newton, F. L. Krumeich, J. A. van Bokhoven, *Nat. Commun.*, **2020**, 11:2409

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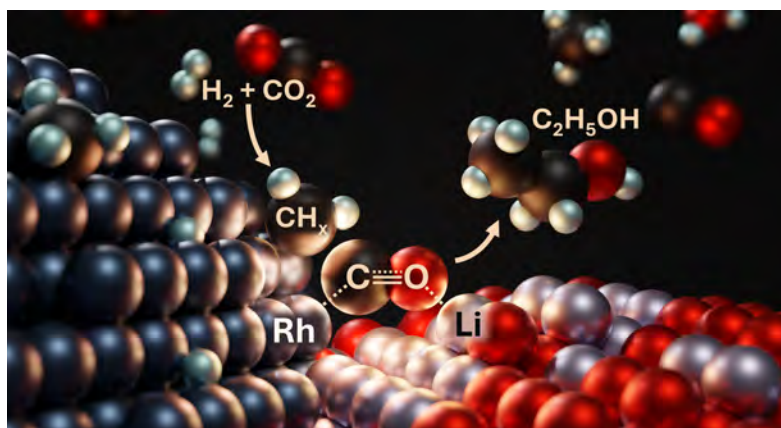
Li-Promotion in Rh-based CO₂ Hydrogenation Catalysts to Ethanol: Enabling Carbon-Carbon Bond Formation at the Interface

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Higher alcohol synthesis from syngas (CO/H₂) has attracted large research efforts in the past decades.^[1] However, the analogous reaction using CO₂ as a feedstock remains relatively underexplored. Due to the net reduction in anthropogenic CO₂ emissions that can be achieved by this approach (provided green H₂ is used), ethanol synthesis from CO₂ has become a highly desirable reaction.^[2] Nevertheless, highly active and selective catalysts for this reaction have remained elusive and poorly understood, and their development presents a formidable task.

By synthesizing well-defined, silica-supported Rh-Li-based catalyst we have improved our understanding of the role of lithium in the formation of ethanol from CO₂.^[3] Using state-of-the-art spectroscopy, such as X-ray absorption spectroscopy, probe molecule infrared spectroscopy and *in-situ* diffuse reflectance infrared spectroscopy, we were able to evidence the presence of an activated CO-species at the interface of metallic Rh and Li⁺ which readily allows the insertion of -CH_x species in the RhLi@SiO₂ system. Complementary computational studies indicate that the insertion of CH_x into CO is drastically facilitated and that the presence of Li⁺ protects -CH_x species from overhydrogenation. The work lays the foundation for deeper understanding of alkali metal promoters in heterogeneous catalysis.



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Enhanced alkene productivity in methanol-to-hydrocarbons conversion using a second catalyst component and hydrogen co-feeds

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Alkenes with three or more carbon atoms (C_{3+}) are essential platform molecules for producing polymers, rubbers, and specialty chemicals, and can also be oligomerized into jet-fuel range hydrocarbons for sustainable aviation fuels (SAFs).[1] Current methanol-to-hydrocarbons (MTH) processes efficiently produce ethene and propene, yet the selective formation of C_{3+} alkenes remains a significant challenge.[2] Unidimensional (1D) zeolites (e.g., ZSM-22, ZSM-23 and ZSM-48) are especially selective for this hydrocarbon fraction, but suffer from rapid catalyst deactivation due to coke deposition.[3] Herein, we introduce a novel multicomponent catalyst (MCC) concept combining a secondary catalyst component with hydrogenating function (e.g., Pd/SiO₂) with the pristine zeolite under ambient pressure H₂ co-feeding. This approach extends catalyst lifetime by up to one order of magnitude, while retaining the inherently high yield of C_{3+} olefins, resulting in a net increase in alkene productivity (**Figure 1a**). The enhancement is maintained across a wide range of H₂ concentrations and Pd/SiO₂:zeolite weight ratios, providing flexibility to minimize both Pd and H₂ use. Kinetic investigations indicate that this effect stems from the selective interception of deactivating intermediates, such as formaldehyde and dienes, curtailing coke-forming pathways. Consistently, *operando* DR-UV-vis spectroscopy (**Figure 1b**) shows that, with H₂, Pd/SiO₂ leads to reduced accumulation of coke species, particularly higher polycyclic aromatics (h-PAHs), ascribed to external coke. Following an induction period, where the system is more hydrogenative, alkene selectivity rises to that of the parent zeolite. *Operando* XAS measurements (**Figure 1c**) indicate that Pd exists as Pd(0) throughout the reaction with no major restructuring, pointing to weaker surface poisoning as the trigger toward milder hydrogenating activity. The drop-in nature of the SCC, together with ambient pressure operation, offers great promise for scalability. Studies are in progress to optimize the Pd speciation within the SCC, and to develop MCC catalysts in technical form.

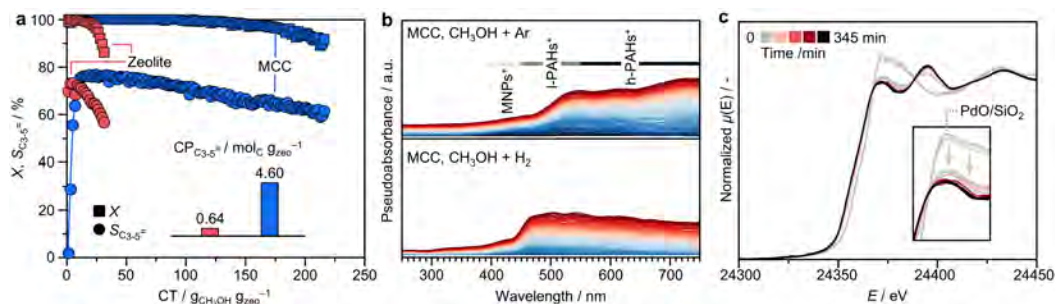


Figure 1. **a** Methanol conversion (X) and selectivity toward C_{3-5} alkenes ($S_{C_{3-5}}$) versus methanol cumulative turnover (CT). The cumulative olefin productivity ($CP_{C_{3-5}}$) is shown in inset. **b** DR-UV-vis spectra acquired during the MTH reaction over the MCC, with/without H₂ co-feed, with band assignments for the main coke species, and **c** Pd K-edge XANES spectra of the MCC acquired during MTH operation.

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Data-Driven Design of High-Entropy Oxides as Multicomponent Catalysts for CO₂ Hydrogenation

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The conversion of CO₂ into value-added chemicals and fuels is a key strategy towards sustainable decarbonization routes and renewable energy storage [1]. However, the development of novel catalytic materials that can simultaneously result in high CO₂ conversion, selectivity and resistance to deactivation under relevant conditions remains as a major challenge. High-entropy oxides (HEOs), composed of at least 5 different metals in a single-phase lattice, have recently emerged as promising materials given their thermal stability, tunable redox properties and unique synergistic effects [2]. In this work, HEOs are tailored for thermocatalytic CO₂ hydrogenation towards optimal methanol yield via a data-driven workflow [3] integrated with automated synthesis, high-throughput catalytic testing and machine-learning iterations to address the vast compositional space. The number of elements was fixed between 5-10 different metals (Al, Mg, Ca, Cr, Fe, Mn, Co, Ni, Cu, Ga, In, Y, Sr, Ce, Ho, Er, Yb), and the high-entropy materials were synthesized with a coprecipitation method in an automated robotic platform, followed by subsequent calcination. Catalytic tests were performed in a 16-fold fixed bed reactor at CO₂ hydrogenation conditions (250-300°C, CO₂/H₂ 1:4 ratio, 34 bar, 40 L.g_{cat}⁻¹.h⁻¹), with a prior activation in H₂ atmosphere at 450°C for 1h. Insights into the catalytic performance using an AI-assisted Bayesian optimizer led to a maximum methanol yield (0.023 mol.g_{cat}⁻¹.h⁻¹) at 300°C after six iterative rounds, comparable to commercial Cu/ZnO/Al₂O₃ catalyst. Hence, this demonstrates the potential of high-throughput experimentation and machine learning to guide the complex design of high-entropy oxide catalysts for selective CO₂ hydrogenation pathways.

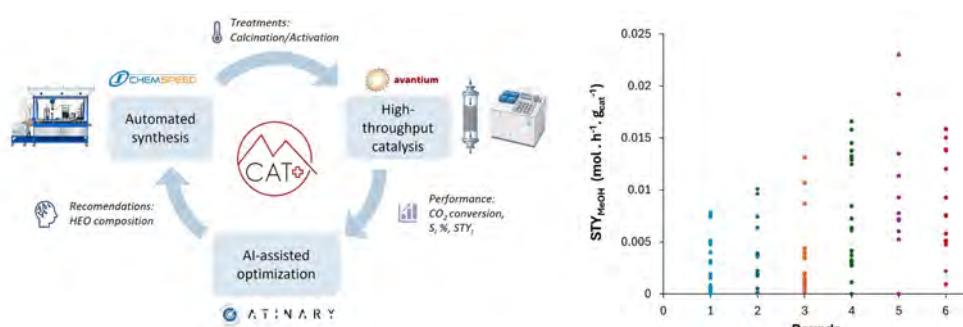


Figure 1. Data-driven design (left) and HEOs catalytic performance (right) from iterative rounds

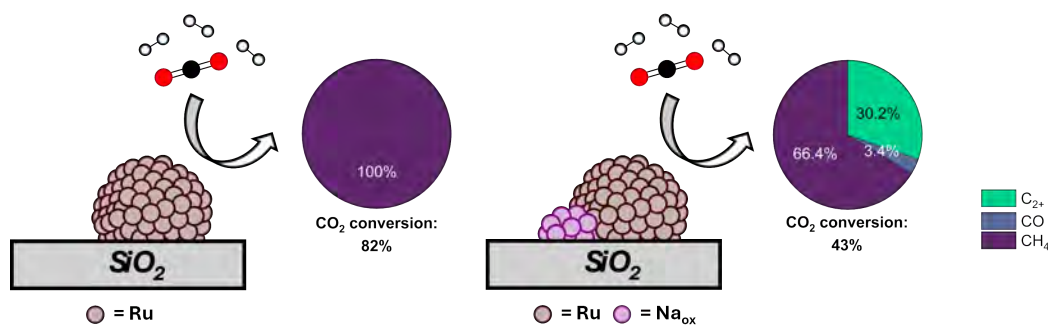
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Conversion of CO₂ to Light Hydrocarbons over Alkali Metal-Promoted Ruthenium Nanoparticles Supported on Silica

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Mitigating the large carbon footprint of traditional chemical processes requires a fundamental shift away from conventional syngas (CO/H₂) feedstocks toward sustainable energy solutions. In this context, carbon capture and utilization (CCU) has emerged as a prominent research field, where CO₂ is transformed into value-added chemicals *via* the use of green or blue hydrogen. Aside from methane and methanol, higher hydrocarbons (C₂₊) are of particular interest due to their wide-spread use as liquid fuels.¹⁻³ However, while the production of higher hydrocarbons from syngas is well established in Fischer-Tropsch Synthesis (FTS), the analogous transformation with CO₂ as feedstock remains underdeveloped. While ruthenium is well-known to be the most active metal for FTS from syngas⁴, exhibiting higher activity, stability and selectivity towards long-chain hydrocarbons, reports on Ru-based systems for CO₂-FTS have been very scarce to date.⁵ In this context, we have studied alkali metal (Li, Na, K, Rb, Cs) doping of silica-supported Ru nanoparticles for CO₂ hydrogenation. Herein, we found that doping of Ru/SiO₂ with Na, K, Rb and Cs leads to a significant increase in the C₂₊ product formation, with Ru-Na/SiO₂ being the most active catalyst. The Li- and unpromoted catalysts on the other hand only produced methane. The reaction is proposed to proceed via a modified FT pathway, where CO is first produced in the reverse water gas shift reaction, followed by C-C coupling to produce higher hydrocarbons.



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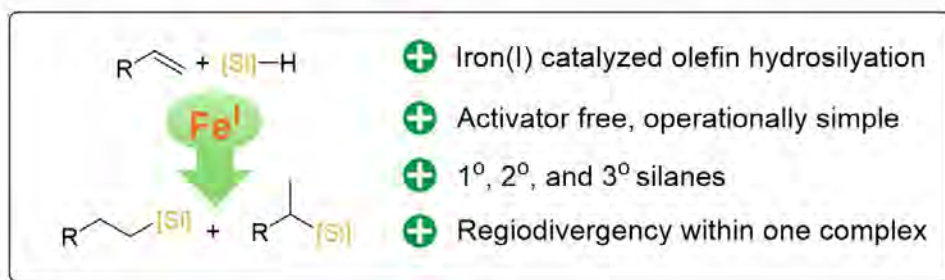
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Unlocking Fe(I) Catalysis: Efficient Hydrosilylation of Terminal Olefins

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Olefin hydrosilylation is an atom-economical reaction used to produce C–Si bonds and represents one of the largest-scale industrial applications of homogeneous catalysis [1]. For decades industrial hydrosilylation has relied on noble metal catalysts, most prominently the platinum-based system developed by Karstedt [2,3]. However, platinum-based hydrosilylation catalysts suffer from high cost, environmental concerns from mining, challenges with metal contamination of products, and undesired side reactions such as alkene isomerization, hydrogenation, and silane redistribution [1,2,4–6].

Herein, we report the first example of iron(I)-catalyzed hydrosilylation of terminal olefins using an isolated low-valent Fe complex without the need for activators. The catalyst efficiently promotes hydrosilylation of terminal aliphatic alkenes with primary, secondary, and tertiary silanes under mild conditions at room temperature, affording anti-Markovnikov products in excellent yields and selectivities. The catalyst also mediates hydrosilylation of styrenes with preferential formation of the Markovnikov product. The Fe(II) analogue, however, is inactive under identical conditions, emphasizing the unique power Fe(I) in this transformation.



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Gold-modified rare earth oxides with tunable lattice oxygen reactivity for N₂O synthesis

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Controlling lattice oxygen reactivity in redox-active oxides is key for catalytic NH₃ oxidation to N₂O, a selective oxidant for organic synthesis.^[1] Still, the long-standing focus on CeO₂ has narrowed exploration of the broader rare earth oxide (REO) family, where systematic variation of cation valence and lattice oxygen reactivity can reveal transferable structure–performance relationships.

Here, we employ flame spray pyrolysis to introduce gold (1 wt% Au) as nanoparticles (NP, ca. 10 nm) across eight REOs (**Figure 1**). In the Au-REO catalysts, N₂O productivity follows support redox activity, rising from trivalent (RE³⁺) to tetravalent (RE⁴⁺) and peaking on mixed-valent oxides. ¹⁸O₂ isotope exchange establishes the activation temperature of oxygen-exchange sites and their homogeneity as the governing selectivity descriptors.^[2] A pioneering operando microwave conductivity approach developed to linking semiconductor response with oxygen-vacancy dynamics reveals that RE cation redox switching (RE³⁺/RE⁴⁺, p-type) governs both the dominant charge carrier and the ease of vacancy formation/healing. The best-in-class catalyst is Au-PrO_x, combining 87% N₂O selectivity at full conversion and long-term stability. By combining operando near ambient pressure X-ray photoelectron and absorption spectroscopies, we identify cationic Au³⁺ over Au-PrO_x as Lewis-acid sites that withdraw electron density from NH₃, facilitating N–H cleavage by lattice oxygen. The Au–O–Pr ensembles promote redox-cooperation between cationic Au species and PrO_x lattice, mediating oxygen transfer to surface NH* species forming short-lived nitroxyl (HNO*) intermediates, the rate-determining step preceding rapid HNO* coupling to N₂O.

These findings introduce a new benchmark for N₂O synthesis and provide general design principles to tune Mars-van Krevelen chemistry across selective oxidations.

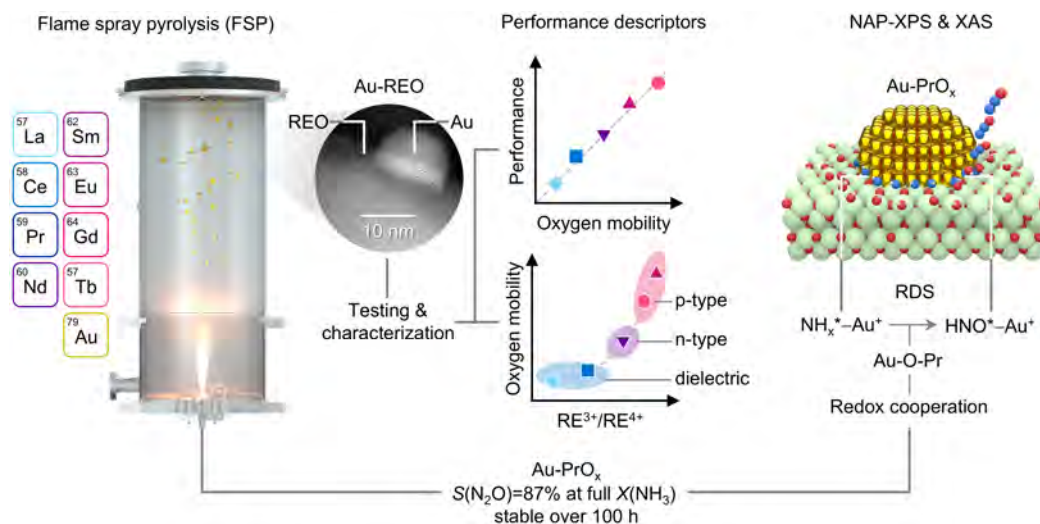


Figure 1. FSP enables the controlled introduction of Au nanoparticles across REO supports, providing a standardized platform for the systematic investigation of Au-REO. The resulting structure-performance relationships identify Au-PrO_x as the benchmark catalyst, which is further examined by operando NAP-XPS/XAS.

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Role of oxidative pulse parameters in long-term CO₂ electroreduction on silver

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Electrochemical CO₂ reduction (eCO₂R) using gas diffusion electrodes with silver as catalyst offers a promising pathway to convert CO₂ to CO^[1]. However, maintaining high CO selectivity at industrially relevant current densities (>200 mA cm⁻²) remains challenging due to the onset of the competing hydrogen evolution reaction (HER). Alternating continuous eCO₂R with short oxidative pulses has emerged as a potential strategy to maintain high selectivity, but its effectiveness depends heavily on the operating parameters^[2-4]. A mechanistic understanding of these effects is thus needed to optimize the pulsing protocol. In this work, we fabricate silver GDEs using electrospun PVDF-HFP substrates and operate them in a three-compartment electrochemical cell at current densities above 200 mA cm⁻² using KHCO₃ as catholyte. Selectivity is monitored continuously by online gas chromatography, and post-mortem structural characterization is performed by scanning electron microscopy and electrochemically active surface area measurements. We systematically vary the oxidative pulse potential, frequency, and duration to map their individual impacts on selectivity retention and catalyst morphology over operation periods of more than 100 hours. We identify a critical pulse potential threshold that separates two distinct behavioral regimes, linked to distinct structural outcomes of the silver catalyst. Guided by this mechanistic understanding, we find a pulsing protocol that substantially extends selectivity retention relative to continuous electrolysis^[5].

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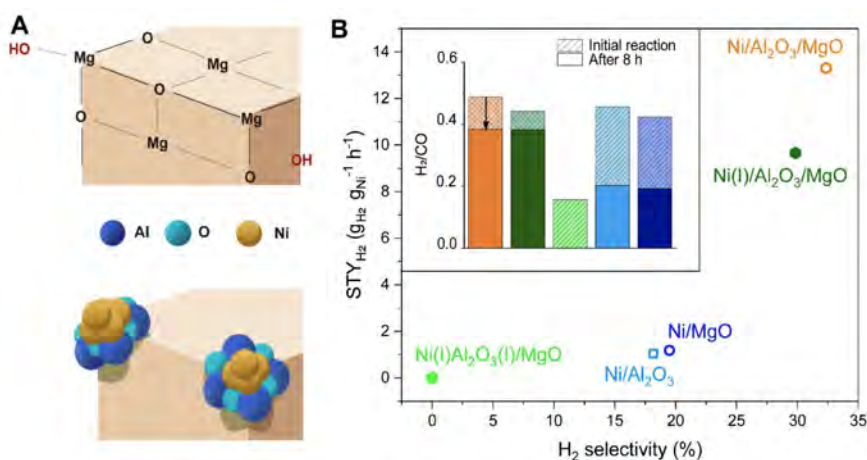
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Atomic Ni/Al₂O₃ clusters for enhanced H₂ production from low-temperature dry methane reformingE. Bonaglia¹, S. Jin², J. S. Luterbacher^{1*}¹École Polytechnique Fédérale de Lausanne (EPFL), CH-1015, Lausanne, Switzerland, ²Korea Institute of Science and Technology (KIST), Clean Energy Research Centre, Seoul, South Korea

Dry reforming of methane (DRM) represents an attractive pathway for renewable biogas valorization and simultaneous utilization of greenhouse gases like CO₂ and CH₄. However, its industrial implementation remains limited to bireforming systems, combined with steam reforming, due to severe kinetic and catalyst stability challenges. The high thermodynamic stability of CH₄ and CO₂ requires operating temperatures above 800 °C, where conventional Ni-based catalysts suffer from rapid deactivation caused by metal sintering and coke formation via methane decomposition [1]. Furthermore, competition between DRM, reverse water–gas shift, and coking reactions typically lead to low H₂/CO ratios, which are undesirable for syngas applications and necessitate additional hydrogen input downstream. In this work, we report a liquid-phase atomic layer deposition (L-ALD) approach to engineer low-nuclearity Ni cluster catalysts with near-atomic precision [2], aimed at enabling stable DRM operation in a lower temperature regime (600 °C). We deposit Ni/Al₂O₃ clusters on MgO, combining the tunable adsorption energy of single-atom catalysts with the improved adsorption capability associated with small metal ensembles. Al₂O₃ clusters were deposited onto dehydroxylated MgO supports through sequential controlled titrations of trimethylaluminum and water [3], followed by anchoring of an organometallic Ni precursor to surface hydroxyl groups (Fig. A). Compared to catalysts with identical composition but prepared with conventional methods like wet impregnation, and to reference catalysts, Ni/Al₂O₃/MgO exhibited improved DRM performance, including higher and more stable H₂/CO ratios and substantially reduced coke formation over 8 h time-on-stream (Fig. B), which demonstrated the importance of the synthetic control afforded by L-ALD. Electron microscopy reveals that Ni sintering is preferentially stabilized at MgO corner sites, leading to an average particle size of ~9 nm after reduction with no significant growth under reaction conditions.

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Determining the electroenzymatic behavior of diverse [FeFe]-hydrogenases on mesoporous electrodes for hydrogen production

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With the current concern about the energy crisis, the transition towards renewable energy has become essential. Among alternative energy carriers, hydrogen (H₂) is emerging as one of the most attractive fuels due to its carbon neutrality and high gravimetric energy density. Unfortunately, low-emission H₂ production remains limited by high costs and harsh operating conditions, such as the need for precious metal catalysts, high pH or elevated temperatures. Interestingly, nature has evolved [FeFe]-hydrogenases, metalloenzymes capable of producing H₂ under mild conditions (rt, pH 7, 1 atm) and this, with a near-zero overpotential and turnover frequencies reaching up to 10⁴ H₂·s⁻¹, which makes them promising catalysts for bio-electrocatalytic H₂ production. Typical limitations to their utilization in biotechnologies for H₂ production include low catalytic currents and/or stability.

In previous studies from our group, a simple two-step electrode preparation procedure using mesoporous indium–tin oxide nanoparticles (nanoITO) on glassy carbon electrodes allowed an efficient immobilization of the [FeFe]-hydrogenase *CpI*. These electrodes exhibit direct electron transfer (DET) with current densities >8 mA·cm⁻² at -0.8 V vs. SHE (pH 7) and with no overpotential, while maintaining □94% of electrocatalytic current after 5 days of constant operation.

In this work, different [FeFe]-hydrogenases with distinct structural features and catalytic properties were immobilized on nanoITO electrodes to determine whether enhanced electroenzymatic activity or stability can be obtained. *CrHydA1*, a minimal [FeFe]-hydrogenase and *DdH*, known as the most active [FeFe]-hydrogenase for H₂ generation, were investigated under identical conditions. While *DdH* exhibited current densities comparable to those previously reported for *CpI*, *CrHydA1* displayed low current densities and poor reproducibility. Surface functionalization with synthetic active site cofactors (or inactive mimics) improved the electrochemical behavior of *CrHydA1*, suggesting a strong influence of the electrode microenvironment on the performance.

We anticipate that further exploration of nanoITO-enzyme interfaces, including surface modification, will facilitate the broader application of this platform to a wider range of metalloenzymes for which DET remains challenging.

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Interfacial W–O–Zr ensembles in tungstated zirconia catalysts enable efficient hydrogen-free recycling of polypropylene waste

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Polyolefins are plastics at the core of modern life with no foreseeable replacement in sight, making chemical recycling technologies play a central role in advancing a sustainable society.^[1] Alternative strategies to the largely studied and commercially available pyrolysis, such as hydrotreatments have gained momentum in research laboratories worldwide due to their milder conditions and lighter downstream processing.^[2] Their practical deployment, however, relies on enhancing catalytic performance and resolving uncertainty related to future green hydrogen supply. Hydrogen-free depolymerization under mild conditions has recently been demonstrated, although studies to date have primarily focused on polyethylene.^[3] Meanwhile, these first catalytic systems exhibit considerable structural complexity, hindering unambiguous structure-performance correlations. Here, we address these gaps by demonstrating the first efficient catalytic depolymerization of polypropylene (PP) in the absence of hydrogen, reductants, or auxiliary agents under mild-temperature conditions. We developed a library of tungstated zirconia catalysts synthesized via flame spray pyrolysis with controlled tungsten speciation (**Fig. 1a**), achieving >80% yields of gasoline-range hydrocarbons (**Fig. 1b**) with stable catalytic performance.^[4] By correlating catalytic performance with catalyst structure, we identify the density of W–O–Zr ensembles, predominantly present in subnanometric clusters, as the key descriptor governing activity, with a W:Zr ratio of 1:9 emerging as optimal. *Operando* spectroscopic analyses reveal the formation of these interfacial linkages under reaction conditions and their role as transient electron- and hydrogen-accepting sites that activate C–H bonds and direct selective C–C bond scission through internal hydrogen transfer pathways. Life-cycle and techno-economic assessments, benchmarked against hydrotreatment-based recycling within a harmonized framework, indicate competitive environmental and economic benefits. Collectively, this work establishes the promise of this hydrogen-free route and highlights the importance of precision catalyst synthesis for polyolefin valorization.

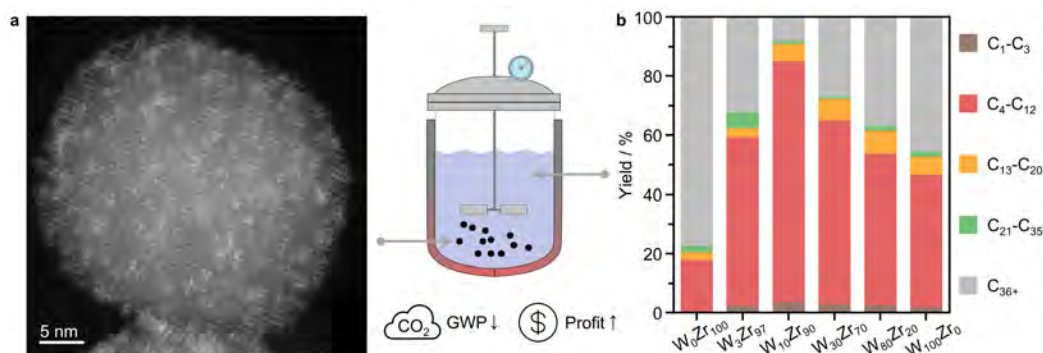


Fig. 1 **a** Representative STEM-HAADF image of as-prepared W₁₀Zr₉₀ showing isolated [WO₄]²⁻ species and WO_x subnanoclusters. **b** Performance for PP_{12k} (Mw = 12 kDa) depolymerization over catalysts with variable composition. Reaction conditions: 0.25 g catalyst, 0.5 g PP_{12k}, 4 bar N₂, 240 °C, 4 h, 750 rpm.

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Decoupling Catalytic Reactivity from Basicity in Organocatalytic Ring-Opening PolymerizationY. Hu¹, S. Ballal¹, S. Nguyen^{1*}¹Laboratory of Synthetic Polymer Chemistry, Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland

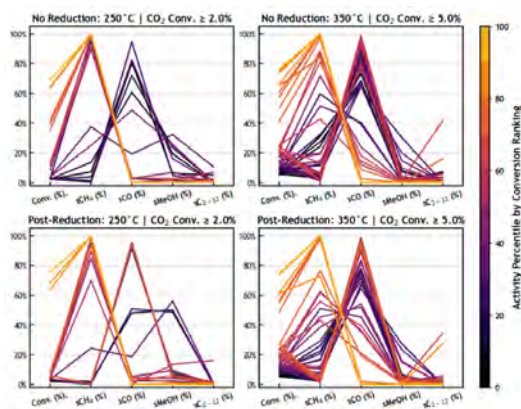
Stereospecific ring-opening polymerization of *O*-carboxyanhydrides (OCAs) is an attractive strategy for accessing stereoregular poly(α -hydroxy acids) with diverse structures and properties. OCAs are readily synthesized from chiral α -amino acids and α -hydroxy acids bearing a wide range of side-chain functionalities; however, their polymerization is often complicated by racemization at the acidic α -stereocenter, limiting stereochemical control. To address this challenge, we developed a new catalyst scaffold that decouples catalytic reactivity from intrinsic basicity, enabling efficient monomer activation while suppressing epimerization. Using these catalysts, controlled polymerization was achieved across a range of OCA monomers, including the particularly challenging mandelic acid-derived OCA. The resulting polyesters exhibited well-defined stereochemistry and predictable molecular weights with minimal epimerization. This work establishes a new platform for stereocontrolled OCA polymerization and provides guiding principles for the future design of organocatalysts for precision polymer synthesis.

Efficient Chemical Space Exploration in Fischer-Tropsch Synthesis from CO₂ via Mathematically Optimized High Throughput Experimentation

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High-throughput experimentation (HTE) and machine learning (ML) have accelerated discovery in molecular chemistry, however, heterogeneous catalysis remains a challenge due to the complex nature of material surfaces and the vastness of the possible chemical space.¹⁻² To minimize complexity and negative effects of too many catalyst components we construct a trimetallic catalyst library starting with a well-defined chemical space of 21 elements. We then apply a mathematical tool allowing us to screen 210 bimetallic pairs in only 70 experiments, and avoid the redundancy of screening over 1000 possible trimetallic combinations. We applied this framework to thermocatalytic CO₂ hydrogenation, a critical process for the transition to a circular carbon economy.³ The library was synthesized *via* an automated robotic platform and evaluated in a parallel-bed HTE reactor across various temperature regimes. With no initial starting bias, we recover efficient methanation, reverse water gas shift, and MeOH synthesis catalysts consistent with literature reports along with novel combinations.⁴⁻⁶ Ultimately, we discover a novel trimetallic catalyst with high CO₂ to Fischer-Tropsch activity. We narrow down the bimetallic composition responsible for the new catalyst's activity and conduct a thorough Group 1 and Group 2 dopant study. This work demonstrates that combinatorial optimization can replace thousands of manual experiments with a mathematically strategic exploration, significantly improving the discovery rate for complex, multi-component heterogeneous catalysts.



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Cu₂O-Based Photoelectrodes for Photoelectrochemical Valorization of Biomass-Derived ChemicalsN. Kim¹, D. Tilley^{1*}¹Department of Chemistry, University of Zurich, Zurich 8057, Switzerland

The photoelectrochemical (PEC) oxidation of biomass-derived platform chemicals provides an attractive strategy for coupling renewable chemical production with light-assisted electrochemical energy conversion. In conventional PEC water oxidation systems, the oxygen evolution reaction often limits overall efficiency because of its sluggish kinetics and large anodic overpotential. Substituting OER with the oxidation of biomass-derived platform chemicals offers a promising alternative, as it can lower the required operating potential while producing value-added chemicals. However, efficient PEC biomass valorization requires photoelectrodes that can simultaneously promote light absorption, charge separation, interfacial charge transfer, and selective oxidation reactions.

Here, we report Cu₂O-based photoelectrodes for the photoelectrochemical valorization of biomass-derived chemicals. Cu₂O was selected as a cost-effective and low-toxicity visible-light absorber, while multilayer and back-contact engineering were introduced to improve charge extraction, band alignment, and interfacial reaction kinetics. Under illumination and applied bias, the engineered Cu₂O photoelectrodes enabled efficient biomass oxidation at significantly reduced potential compared with conventional OER operation. The optimized system further exhibited selective formation of target oxidation products from representative biomass-derived substrates, along with enhanced operational stability. These results demonstrate that rationally engineered Cu₂O-based photoelectrodes can serve as a promising platform for low-bias, selective, and stable PEC biomass valorization.

Biocatalytic Reduction of Six-Membered Ring Heterocyclic Imines in Continuous FlowD. Lim¹, F. Paradisi¹¹University of Bern, Department of Chemistry, Biochemistry and Pharmaceutical Sciences, Freiestrasse 3, Bern (Switzerland)

Heterocyclic amines are a key structural motif for the synthesis of pharmaceuticals (e.g., antibiotics) as well as pesticides and flavors. In this regard, imine reductases (IREDs) have recently emerged as a highly selective and sustainable alternative for asymmetric reductive amination reactions. Herein, we have applied six IREDs, two of which were newly identified, in the reduction of heterocyclic imines with either a *N*, *S*, or *O* substitution at C-4. Since IREDs are NADPH-dependent enzymes, a commercially available, supported glucose dehydrogenase was added as a cofactor-regenerating system [1]. IREDs were then immobilized on porous microparticles to further improve the efficiency and sustainability of the system.

The strategic combination of bioinformatic analysis and immobilization screening resulted in immobilized biocatalysts with 95% retained activity. This enabled the integration of the bienzymatic system into a continuous-flow reactor leading to >90% conversion of 50 mM of the *S*-heterocyclic amine, 5-methyl-3,6-dihydro-2*H*-1,4-thiazine, with a residence time of 30 min, and reaching space-time yields up to 14.3 g L⁻¹ h⁻¹. In addition, (*S*)- or (*R*)-stereoselectivity of the biocatalytic reduction of the 1,4-disubstituted heterocyclic imines was achieved by using the newly identified IREDs from *Goodfellowiella coeruleoviolacea* and *Labilithrix luteola*, respectively.

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CO₂ Hydrogenation to MeOH over the Cu-containing UiO-66 Metal-Organic Framework Studied by in situ XAS, XRD, and DRIFTS

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The development of advanced catalysts for CO₂-to-methanol conversion is important for reducing carbon emissions while enabling sustainable methanol production. Recently, metal-organic frameworks (MOFs) gained attention as potential dual-function materials combining high CO₂ adsorption capacity with stabilization of catalytically active metal species.[1] Here, we investigate a Cu-Zn/UiO-66 catalyst prepared by wet impregnation of pre-synthesized UiO-66 with Cu and Zn precursor salts (4 wt% Cu, 10 wt% Zn). Under continuous-flow CO₂ hydrogenation conditions (200 °C, 20 bar, CO₂:H₂ = 1:3), the catalyst shows stable methanol formation with average productivity of 2.1 mmol g_{cat}⁻¹ h⁻¹, exceeding Cu/UiO-66 measured under identical conditions (1.8 mmol g_{cat}⁻¹ h⁻¹, same Cu amount). Building on our previous operando studies on UiO-66, we further investigate the dynamic response of the framework under reaction conditions. In situ synchrotron XRD reveals reversible unit-cell expansion of UiO-66 and contraction only during active catalytic operation (Fig. 1a), while high-pressure in situ DRIFTS shows the simultaneous evolution of methanol-related oxygenated intermediates (Fig. 1c-e). Integration of characteristic DRIFTS bands[2] over time demonstrates that these species appear together with catalytic activity (Fig. 1e). In situ Zr K-edge XANES further reveals reversible changes at the Zr nodes, consistent with adsorption and desorption of oxygenated species under reaction conditions (Fig. 1b). Pristine UiO-66 itself remains catalytically inactive, indicating that the metallic Cu-Zn function is required for methanol formation, while the framework may contribute through stabilization and temporary retention of intermediates. Altogether, the results suggest that the porous UiO-66 framework behaves as a dynamic host for methanol-related species, potentially increasing their residence time near the Cu-Zn active sites, which may influence methanol formation under reaction conditions. Ongoing work focuses on kinetics and further high-pressure operando DRIFTS.

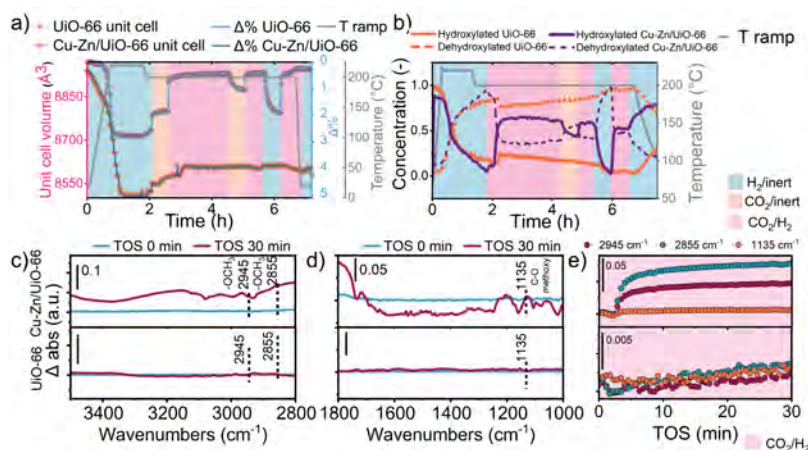


Fig. 1: (a) Unit cell volume of UiO-66 and Cu-Zn/UiO-66 derived from refinement of XRD (75 keV, ID31, ESRF; 200 °C, 15 bar, CO₂:H₂ = 1:3, 30 mL min⁻¹). (b) MCR-ALS analysis of Zr K-edge XANES of UiO-66 and Cu-Zn/UiO-66 (ROCK, SOLEIL; 200 °C, 20 bar, CO₂:H₂ = 1:3, 30 mL min⁻¹). (c-d) DRIFTS spectra: UiO-66 and Cu-Zn/UiO-66 in the O-H/C-H 3500-2800 cm⁻¹ and 1800-1000 cm⁻¹ regions; 20 bar, CO₂:H₂ = 1:3, 180 °C, 15 mL min⁻¹ (e) Evolution of integrated DRIFTS bands assigned to methanol-related species.

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Optimizing aldol reactions via mechanochemistry: Study of potential Dyno[®]-Mill technology

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The need for a more sustainable and greener chemistry is becoming more and more important, and implementing mechanochemistry on an industrial scale could help to decrease the ecological impact by considerably reducing the amount of solvents used. To date there is little data highlighting the benefits of these mechanical technologies with regards to process scale-up. Bead-mill technology (Dyno[®]-Mill) was used for the first time for the sustainable mechanochemical synthesis of Acetaminophen (known as Paracetamol) using Beckmann rearrangement. The optimized solvent-free method was able to deliver around ten grams on a laboratory scale, and gave better yields compared with solvent-based (89 vs. 74 %).^[1] Since C-C bond formation is a key reaction in pharmaceutical chemistry, an asymmetric organocatalysis with an amine acid (L-proline) between a ketone and an aldehyde (aldol reaction) was carried out to study which variables mainly influence the responses : yield, diastereoselectivity, enantioselectivity and Space-Time-Yield (STY). After process optimization, yields and selectivities comparable to those obtained in solution-based syntheses and ball-milling were achieved across a range of substrates. The principal advantage of the developed methodology lies in its significantly enhanced STY, which was at least fivefold higher than that of the reference processes. In addition, the method exhibited markedly improved green metrics, with a substantial reduction in waste generation (including work-up operations) ranging from at least 33 % up to 93 % compared to conventional solution synthesis and ball-milling.

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Cooperativity in Nitrogenases

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The enzyme Nitrogenase catalyses the conversion of atmospheric dinitrogen (N₂) to ammonia (NH₃) in an ATP dependent reaction. It does this at ambient conditions (room temperature and atmospheric pressure). The nitrogenase enzyme also does this in a carbon neutral manner, providing us with an environmentally friendly means of NH₃ production. NH₃ is an extremely important molecule in the production of fertilisers and acts as the main source of nitrogen for all life on Earth.

Nitrogenase occurs in diazotrophic bacteria and archaea. It consists of two metalloenzymes that together form an electron transport chain for the reduction of N₂. The catalytically active protein is the MFe protein (M = Mo, V, Fe) and is a heterotetramer which contains two identical α and β subunits ($\alpha_2\beta_2$) in two symmetrical $\alpha\beta$ halves. The most common variant is the MoFe protein that contains two iron-sulfur (Fe-S) clusters, the active FeMo-cofactor with the formula [Mo-7Fe-9S-C]:homocitrate (FeMo-co) and an electron relay cluster, the P-cluster [8Fe-7S], that reduces the FeMo-co. A set of these clusters are found in each of the two $\alpha\beta$ halves of the MoFe protein.

Cooperativity describes the effect of substrate binding or turnover in one subunit of a multimeric protein on the activity of the other subunits. There are three types. If activity in one subunit causes an increase in the activity of the other subunits, it is positive cooperativity. If there is a reduction in activity, it is negative cooperativity, and if there is no effect on the activity, there is no cooperativity.

In the nitrogenase enzyme, cooperativity focuses on the effect one $\alpha\beta$ half being active has on the second half. To study this, point mutations are made in the α -subunit to reduce or completely eliminate activity in only one half. These proteins are dubbed "asymmetric" MoFe proteins. Activity of the mutated asymmetric protein is measured using standard H₂, NH₃, and C₂H₄ production assays and compared to that of the activity of the wild type enzyme and the symmetric mutated protein which contains the point-mutation in both α -subunits.

The focus of this work is the role of the P-cluster in any possible cooperativity in the nitrogenase MoFe protein. The coordination environment of the P-cluster is mutated to reduce the activity in one half of the active protein and the overall activity is measured to assess any cooperative impact this has on the activity of the unmutated half.

Steam and oxygen effect in MTO catalyst regeneration

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The methanol-to-olefins (MTO) process converts methanol from syngas or CO₂/H₂ into light olefins such as ethylene and propylene. Industrial catalysts SAPO-34 and its zeolite analogue SSZ-13 (CHA topology) exhibit high activity but deactivate quickly due to coke accumulation. Efficient, reliable regeneration strategies are therefore essential to ensure stable long-term operation [1,2].

This work compares oxidative and steam-assisted regeneration of CHA catalysts. Oxidative regeneration efficiently removes coke via combustion, but it is highly exothermic. Reducing O₂ concentration moderates the combustion rate and heat release. In contrast, steam regeneration removes a significant fraction of coke by gasification into CO and H₂ under milder conditions (Fig. 1a).

XRD shows that coke expands the CHA *c*-axis, while steam treatment restores the lattice contraction (Fig. 1b). Thermal aging removes soft coke and promotes condensation of the remaining species. Raman spectroscopy reveals that the combined aging–steam treatment transforms bulky polyaromatic hydrocarbons into smaller, naphthenic, compounds (Fig. 1c). XPS and confocal fluorescence microscopy indicate that steam treatment redistributes carbon rather than fully removing it, forming graphitic coke on the external surface (Fig. 1d-f).

Catalytic testing shows that while oxidative regeneration restores initial activity, steam-regenerated SAPO-34 exhibits enhanced ethylene selectivity compared to both fresh and oxidatively regenerated catalysts. This arises from a dynamic balance between residual internal coke and external graphitic deposits, which introduces diffusion limitations that shape product distribution. Understanding this balance is key to tuning olefin selectivity and to designing regeneration protocols. Ongoing work focuses on correlating coke speciation, spatial distribution and reactivity, alongside detailed investigation of coke oxidation and its influence on framework stability.

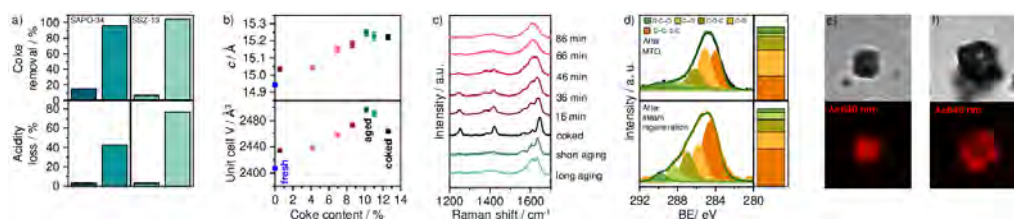


Figure 1. a) Maximum and minimum coke removal and acidity losses for SAPO-34 and SSZ-13 upon steam regeneration. b) Unit cell volume and *c* lattice parameter versus coke content and c) Raman spectra during regeneration by steam and for aged samples. d) C 1s XPS spectra and distribution of different carbonaceous species and e) confocal fluorescence images of SAPO-34 after MTO reaction and f) steam regeneration

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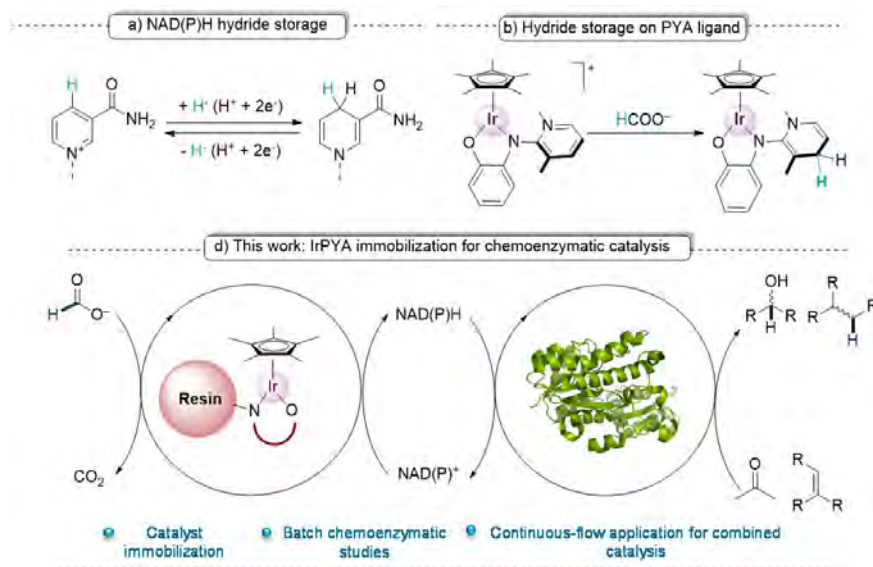
From Inhibition to Integration: Immobilized IrPYA Complexes as Biocompatible NAD(P)H Regeneration Catalysts

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NADH is a crucial cofactor in oxidoreduction enzymatic processes due to its ability to reversibly store hydrides on the nicotinamide moiety (Figure 1a). Despite its importance, its use is limited by high cost, low stability, and stoichiometric utilization.[1] Several regeneration systems have been explored to address these limitations, including organometallic complexes, which have provided numerous promising NAD(P)⁺ regeneration catalysts.[2,3] Nevertheless, integrating these catalysts into biocatalytic systems remains challenging, primarily due to mutual inhibition between the enzyme and the metal catalyst and the difficulty of identifying biocompatible conditions.[4]

We recently developed an iridium complex bearing a pyridylidene-amine (PYA) ligand that mimics NADH-type reactivity and efficiently catalyzes NAD(P)⁺ regeneration (Figure 1b).[5] When combined with enzymes, however, the homogeneous system suffers from significant mutual inhibition.[6] Herein, we report the synthesis of an IrPYA complex designed for covalent immobilization onto enzyme-compatible resin supports, its evaluation as a heterogeneous NAD(P)⁺ regeneration catalyst, and its application in chemoenzymatic transformations both in batch and in flow (Figure 1c).



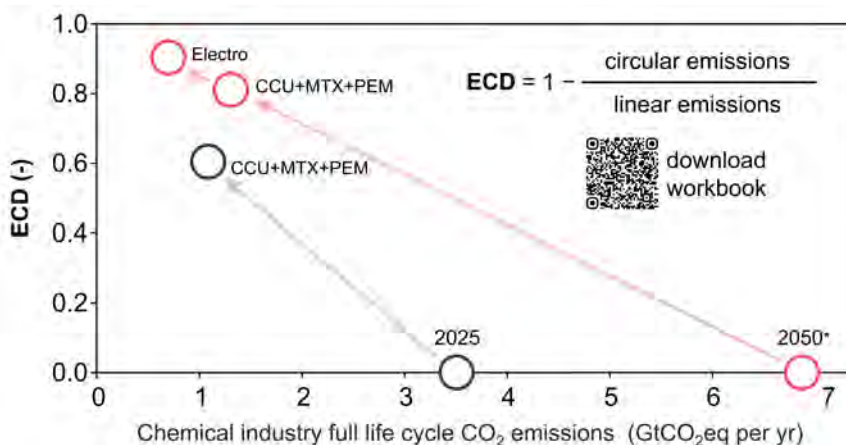
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The emissions circularity degree as a shared compass for a circular chemical industry

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The chemical industry, responsible for ca. 10% of global greenhouse gas (GHG) emissions, is striving for net-zero emissions by 2050 while meeting a demand projected to double.^[1] Closing the carbon loop through circular strategies such as carbon capture and utilization (CCU), bio-based routes, and chemical recycling of used plastics is central to this transition. However, the sector still lacks a consistent way to evaluate how much these technologies reduce life cycle emissions. Existing circularity indicators focus on material flows, while life cycle assessment (LCA) remains inaccessible to most non-experts. To bridge this gap, we introduce the emissions circularity degree (ECD), an emission-based metric ranging from 0 (fully linear, fossil-based) to 1 (fully circular, net-zero across the full life cycle), and apply it to a sector-scale prospective assessment of hundreds of chemicals under different feedstock scenarios. Our findings highlight that current mid- to high-TRL technologies, particularly CCU coupling direct air captured CO₂ with electrolytic hydrogen, could enable a sector-wide ECD of 0.8 (80% circularity) by 2050, reducing emissions by ca. 5.6 GtCO₂eq per yr relative to linear production (**Fig. 1**).^[2] End-of-life emissions appear to be the dominant barrier, and reaching full life cycle net-zero requires an ECD of 0.85, achievable through innovation in low-TRL routes such as direct nitrogen and CO₂ electroreduction, alongside a reasonable allocation of global CCS storage capacity. Furthermore, to broaden adoption beyond LCA experts, we provide an open source ECD workbook that reproduces detailed LCA results within 10% relative error, enabling experimentalists to assess circular technologies using minimal process data. The ECD thus offers a shared compass for catalysis researchers, process engineers, and LCA experts to evaluate, prioritize, and accelerate the technologies for a truly circular net-zero chemical sector. As the first sustainability metric from NCCR Catalysis, it is designed to be widely accessible and readily implemented by the community.



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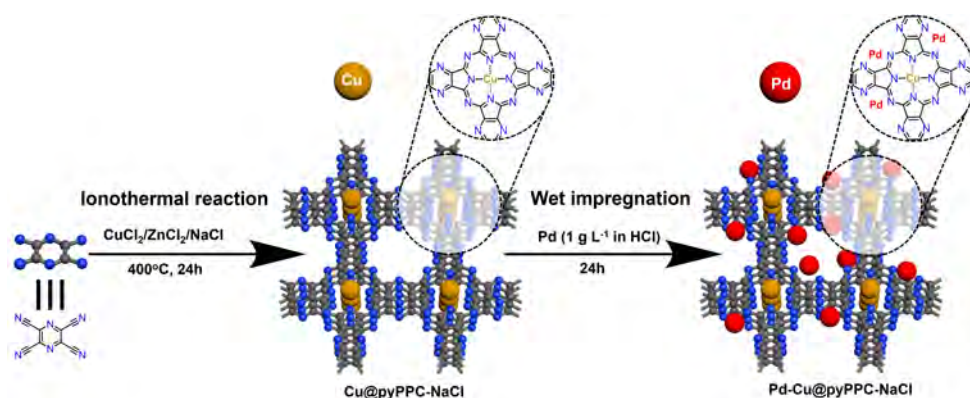
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Pd–Cu Single-Atom Catalysts in Covalent Organic Frameworks for Sonogashira Cross-Coupling Reaction

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Bimetallic single-atom catalysts (SACs) provide a platform for cooperative reactivity, yet achieving precise control over the spatial distribution of distinct metal sites remains challenging. Herein, we report the construction of metallophthalocyanine-based covalent organic frameworks (COFs) featuring well-defined Pd and Cu single-atom sites, thereby extending our previously reported monometallic system [1] to a bimetallic architecture with spatially separated Pd and Cu centres. The material, Pd–Cu@pyPPC-NaCl, is obtained via mixed-metal ionothermal polymerization of tetracyanopyrazine in a CuCl₂/ZnCl₂/NaCl melt, which installs Cu within N₄ phthalocyanine cavities, followed by Pd incorporation into the pores through wet impregnation. This synthetic protocol affords atomically dispersed Pd and Cu sites at high loadings (16.2 wt% Cu, 6.2 wt% Pd).



In the Sonogashira–Hagihara coupling, Pd–Cu@pyPPC-NaCl delivers >95% yield in batch and maintains >90% under continuous-flow operation. Kinetic and time-on-stream analyses indicate enhanced reaction rates and superior performance compared to monometallic counterparts. The catalyst remains stable over 18 h with negligible metal leaching, and its activity can be readily recovered by simple solvent flushing. These findings point to a cooperative mechanism, wherein Pd and Cu sites independently activate the aryl halide and alkyne, respectively. Thereby demonstrating that controlled positioning of Pd and Cu within a COF enables both high activity and sustained stability under flow conditions.

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Sustainability-guided catalyst optimization for CO₂ hydrogenation

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Catalyst development in academia commonly prioritizes the optimization of reaction-level metrics such as conversion or selectivity,^[1] while the consideration of techno-economic (TEA) and life cycle analyses (LCA) comes at later stages. However, the extent to which reaction-level metrics can predict process-level sustainability metrics such as cost and global warming potential (GWP) remains unclear. This issue becomes increasingly complex for processes with broad product distributions and/or lacking preliminary reports of environmental and economic viability.^[2] Early integration of sustainability metrics can thus help advance catalysis research. By integrating catalyst design, process-level analyses and machine learning, we establish a sustainability-guided optimization framework wherein the algorithm directly recommends catalyst compositions and reaction conditions based on sustainability metrics (**Fig. 1a**), using CO₂ hydrogenation to higher alcohols (HA) and olefins (CH=) as a case study. Here, we demonstrate the potential of a novel NaZrFeCo catalyst family for attaining high yields of valuable long-chain products following the standard approach. XRD and XAS characterization revealed a unique balance between carbide and oxide phases in these materials stemming from the Na and Zr promoters. When optimizing this system using the proposed framework, three cycles of active learning (AL) resulted in an improved Na₁₁Zr₉Fe₅₈Co₂₂ system after 15 experiments (**Fig. 1b**), showing a 33% higher profit margin and 20% lower CO₂ emissions than the standard approach. While the process achieves lower carbon footprint gains compared to the fossil route, prospective analyses for 2050 suggest profitability under favorable IPCC scenarios. This work highlights a promising catalyst for CO₂ valorization and demonstrates how new tools enable the early adoption of sustainability metrics to guide catalyst development.

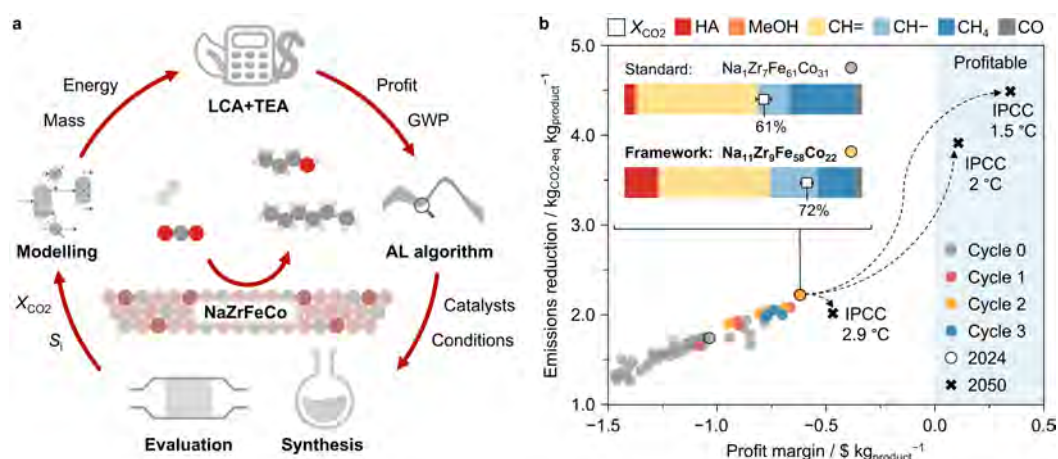


Fig. 1 **a** Sustainability-guided optimization framework consisting of catalyst synthesis and evaluation, process-level analyses, and active learning stages repeated across several cycles. **b** Evolution of profit margin (economic metric) and reduction in CO₂ emissions (environmental metric) compared to the fossil route. The inset shows product distributions for NaZrFeCo catalysts from the standard approach and after sustainability-guided optimization.

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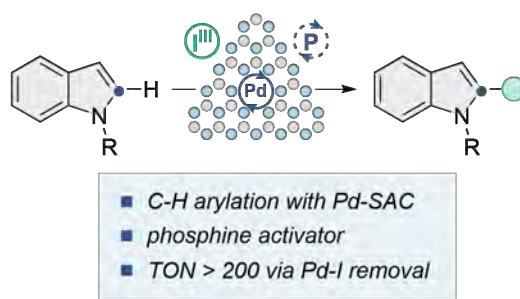
Direct C-H Arylation with Regenerable Heterogeneous Palladium Single-Atom Catalysts

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Transition-metal-catalyzed modification of ubiquitous C–H bonds is a powerful strategy to introduce new moieties into molecules. It has rapidly become one of the most researched topics in synthetic chemistry. However, there was little progress on process industrialization as many existing catalytic C–H functionalizations require high precious metal loadings, elevated temperatures, strong oxidative, acidic, or basic conditions to achieve efficient catalysis.^{1–4}

Single-atom catalysts (SACs) emerged as tunable, recoverable heterogeneous alternatives to homogeneous metal complexes.^{5–6} However, direct C–H bond functionalization, which surpasses the need for pre-functionalization, remains unexplored with palladium SACs, owing to harsh reaction conditions that can lead to rapid catalyst degradation.



Here, we developed the first Pd single-atom catalyzed C–H arylation of indoles, achieving TON > 200.⁷ Nitrogen-coordinated Pd sites ensured high stability and metal retention but were intrinsically inactive, necessitating *in situ* activation with a catalytic phosphine additive. The role of phosphine was investigated in detail, showing rapid and selective phosphonium formation, which acts as a reservoir of acid. Recycling studies, including *in situ* X-ray absorption spectroscopy, revealed Pd–I formation as the dominant catalyst deactivation pathway, which had not been observed previously for SACs. Guided by this insight, post-reaction treatment in aqueous ammonia overcame iodide poisoning, restoring catalytic activity for multiple cycles. These findings establish strategies to balance activity, stability, and regenerability and extend palladium single-atom catalysis to direct C–H functionalizations, paving the way for a greener, more step-efficient chemical synthesis.

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Low-Potential Viologen-Based Electron Donors for Enzymatic H₂ Production with [FeFe]-Hydrogenases

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“Green” dihydrogen (H₂) is developing into a key player in solving the global energy crisis and reducing CO₂ emissions, as its combustion only produces water as a side product. However, current technologies for producing, transporting and storing green H₂ are somewhat limited and more than 99% of globally utilized H₂ is still traced back to fossil fuels and thus considered to be economically unfriendly.^[1] In order to access more sustainable H₂ evolution technologies, the enzyme class of hydrogenases can act as a blueprint for building ecofriendly model systems. Hydrogenases are capable of catalyzing the reversible interconversion of protons and electrons into H₂ with exceptionally high rates under mild conditions, *i.e.*, neutral pH and ambient temperature and pressure.^[2]

As a model, we study the [FeFe] hydrogenase *CpI* from the organism *Clostridium pasteurianum*, due to its relative ease of production and a high bias towards H₂ evolution. To mimic the biological environment, where electrons are delivered by oxidoreductase enzymes, the application of an electrochemical potential (that itself can be generated by renewable energy sources) to these enzymes opens a new possibility for green H₂ production.^[3] To enable electrochemical electron transfer to *CpI*, there are two possible strategies, utilizing either a direct electron transfer (DET) configuration, where the enzyme is efficiently immobilized onto the electrode, or a mediated electron transfer (MET) configuration, using an electrochemically reduced mediator.^[4] For the latter, viologens have been shown to act as efficient redox mediators to oxidoreductase enzymes. However, the most studied and commonly employed viologen, methylviologen, is limited in terms of stability and the two-electron low-potential reduced state is inaccessible in aqueous media. Herein, we report a low-potential two electron viologen-based donor that is able boost the enzyme's specific activity beyond those reported previously.^[5]

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Agentic AI for Homogeneous Catalyst Design

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De novo discovery of catalytic systems remains one of the most complex challenges in chemistry, traditionally defined by a "trial-and-error" paradigm where mechanistic understanding is often retrospective. While AI has streamlined discovery in other fields, its application in homogeneous catalysis is frequently hindered by complex predictability and a "data scarcity" problem where systems are modeled *ad hoc* after significant experimental data exists. Herein, we propose an **Agentic AI framework** designed to operate in the **low-to-no-data regime**.

We began by benchmarking the ability of Large Language Models (LLMs) to distill qualitative and quantitative mechanistic knowledge from diverse systems, including organocatalyzed Morita-Baylis-Hillman (*MBH*) reactions [1], Pd-catalyzed C-H fluorination [2] and Ni/photo-redox [3], Cu [4], and Pd-catalyzed couplings [5, 6]. Preliminary results demonstrate that while context-blind distillation remains a hurdle for older models, current frontier architectures exhibit a reasoning capacity for chemical properties that is comparable to, and in specific benchmarks exceeds, that of seasoned experimental chemists.

We validate this Agentic Framework through three prospective studies:

1. We utilize a **generative model** [7] coupled with an **LLM oracle** to explore the space and propose organocatalyst for the *MBH* reaction. We showcase that LLMs can overcome the limitations of DFT modeling [8] by leveraging every mechanistic step as proxy for catalytic activity at a fraction of the cost.
2. We utilize different frontier LLMs to explore the complex ligand space of **Pd-catalyzed C-H activation** [9]. Taking this versatile butenolide synthesis as benchmark, we demonstrate how an autonomous agent loop could performed ligand optimization after warm-start initialization.
3. We propose a **palladium-catalyzed decarbonylative fluorination of aroyl fluorides** enabled by cooperativity. Developed as part of an application to the **UZH & EPFL Self-Driving Lab Hackathon**, this project will serve as a preliminary showcase for the "chemistry of the future," where chemists' hypotheses are tested via automated experimental workflows fully guided by an AI Agent.

By integrating LLM reasoning into catalyst design, we provide a blueprint for moving from retrospective modeling toward a prospective, agent-guided discovery paradigm in the laboratory.

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Surface-enhanced infrared absorption spectroscopic elucidation of the electrochemical promotion of the thermocatalytic hydrogenation of 3-nitrostyrene

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Surface-enhanced infrared absorption spectro-electrochemistry (EC-SEIRAS) is as a powerful analytical technique to study surface-bound species and electric field effects at electrified solid-fluid interfaces.^[1] EC-SEIRAS could thereby provide key information on the interfacial chemistry that directs heterogeneous catalysis.^[2] Electrochemical promotion of catalysis (EPOC) offers an elegant way to enhance catalytic performance *in situ* with applied electric fields. For instance, recent work has demonstrated spectacular rate enhancements of thermal catalysis by applied electrochemical potentials in a few transformations, including hydrogenation reactions.^[3-8] We hypothesized that with a better fundamental understanding of such processes through EC-SEIRAS, EPOC may be further developed, for instance, to also allow enhancement of chemoselectivity in thermal reactions.

Here, we show that the application of a positive potential during the thermocatalytic hydrogenation of 3-nitrostyrene with H₂ on a heterogeneous Pt catalyst delivered one single product (1-ethyl-3-nitrobenzene) with six-fold enhanced yield, meanwhile a complex product mixture was obtained at open circuit voltage.^[9] Examining this system by EC-SEIRAS combined with kinetic studies suggested that a tuned surface coverage and a modified affinity of the Pt catalyst for electron-rich versus electron-poor functional groups at positive applied potential is responsible for the enhancements in rate and chemoselectivity. Our work thereby provides fundamental understanding of the effect of an applied potential on a thermal hydrogenation and opens the road for tuning chemoselectivity in other transformations.

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β -PdH_x as selective CO₂ reduction catalysts to formate via palladium membrane reactorL. Poon¹, V. Mougel^{1*}¹Laboratory of Inorganic Chemistry, Department of Chemistry and Applied Biosciences, ETH Zürich, CH-8093 Zürich, Switzerland

Electrocatalytic transformation of CO₂ into fuels or value-added chemicals are emerging as attractive alternatives to traditional petroleum-based chemistry and viable route to mitigate carbon emissions. Palladium stands out, amongst various electrocatalysts studied to this date, by displaying two distinct catalytic pathways depending on the overpotential applied: selective formate production at almost zero overpotential, and CO and H₂ eventually at higher overpotentials. Such diverge behaviours have been proposed to stem from the shift of PdH_x active species from the α -hydride phase to the β -hydride phase as potential goes more cathodic or as time evolves, with each phase assumed to be responsible for a different set of products. [1][2] Recent efforts to elucidate the exact mechanism of CO₂RR catalysed by Pd or PdH_x mostly focused on following the morphology and structural change of Pd/PdH_x over the course of reaction via some *operando* measurements. [2][3][4] While some of such work demonstrated the correlations between the evolution of PdH_x phases and the respective diverging catalytic activity towards CO₂RR, the very nature of generating the hydride **while** conducting CO₂RR in these works mean that the causality between the phase(s) of PdH_x and its reactivity cannot be unequivocally established and remained elusive.

Herein, we report the use of pre-generated and continuously-formed bulk β -PdH_x as electrocatalysts for CO₂RR. The generation and consumption of PdH_x were separated, both temporally and spatially, by utilising a palladium membrane reactor setup. Remarkably, such β -PdH_x catalyst in CO₂RR yielded similar trends as when pristine Pd nanoparticles were used, affording selectively formate at low overpotential and shifting to CO and H₂ upon more negative potentials, providing strong evidence against the aforementioned postulations. Such findings demonstrated the ability of β -PdH_x to selectively reduce CO₂ into formate or CO/H₂ under different conditions, and that a better descriptor other than the bulk PdH_x phases is needed to predict its reactivities.

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Combined SSITKA-FTIR studies on Cu/ZnO/oxide materials for CO₂ hydrogenation reaction reveal different formate species impacting the catalytic activity

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The accumulation of greenhouse gases in the atmosphere is a pressing environmental challenge, CO₂ emissions receiving particular attention. A promising strategy is the CO₂ conversion into platform chemicals such as methanol, a well-established industrial process performed over the Cu/ZnO/Al₂O₃ (CZA) catalyst. The precise reaction mechanism and the active sites under catalytic conditions (50-100 bar and 200-300 °C) remain highly debated topics, with the majority of the most recent works focusing on deciphering the dynamic interaction between the Cu and Zn species.^[1] The role of Al₂O₃ has been largely neglected in this picture, though it has been hypothesized that it may be involved in CO₂ activation. To the best of our knowledge, a systematic study exploring the role of the third component on the reaction mechanism has yet to be carried out.^[2]

This work fills this knowledge gap by investigating the role of the oxidic components' acid/base properties in the mechanistic pathway. For this purpose, several metal oxides of different acidities are impregnated with 10 wt% Cu and 5 wt% Zn and catalytically tested in the CO₂-to-methanol reaction, revealing entirely different activities and methanol selectivities (Fig. a). Combined SSITKA-FTIR experiments reveal that the reaction follows the formate-mechanism over all the catalysts (Fig. b). In fact, two different formate species can be identified on most materials, likely corresponding to ZnO- and MO_x-bound species, respectively. The different supports affect the stabilization of the formate intermediate (Fig. c): the characteristic vibrational bands shift depending on the acidity of the support and their intensities correlate with the total amount of basic sites. There is no direct relationship between the intensity of the formate band and the catalytic performance (STY (mg_{MeOH}/DME g_{cat}⁻¹ h⁻¹)), suggesting that not all formate species are further reacted to methanol. Nonetheless, there appears to be a direct relationship between the STY and the frequency of the asymmetric HCOO stretching vibration, highlighting the effect of the support's basicity on the catalytic performance. Our results show the direct influence of the support on the stabilization of key reaction intermediates, emphasizing the importance of the oxidic support in the rational design of catalysts for the CO₂ reduction reaction.

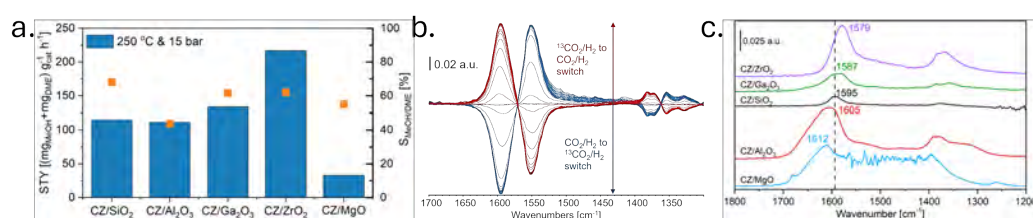


Figure: **a.** Catalytic data collected at 250 °C and 15 bar; **b.** Isotopic switch ¹²CO₂/H₂ to ¹³CO₂/H₂ (blue) and reverse switch (red) on the CZ/SiO₂ and **c.** formate region vibrational frequencies for the five catalysts.

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Assessing the Cooperative Role of Brønsted-Lewis Acid Synergy in Ferrierite Zeolites for Methanol-to-Hydrocarbons Process

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The methanol-to-hydrocarbons (MTH) process offers a promising non-petroleum route to produce light olefins, particularly C₃–C₅ olefins that serve as valuable intermediates for oligomerization to sustainable aviation fuels (SAF) process.[1,2] Among zeolite frameworks, ferrierite (FER) exhibits a distinctive 2D pore topology with intersecting 8- and 10-membered ring channels that intrinsically favors the formation of C₃–C₅ olefins. However, the rapid coke-induced deactivation of FER zeolite under MTH conditions occurring on Brønsted acid sites (BAS) remains a critical challenge in obtaining long-term stability.[3] In this research, we aim to study the impact of acid site density (ASD), a key descriptor in MTH catalysis,[1] on the performance of FER. The ASD is modified through various post synthetic treatments. Dealumination and desilication treatments, exhibited negligible improvements in catalytic stability, reflecting the inherent structural resistance of FER to these approaches of ASD modifications.[4] To circumvent this, we explore the cooperative role of BAS and LAS, through incipient wetness impregnation of alkali and alkaline earth metals (0.1-2.5 wt.% Na, Mg, Ca, Sr, Ba), targeting the reduction of strong BAS strength and generation of tunable Lewis acidity.[5,6] Alkali metal impregnation showed marginal catalyst stability improvements with Na-FER (0.5 wt.%) significantly enhancing C₅ olefin selectivity. In contrast, alkaline earth metal incorporation, particularly Mg- and Ca-FER (1.2 wt.%), enhanced C₄–C₅ olefin selectivity favoring olefins over aromatic products, while concurrently suppressing the methane formation. Building on these findings, transition metal impregnation such as Fe, Co, Ni are further explored to introduce redox functionality and suppress hydrogen transfer reactions that accelerate coke formation.[7] In our ongoing research, we investigate the influence of extra framework cations on acidity of FER and their correlation with MTH catalytic performance. In this regard, the quantification of the acid sites by NH₃-TPD and isopropyl-amine probed FTIR is used to distinguish different acid sites. To gain insights into the structural modifications induced by acid/base treatments and metal incorporation, ²⁷Al, ²⁹Si, and ¹H MAS-NMR will be performed, directly supporting ASD regulation across the modified series of FER catalysts. Furthermore, to elucidate the deactivation mechanism, operando UV-Vis spectroscopy will be employed, offering time-resolved insights into the evolution of carbonaceous species during MTH.

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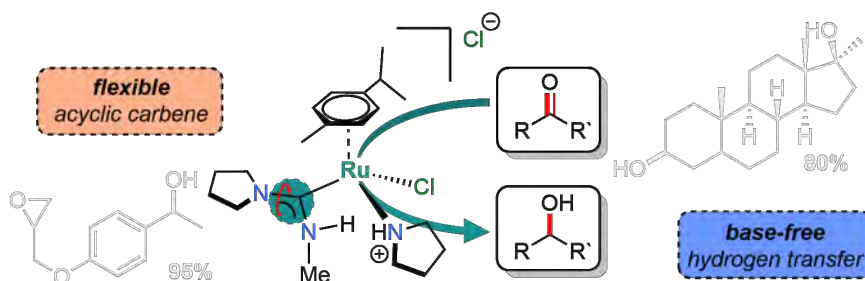
Ligand flexibility as a concept to unlock catalytic activity: acyclic carbenes for base-free transfer ruthenium hydrogenation catalysis

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N-Heterocyclic carbenes (NHCs) are key ligands in homogeneous catalysis owing to their strong σ -donor properties and high thermal and oxidative stability [1]. Their rigid framework and well-defined steric environment make them particularly valuable for controlling the reactivity of transition-metal catalysts [2]. However, this structural rigidity may limit ligand adaptability at the metal centre and typically does not provide a proximal proton source to assist proton shuttling in hydrogen transfer processes.

To address these limitations, acyclic diamino carbenes (ADCs) have emerged as attractive alternatives [1]. In contrast to their cyclic analogues, ADC ligands possess an open-chain structure that introduces enhanced conformational flexibility while maintaining strong donor ability and steric control around the metal centre [1,3,4]. This flexibility can modulate the local environment at the catalytic site and facilitate cooperative proton transfer.



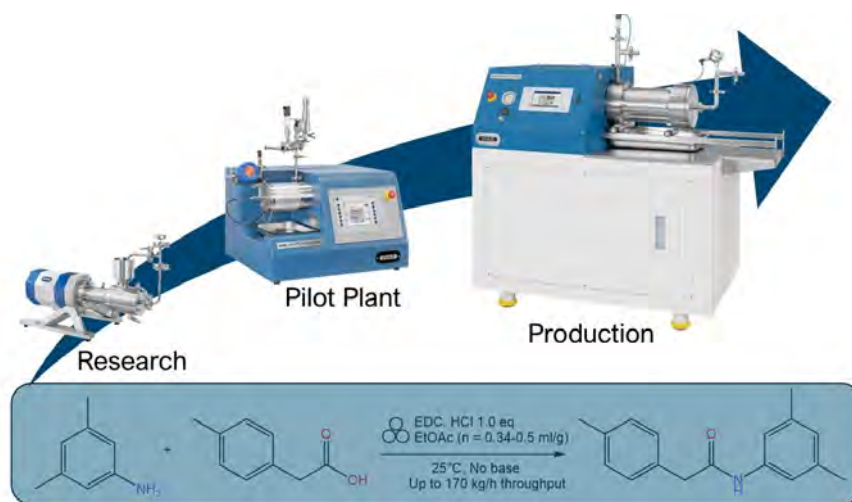
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Reinventing Amide Bond Formation: Semi- and Fully Continuous Mechanochemistry at Scale

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Mechanochemistry is emerging as a sustainable alternative to solvent-based chemical manufacturing, offering significant reductions in waste, energy use, and hazardous solvents. To support industrial adoption, this presentation introduces WAB-GROUP®'s mechanochemical technologies, with emphasis on the WAB IMPA[°]CT REACTOR®, which integrates continuous flow chemistry with bead milling for efficient, solvent-reduced synthesis at scale. Equipment characterization, application examples, and strategies for process control and energy optimization will be discussed, along with pharma-relevant applications such as API particle-size control, co-crystal formation, and formulation-oriented milling.



Building on this foundation, the talk highlights a major advance: the large-scale mechanochemical synthesis of amides [1], performed in semi-continuous and fully continuous modes using bead-milling technology. The process achieved productivities above 100 kg h⁻¹ with minimal ethyl acetate and without excess reagents, added base, or bulk solvent—showing a practical and environmentally responsible route to scalable amidation using commercially available equipment. The session concludes with a green-impact analysis and an outlook on mechanochemistry's expanding role in sustainable pharmaceutical and chemical manufacturing.

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Co/Ni POM–cubane hybrids as reconstructive precursors: comparing HER behaviour and OER activityA. A. Schultz¹¹Institut für Chemie Universität Zürich Winterthurerstrasse 190 CH-8057 Zürich

Polyoxometalates (POMs) and Co/Ni-based coordination complexes are both promising and well studied electrocatalysts. However, a systematic comparison of their combined hybrid properties under HER and OER conditions remains rare. Here, Co and Ni POM–cubane hybrids based on CoCoW₃ and Co₄O₄-dpk precursor are synthesized and structurally characterized by Raman and FT-IR spectroscopy. Further, their HER and OER performance and behavior is investigated and compared to their precursor materials. Under acidic HER conditions, all CoCoW₃-based electrodes (POM, cubane and hybrids) undergo activation and converge to similar overpotentials, with the hybrids matching but not surpassing the performance of the parent POM while showing pronounced surface area changes. In alkaline OER, the Co/Ni POM–cubane hybrids significantly outperform both POM and cubane precursors, with the Ni-hybrid giving the lowest overpotential and shallowest apparent Tafel slope. Operando Raman, SEM–EDX, ICP–MS and EIS collectively point to reconstruction into Co/Ni (oxy)hydroxide-like films with POM-derived motifs, linking molecular precursor design to emergent catalytic behaviour.

Versatile Functionalization Platform Using Iodonium Salts for Cobalt Phosphide Enables Enhanced Hydrogenation Selectivity

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The use of surface ligands is an effective strategy for tuning the catalytic performance of solid catalysts. Especially noble metal catalysts have been extensively investigated in this area.^{1,2} However, this strategy has been much less explored for more earth-abundant material catalysts. For instance, transition metal phosphides (TMPs) have attracted enormous interest as promising candidates for hydrotreating processes,^{3,4} but current strategies for introducing ligands to TMP surfaces are restricted to a small selection of possible organic groups.^{5,6} In addition, current strategies for modifying TMP surfaces often suffer from poor control over surface coverage. Therefore, a more versatile and controllable surface functionalization approach is needed for these materials to enable a rational design of TMP-based catalysts.

Herein, we present a novel approach for the organic modification of cobalt phosphide (CoP) surfaces with a range of organic groups.⁷ For this, we used iodonium salts, which enabled the attachment of alkyl- and aryl-groups, including phenyl-groups with systematically varied steric and electronic properties onto CoP surfaces. Furthermore, our strategy allows controlling surface coverage and prevents the formation of multilayers. This is a common challenge for conventional diazonium salts- based strategies.⁵ We demonstrate that our strategy for surface modification can be applied to tune hydrogenation catalysis. Specifically, we show that the selectivity in the hydrogenation of α,β -unsaturated aldehydes for the unsaturated alcohol can be substantially improved by use of the surface-modified CoP catalysts. Additionally, systematic tuning of the surface properties of the modified CoP catalysts permits a detailed analysis of ligand effect on hydrogenation selectivity and identification of optimal surface properties. Our functionalization approach thereby significantly expands the chemical space available for TMPs and provides a foundation for the optimization of catalytic systems based on these more earth-abundant materials.

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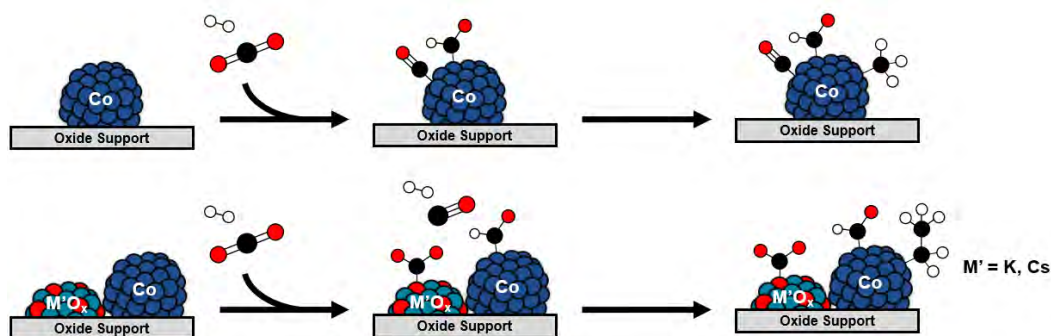
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Making Carbon-Carbon Bonds from CO₂: The Effect of Alkali Metals on Cobalt-Based Catalysts

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At present, most large-scale catalytic processes rely on syngas (CO/H₂) as chemical feedstock for the production of e.g. higher hydrocarbons. These processes are however associated with a large carbon footprint and need to be rethought in the coming years to meet the growing demand for sustainable energy solutions. In this context, carbon capture and utilisation (CCU) has emerged as a prominent research field, where the transformation of CO₂ to value-added chemicals presents a promising avenue. Among these, higher hydrocarbons (C₂₊) are of particular interest due to their wide-spread use as liquid fuels. [1, 2] Cobalt is well-known for its activity in the Fischer-Tropsch (FT) process, but remains challenging and relatively underdeveloped for analogous reactions with CO₂ as feedstock. [3, 4] In this context, we have studied alkali metal doping of supported cobalt nanoparticles for CO₂ hydrogenation to higher hydrocarbons. We found that doping SiO₂-supported Co catalysts with alkali metals led to the suppression of methanation and a significant increase of the C₂₊ (Na and K) and CO (Rb and Cs) selectivity. Moreover, a strong support effect was observed, where TiO₂ appeared to be beneficial for C-C coupling compared to SiO₂. Initial *in-situ* DRIFTS experiments were performed for the Co, KCo, and CsCo@TiO₂ systems. Notably, the alkali metal promoted materials showed very low-lying CH_x species, coinciding with their ability to form higher hydrocarbons in CO₂ hydrogenation. It is thus proposed that the reaction towards higher hydrocarbons proceed via a modified FT mechanism, where the alkali metal promoted systems form CO via the reverse water-gas-shift reaction, followed by C-C coupling to form C₂₊ products.



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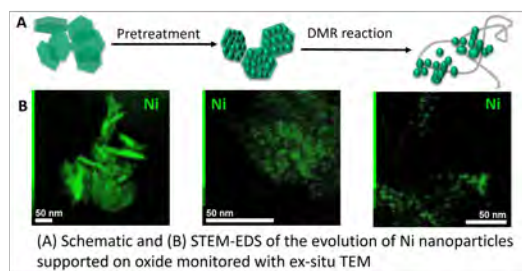
Influence of support material on the structural evolution of Ni-oxide support catalysts in dry methane reforming

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Metal-oxide support catalysts have been widely used for energy and chemical conversion including water gas shift reactions, CO₂ hydrogenation, dry methane reforming (DMR). These oxide supports may serve as inert material improving the dispersion of active metal or can interact with the active metal by charge, metal, oxygen or adsorbate transfer between the metal and support [1]. The strength of metal-support interaction and its manifestation is sensitive to the metal-support material selection as well as the reaction environment and conditions. Such interactions can help mitigate sintering, coking and phase transformation of the catalyst under the harsh operating conditions required for heterogeneous thermal catalysis [2]. With renewed interest in dry methane reforming (DMR) in recent years as a lucrative alternative to produce syngas with a balanced ratio (H₂:CO =1) from two major greenhouse gases, namely CO₂ and CH₄, supported Ni catalysts are being explored extensively for their cost-performance balance [2]. However, the development of high-performance supported Ni catalysts for DMR is limited by the lack of understanding of the influence of support materials on the structural and chemical evolution of these catalysts during DMR and their correlation to catalyst stability.

Here we study the structural evolution of Ni nanoparticles (NPs) on technologically relevant oxide supports for DMR reaction using ex-situ TEM. We leverage the atomic resolution imaging along with complementary STEM-EDS capabilities of a TEM to investigate changes in Ni NP size and morphology, and coke formation in the catalyst when subjected to pretreatment followed by DMR reaction. We identify the impact of support materials on the restructuring of Ni NPs during DMR reaction resulting in widely different size distributions and particle shapes depending on the support used. Such a strong restructuring of Ni NPs may be beneficial or detrimental to the catalyst performance. Furthermore, we show that pretreatment of the catalysts can help to control the dispersion of Ni NPs on oxide support. Our study therefore highlights the multifactorial structural evolution of the supported Ni catalysts and the need to gain further insight from complementary structural and spectroscopic in-situ/operando studies.



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Selective Shuttle Hydrochlorination of Alkynes over Carbon-Supported Gold Single Atoms

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Shuttle catalysis enables the transfer of reactive functional groups without relying on toxic or corrosive reagents. However, it remains largely confined to homogeneous systems, which typically suffer from limited catalyst recyclability, posing significant economic and environmental challenges. In this study, we address this challenge by developing recyclable gold single-atom catalysts (SACs) supported on activated carbon that can be employed for the selective shuttle hydrochlorination of terminal alkynes to vinyl chlorides (**Fig. 1a**), a key class of intermediates in pharmaceutical synthesis. We demonstrate that this transformation can only be achieved with Au, whereas SACs of other metals, including Ir, which was initially developed in a homogeneous system, either remain inactive or are unselective towards the desired product (**Fig. 1b**). Spectroscopic and catalytic studies indicate that the combination of Au(I) single-atoms with the activated carbon carrier is essential for the unique chemo- and stereoselectivity observed, with the support contributing to the hydrochlorination step. The catalytic system shows broad functional group tolerance and affords the corresponding vinyl chloride derivatives of highly sterically hindered substrates, heteroaromatics, and drug conjugates (**Fig. 1c**), which have remained inaccessible for most heterogeneous systems in various organic reactions. Stability and recovery studies indicate the absence of Au leaching. Nevertheless, Au aggregation eventually leads to activity loss after repeated cycles (**Fig. 1d**), which could be reversed by an oxidative regeneration treatment. Overall, these insights present an efficient and recyclable Au SAC for the shuttle hydrochlorination of alkynes, paving the way towards more sustainable shuttle reactions and highlighting the critical role of tailored catalyst design approaches of SACs.

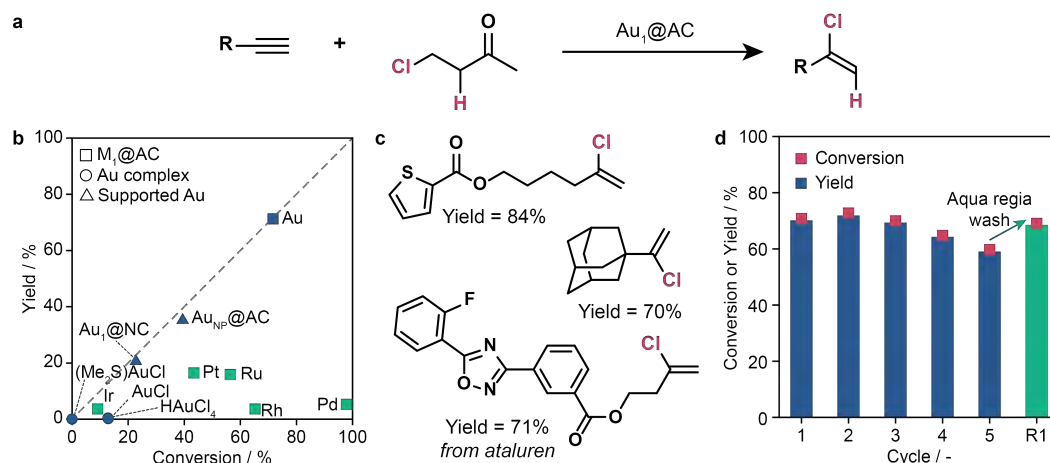


Fig. 1a Scheme of the shuttle hydrochlorination of alkynes and 4-chlorobutan-2-one over $Au_1@AC$. **b** Conversion-yield map of different single-atom catalysts and Au catalyst in the shuttle hydrochlorination of 5-phenylpent-1-yne. **c** Selected vinyl chlorides that could be formed with $Au_1@AC$. **d** Reusability of $Au_1@AC$ over multiple cycles, including regenerative treatment after the 5th cycle.

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Overcoming ATP hydrolysis-driven conformational changes in nitrogenaseN. Vorontsova¹, R. D. Milton^{1*}¹Department of Inorganic and Analytic Chemistry

Nitrogenase is the enzyme responsible for dinitrogen (N₂) fixation into ammonia (NH₃).^[1] It consists of the two proteins - the Fe protein and the MoFe protein. The Fe protein transiently binds and transfers the electrons to the MoFe protein, where N₂ is bound and reduced. Each electron transfer requires hydrolysis of two molecules of adenosine triphosphate (ATP), and the reaction requires a minimum of eight electrons to be transferred.^[2] ATP binding and hydrolysis is coupled to conformational change in the Fe protein, and recent Cryo-EM studies provide evidence for the conformational change of the MoFe protein during turnover. This project focuses on understanding the role of conformational change in the MoFe protein during transient association with the ATP-bound Fe protein.^[3] The hydrolysis of ATP for the fixation of each dinitrogen represents a $\Delta_r G^{0'}$ of up to approximately $-1'250 \text{ kJ mol}^{-1}$, and thus, approaches to bypass this demanding step while still permitting dinitrogen fixation could be valuable. Here, the MoFe protein was modified with the azobenzene di-maleimide (ABDM) molecule proximal to the Fe protein binding side. The ABDM switches conformation from trans- to cis- upon UV light illumination (representing an end-to-end change of 10 Å),^[4] and we present preliminary evidence that the MoFe conformation can also be affected by this switch.

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Ligand-Engineered Ni–Mo Oxides for Ethylene-Glycol ElectrooxidationY. Wang¹¹University of Zurich

Organic–inorganic hybrid materials combine the robust redox chemistry and electronic conductivity of transition-metal oxides with the chemical tunability of organic ligands. In layered Ni–Mo oxide systems, introducing molecular ligands into the interlayer space or directly into the metal coordination sphere provides an efficient, bottom-up strategy to tune the local geometry, layer spacing, and — critically — the electronic environment of the catalytically active Ni centers. Such molecular control opens routes to modulate adsorption strengths of reaction intermediates, charge-transfer kinetics, and proton/electron transport pathways — all key parameters for small-molecule electrooxidation reactions like ethylene glycol oxidation (EGOX).

In this study we systematically examine how a set of structurally and electronically diverse N-donor ligands alter the structural and electronic properties of Ni–MoOx and how those changes translate into EGOX performance. This library was chosen to probe three mechanistic levers by which ligands affect catalysis: (i) electronic donation/withdrawal (σ -donor vs. π -acceptor character) that shifts the Ni d-band center; (ii) multidentate vs. monodentate coordination that changes Ni coordination number and local geometry; and (iii) molecular rigidity/size that controls interlayer expansion and π – π or van der Waals interactions that affect charge transport and active site accessibility.

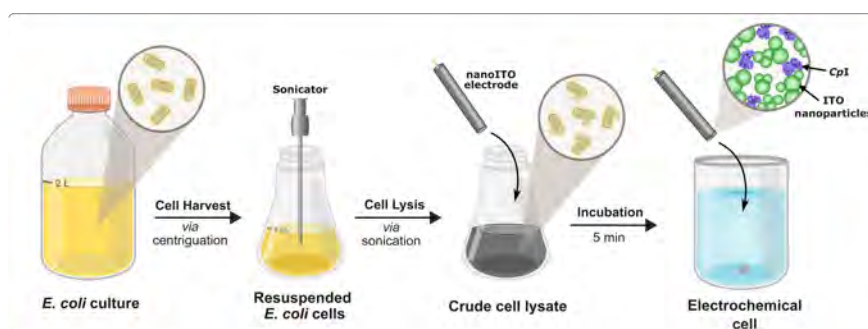
We hypothesize that stronger σ -donor ligands and multidentate amines will increase electron density at Ni, tuning adsorption energies of hydroxyl and alkoxide intermediates toward more favorable reaction energetics, while rigid aromatic spacers that mediate π -interactions could facilitate electronic delocalization across layers and influence long-range conductivity. Conversely, bulky or flexible ligands may hinder substrate access to Ni sites or create heterogeneous microenvironments that alter selectivity and stability.

Purification-Free Electrocatalytic Hydrogen Production with [FeFe]-HydrogenaseS. Webb¹, P. Maroni¹, U. Apfel^{2,3}, R. D. Milton^{1*}¹University of Geneva, ²University of Bochum, ³Fraunhofer Institute for Environmental, Safety, and Energy Technology UMSICHT

The demand for renewable fuels such as H₂ continues to rise during the climate crisis. Metalloenzymes such as [FeFe]-hydrogenases are an attractive option for electrocatalytic H₂ evolution as they operate under mild conditions. To produce hydrogen electroenzymatically, the biocatalyst can be immobilized on (and electronically wired to) an electrode surface, where a potential is applied to drive H⁺ reduction. However, these bioelectrocatalytic systems often suffer from reduced stability.

We developed a simple method to functionalize carbon electrodes with a mesoporous indium tin oxide (nanoITO) layer, onto which the [FeFe]-hydrogenase *CpI* from *Clostridium pasteurianum* was directly immobilized.¹ The resulting bioelectrode produced H₂ at current densities exceeding 8 mA cm⁻² at -0.8 V vs. SHE (pH 7), while retaining ~92% of its initial activity after 5 days of continuous operation. Surface analysis revealed the nanoITO film possesses a hierarchical porous structure with cavities and nanoparticle agglomerates, whilst electrochemical quartz crystal microbalance (EQCM) measurements further revealed that *CpI* adsorbs more stably and operates with higher catalytic activity on nanoITO compared to planar ITO surfaces.²

In this work we further simplify the enzyme preparation procedure to make it better suited for practical application. A significant limitation to the widespread biotechnological application of such enzyme electrodes is the costly and time-consuming purification step necessary to isolate *CpI* from complex protein lysate mixtures prior to its immobilization on the electrode surface. In this work we circumvent the need for enzyme purification by directly immobilizing *CpI* on nanoITO from the lysate protein mixtures (see below). Importantly, the lysate-modified electrode exhibited similar electrocatalytic current densities to that of purified *CpI* and was stable over 16 h of continuous operation. We also highlight the remarkable stability of the lysate solution, which could be stored at room temperature for 80 days with only a 1 % decrease in electroenzymatic activity. We hope that this drastically simplified procedure for preparing [FeFe]-hydrogenase enzyme electrodes will aid in the development of new hydrogenase-based electrocatalytic systems in the future.



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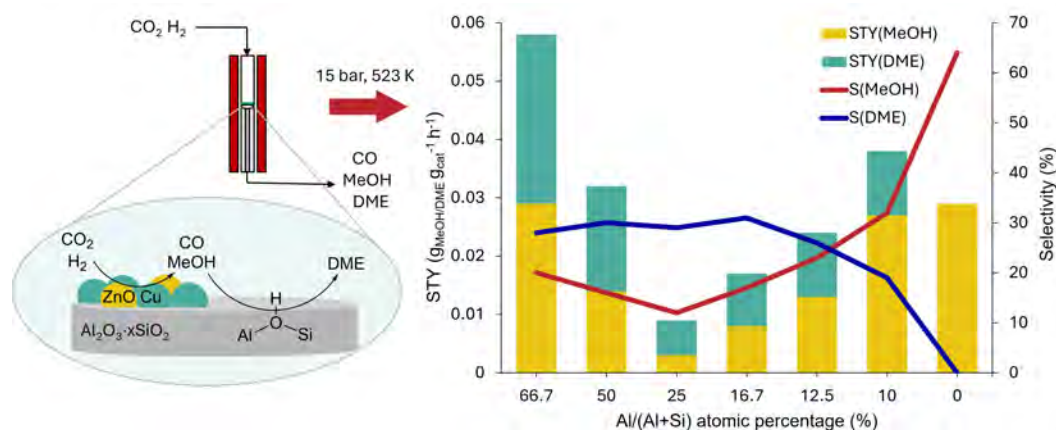
Tuning Acidity in CuZn-Based Catalysts for Direct CO₂ Hydrogenation to Dimethyl Ether

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Dimethyl ether (DME) is a promising low-emission fuel because it can be handled like liquefied petroleum gas (LPG), burns with low soot formation, and can also serve as an intermediate for olefins and other valuable chemicals. A favorable route to DME is the direct hydrogenation of CO₂, which is first converted to methanol over Cu-based catalysts and then dehydrated to DME over acid sites.^[1] However, common dehydration catalysts such as zeolites and γ -Al₂O₃ can suffer from coking, water inhibition, side reactions, or instability.^[2] Cu/ZnO/Al₂O₃ is the benchmark catalyst for CO₂ hydrogenation to methanol,^[3] but the acidity associated with the alumina component has not been fully exploited as a tunable function for directing methanol-to-DME conversion. This work investigates Cu/ZnO/Al₂O₃·xSiO₂ catalysts with varied Al/Si ratios to tune acidity and studies the influence of acid sites on methanol and DME selectivity.

The synthesized supports, covering a broad compositional range, were impregnated with 10 wt% Cu and 5 wt% Zn and tested for CO₂ hydrogenation at 15 bar and different temperatures. The results (Figure) show that alumina-rich catalysts favor DME formation, while silica-rich catalysts enhance methanol selectivity, with an inverse volcano-like trend where the Al/(Al+Si) = 25 catalyst shows the poorest performance. Notably, the catalysts show no deactivation for at least 4 hours on stream. NH₃-TPD shows an increase in both total acidity and acid site strength as the Al-content is raised, while pyridine-FTIR measurements suggest that the nature of acid sites (Lewis/Brønsted) plays a crucial role in controlling the methanol/DME product distribution. Overall, this study supports the rational design of CuZn-based catalysts for one-pot CO₂ hydrogenation to DME.



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Substrate Scope and Structural Basis of Ergothioneine-Like Lyases in *S*-Alkyl Ergothione Catabolism

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Ergothioneine is a histidine-derived betaine of bacterial and fungal origin that is taken up by higher organisms, including humans, as a micronutrient. While the biosynthesis of ergothioneine is well established, the enzymatic processes that utilise, modify and degrade this compound remain poorly understood.² For example, *S*-methyl ergothioneine has been detected as a circulating metabolite of ergothioneine in mice and humans.¹ Still, the function of this compound, its origin and its broader distribution in the environment are unknown. We have recently discovered a set of enzymes from soil bacteria that degrade *S*-methylated ergothioneine in a pathway related to, but distinct from, the ergothioneine degradation pathways.^{2,3} In this presentation, we will discuss our most recent efforts to decipher the degradation of ergothioneine derivatives by bacteria, with the goal of establishing a physiological role of ergothioneine alkylation.

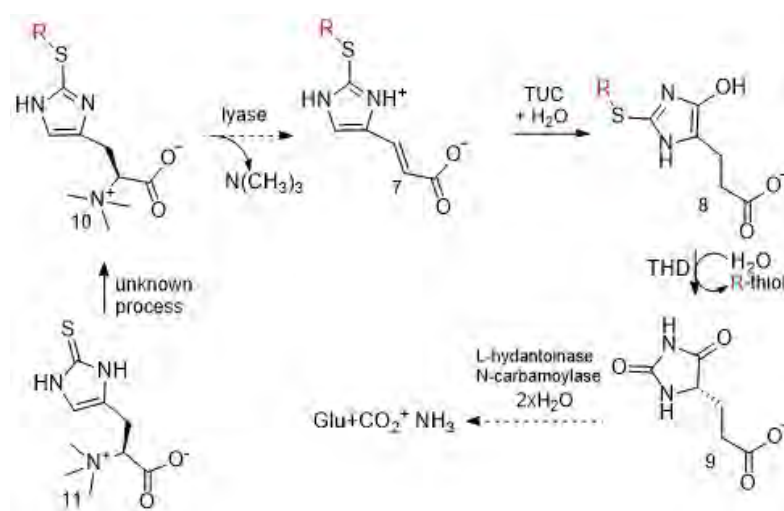


Figure 1. Proposed pathway for the bacterial utilization of *S*-alkyl ergothioneine (10).

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Bayesian Optimization–Guided Development of P450_{BM3}-Catalyzed Metal–Hydride Hydrogen Atom Transfer

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Metal–hydride hydrogen atom transfer (MHAT) reactions catalyzed by engineered enzymes offer a promising platform for enantioselective alkene functionalization under mild conditions. We recently reported a repurposed cytochrome P450_{BM3} that catalyzes enantioselective MHAT cyclization reactions using hydrosilanes as hydride sources. A practical limitation of this enzymatic transformation is the requirement for superstoichiometric amounts of hydrosilane, which limits its practicality and industrial relevance. To overcome this limitation, we applied a Bayesian optimization algorithm based on Gaussian regression to minimize hydrosilane usage while maintaining high yield and enantioselectivity. Using either PhSiH₃ or MePhSiH₂ as hydride source, we simultaneously optimized multiple reaction parameters, including pH, substrate concentration, surfactant loading, and hydrosilane stoichiometry. For reactions employing PhSiH₃, hydrosilane consumption could be reduced from 20 equivalents to 4 equivalents without compromising yield or enantioselectivity. These optimized conditions were broadly applicable across different diene substrates. When MePhSiH₂ was used, the Bayesian optimization identified distinct parameters, affording twofold higher yields than under the reported conditions. Collectively, this study confirms the power of Bayesian optimization for efficiently navigating the parameter hyperspace and provides practical conditions that enhance the applicability of enzymatic MHAT chemistry.