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Enzyme discovery in non-canonical natural product pathwaysL. Berra¹¹University of Konstanz, Fachbereich Chemie, Universitätsstrasse 10, 78464 Konstanz, Germany

Natural products have been and continue to be of tremendous importance for human health purposes. They have captivated researchers for decades with their remarkable structural complexity, bioactivity, and the intricate enzymatic reactions underlying their biosynthesis. While much attention has been focused on traditional classes such as non-ribosomal peptides, polyketides, and terpenoids, our research program specifically aims to expand upon these systems by uncovering and investigating distinct specialized metabolic pathways to unlock access to truly novel chemical entities and the associated enzyme-catalyzed chemical transformations.

The talk will focus on our on-going endeavors in exploration of non-canonical SAM-derived enzyme chemistry by combining genomics-driven computational methods with functional, structural, and mechanistic investigations.

Non-oxidative dehydrogenation of alkanes over Cu(I)-exchanged Mordenite.

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The non-oxidative dehydrogenation of light alkanes offers a promising route for the production of olefins - one of the key reagents in the chemical industry [1]. Our group recently demonstrated that Cu-exchanged zeolites to be effective catalysts for this transformation when operated in a chemical looping mode under significantly milder conditions compared to conventional high-temperature processes [2]. In particular, CuIMOR zeolite has been shown to dehydrogenate alkanes forming π -complexes with olefins, as evidenced by *in situ* solid-state NMR and FTIR spectroscopies, showing characteristic signals of Cu–olefin intermediates.

To further elucidate the reaction mechanism, we extended our study to n-butane as a reactant. This system presents greater mechanistic complexity, given the possibility of multiple products. The application of ¹³C-labeled n-butane in combination with *in situ* solid-state NMR and FTIR spectroscopies, alongside with online gas chromatography detection, allowed us to detect and differentiate between possible products such as 1-butene, *iso*-butene, and *cis*-/*trans*-2-butene. To gain deeper mechanistic insight into the role of Cu-speciation in guiding selectivity and reactivity, we compared reaction rates using a series of alkanes – ethane, propane, *n*-butane and *iso*-butane. This comparative kinetic study was further supported by a Hammett plot analysis, which correlates the reaction rates to the electron-donating properties of the reactants. The observed trends provided additional evidence for the proposed mechanism, suggesting that electronic effects play a significant role.

Our findings highlight the potential of Cu-zeolites for low-temperature alkane dehydrogenation and underscore the value of advanced spectroscopic techniques in unveiling reaction mechanisms under realistic operating conditions. This work advances the development of Cu-containing zeolites for energy-efficient catalytic applications.

[1] Z. Nawaz, *Reviews in Chemical Engineering* **2015**, 31.5, 413-436.

[2] M. Artsiusheuski, et al., *J. Am. Chem. Soc.* **2025**, 147, 18, 15880–15889

One-step Electrochemical Ammonia Synthesis and Recovery via Joule-Stripping Strategy

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In recent years, the overabundance of reactive nitrogen species in the environment, especially nitrate, due to the over fertilization of crop fields, has received considerable amount of attention in the scientific community. Related results, such as a severe transgressed planetary boundary of the N-cycle, eutrophication of aquatic ecosystems, and direct threat to human health has started the surge to remove excessive nitrate from the environment.^[1] In particular, electrochemical methods have emerged as a promising approach since it not only allows to remove nitrate under ambient conditions, but also to convert the toxic pollutant into a value-added product, such as ammonia.^[2] Despite recent progress in the development of active, selective, and stable electrocatalysts for the nitrate to ammonia reduction, a severe challenge to date is the recovery of the produced ammonia from the dilute aqueous solutions.

In our work we have demonstrated how operating the electrochemical nitrate reduction at high current densities ($>700 \text{ mA cm}^{-2}$) in alkaline media allows to turn the undesired but unavoidable Joule-losses into a beneficial process by using the *in situ* generated heat to directly volatilize the produced ammonia in the electrolyte.^[3] The so termed “Joule-Stripping Strategy” of ammonia combined with a subsequent acid trap enables to collect $>95\%$ of the formed ammonia as solid, avoiding additional post-catalytic time and energy intensive extraction steps to obtain ammonia from the aqueous electrolyte.

[1] Y. Xiong, Y. Wang, J. Zhou, F. Liu, F. Hao, Z. Fan, *Advanced Materials*, **2024**, 36, 2304021

[2] Y.-Z. Xu, D. F. Abbott, R. N. Dürr, T. N. Huan, V. Mougél, *Advanced Energy Materials*, **2024**, 14, 2402294

[3] Y.-Z. Xu, R. N. Dürr, F. Häfliger, D. F. Abbott, V. Mougél, *Angewandte Chemie International Edition*, **2025**, e202504174

Disentangling the Effects of Alloying and Interfacial Sites in PtCr-Catalyzed CO₂ Hydrogenation

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Promotional effects are ubiquitous across catalytic processes involving supported nanoparticles, where the addition of a second element – promoters – significantly improves the catalytic performance, such as activity, selectivity, and stability. However, the inherent complexity of these catalysts makes it difficult to pinpoint the roles played by promoters at the molecular level. In this study, we prepare well-defined PtCr bimetallic catalysts with or without Cr interfacial Lewis acidic sites via two different surface organometallic chemistry (SOMC) approaches.¹ Extensive characterizations are conducted to confirm the structural difference resulting from the different synthetic approaches. Notably, the catalyst containing exclusively PtCr alloys displays a substantial promotional effect in reverse water gas shift (RWGS) compared to monometallic Pt@SiO₂, while having additional Cr-interfacial sites further improves the catalytic activity. This difference in reactivity was explained by CO₂ adsorption IR and *in situ* spectroscopic studies, which reveal that PtCr alloy facilitates a redox reaction pathway, whereas an additional formate-mediated pathway takes place at the interface between PtCr alloy and Cr(III) Lewis acid sites. These findings highlight that both PtCr alloy formation and Cr interfacial sites contribute to improving the RWGS activity. The ability to synthesize well-defined bimetallic catalysts with SOMC approaches gives us the opportunity to dissect the roles of different species and establish a better understanding on the structure-activity relationship.

Christophe Copéret, Aleix Comas-Vives, Matthew P. Conley, Deven P. Estes, Alexey Fedorov, Victor Mougél, Haruki Nagae, Francisco Núñez-Zarur, Pavel A. Zhizhko, *Chemical Reviews*. **2016**, 116, 323-421.

Oxygen Vacancy Dynamics in Indium Oxide Drive the Catalytic Activity and Stability during CO₂ Hydrogenation to Methanol

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Indium oxide (In₂O₃) based catalysts are active for the selective hydrogenation of CO₂ to methanol that likely proceeds over oxygen vacancy sites ($V_{\text{O}}^{\bullet\bullet}$ sites) of an active In₂O_{3-x} phase formed in situ.[1–3] However, an excessive generation of $V_{\text{O}}^{\bullet\bullet}$ sites leads to their precipitation to In⁰ (deactivation due to over-reduction of In₂O₃).[3] An atomic-scale understanding of how to modulate the reactivity of $V_{\text{O}}^{\bullet\bullet}$ sites in In₂O₃ is currently incomplete.[4,5] We hypothesized that the abundance and stability of $V_{\text{O}}^{\bullet\bullet}$ sites in In₂O₃ is tunable by changing its defective structure through doping, eventually aiming to improve the overall catalyst performance. Using Sn- or Zr-doped In₂O₃, we observed diverging dopant-induced catalytic performances under CO₂ hydrogenation conditions, i.e., a rapid deactivation in Sn-doped In₂O₃ and a stable, high activity in Zr-doped In₂O₃. Relying on various operando techniques, we uncovered that the $V_{\text{O}}^{\bullet\bullet}$ sites in Sn-doped In₂O₃ were unreactive towards CO₂, agglomerated, and precipitated to In⁰ and Sn⁰ that were molten under reaction conditions. At the same time, $V_{\text{O}}^{\bullet\bullet}$ sites in Zr-doped In₂O₃ were highly reactive towards their replenishment by CO₂, resulting in high catalyst activity and stability of the *c*-In₂O₃ phase.

Fresh Sn- and Zr-doped In₂O₃ (In_{1.9}Sn_{0.1}O_{3.05} and In_{1.9}Zr_{0.1}O_{3.05}) were phase pure (*c*-In₂O₃ structure) based on XRD measurements. The analysis of the local atomic structure probed by PDF (Figure a, top) revealed dopant-induced local strain in both In_{1.9}Sn_{0.1}O_{3.05} and In_{1.9}Zr_{0.1}O_{3.05} relative to the reference undoped nano-In₂O₃. The strain due to the dopant insertion is evident from the peak in the difference PDF for the doped materials, while no such peak was observed for nano-In₂O₃ (Figure a, bottom). Despite their structural similarity, In_{1.9}Sn_{0.1}O_{3.05} and In_{1.9}Zr_{0.1}O_{3.05} exhibited contrasting catalytic performances for the hydrogenation of CO₂ to methanol (Figure b). In_{1.9}Sn_{0.1}O_{3.05} showed a low initial activity and underwent rapid deactivation, while In_{1.9}Zr_{0.1}O_{3.05} displayed a high methanol yield with no deactivation. Operando PDF data of the catalysis after 4 h time on stream (TOS) revealed that the structure of In_{1.9}Zr_{0.1}O_{3.05} remained in the *c*-In₂O₃ type, while In_{1.9}Sn_{0.1}O_{3.05} (and nano-In₂O₃) displayed a strongly altered PDF after 4 h TOS (Figure c), originating from molten metallic indium (and tin).

Our study demonstrates the structural dynamics of In₂O₃-based catalysts during CO₂ hydrogenation to methanol. Altering the defective structure of *c*-In₂O₃ through doping is an effective approach to tune the structural dynamics towards the desired improvement of the catalytic performance.

- [1] J. Ye, C. Liu, D. Mei, Q. Ge, *ACS Catalysis*, **2016**, 3, 1296–1306.
- [2] O. Martin, A. J. Martín, C. Mondelli, S. Mitchell, T. F. Segawa, R. Hauert, C. Drouilly, D. Curulla-Ferré, J. Pérez-Ramírez, *Angewandte Chemie International Edition*, **2016**, 55, 6261–6265.
- [3] A. Tsoukalou, P.M. Abdala, D. Stoian, X. Huang, M.-G. Willinger, A. Fedorov, C. R. Müller, *Journal of the American Chemical Society*, **2019**, 141, 13497–13505.
- [4] A. Tsoukalou, P. M. Abdala, A. Armutlulu, E. Willinger, A. Fedorov, C. R. Müller, *ACS Catalysis*, **2020**, 10, 10060–10067.
- [5] T. P. Araújo, S. Mitchell, J. Pérez-Ramírez, *Advanced Materials*, **2024**, 2409322, 1–22.

Regulating the Long- and Short-Range Interaction in Cu-Based Single-Atom Catalysts for Oxygen Electroreduction

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The oxygen reduction reaction (ORR) has emerged as an electrochemical approach for efficient fuel cells and metal-air batteries, which are promising and environmentally friendly strategies for achieving high-performance sustainable energy conversion and storage systems. Single-atom catalysts (SACs) have demonstrated significant potential for electrocatalytic ORR, which can be further enhanced by introducing heteroatom doping within the carbon matrix. However, the complex structure-function relationships between the doping positions and catalytic activity remains poorly understood. In this study, we synthesized Cu-based SACs comprising coordinated/uncoordinated S atoms on a nitrogen-doped carbon matrix. We introduced a ligand-modification strategy to precisely control the spatial distance between S dopants and the Cu active sites. Three different catalysts with distinct S positions were prepared and systematically evaluated for ORR. Furthermore, we systematically studied how the positions of S dopants affect catalytic behavior and set up structure-performance relationships for the first time. Operando Raman and X-ray absorption spectroscopy revealed the dynamic behavior of the catalytic Cu sites. In addition, density functional theory (DFT) calculations revealed a volcano-type relationship between the free energy (ΔG_{OH^*}) and the Cu-S interatomic distance, highlighting an optimal S-doping configuration. This work provides deeper insights into the mechanistic role of the position of heteroatom in SACs, which is important for tuning their catalytic performance.

Present and Future of Environmental Catalysis in Industry

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The green chemicals sector is rapidly expanding, with global market value exceeding \$100 billion in 2022 and projected to surpass \$270 billion by 2032 [1]. Environmental catalysis has emerged as a critical enabler of this growth, offering robust solutions for industrial decarbonization through emission reduction, enhanced energy efficiency, and compliance with increasingly stringent environmental regulations. From an industrial standpoint, catalytic technologies are not only essential for environmental stewardship but also for maintaining operational competitiveness and long-term sustainability.

The transition to renewable energy sources—characterized by intermittency and variability—introduces significant challenges for catalytic systems traditionally designed for steady-state operation. These challenges necessitate a paradigm shift in process design, control strategies, and catalyst development to ensure performance stability under dynamic conditions. Particular attention is directed toward the deployment of green ammonia and green methanol technologies, which are reshaping chemical production paradigms. Companies such as Casale SA are at the forefront, integrating advanced catalytic systems into modular, scalable platforms capable of utilizing hydrogen from electrolysis and captured CO₂, thereby aligning with global decarbonization targets [2-4].

To address the operational variability introduced by renewable energy, the industry is adopting flexible process integration strategies, advanced control architectures, and real-time digital monitoring. Hybrid energy storage systems—including batteries, thermal storage, and hydrogen buffers—are increasingly employed to decouple energy supply from demand, ensuring continuous catalytic operation. Concurrently, innovations in catalyst materials and configurations are enhancing system resilience and performance under fluctuating conditions.

Beyond technological advancements, the adoption of environmental catalysis is strongly influenced by policy frameworks and market dynamics [5]. Regulatory instruments such as carbon pricing, green hydrogen incentives, and emissions mandates are accelerating the shift toward cleaner technologies. Simultaneously, growing demand for low-carbon products is reinforcing the strategic importance of catalytic innovation [6].

In summary, environmental catalysis is not merely a scientific advancement but a foundational pillar of sustainable industrial transformation. Its integration into chemical manufacturing systems supports the transition to renewable energy and low-carbon production while preserving industrial viability and competitiveness. As such, it represents a cornerstone of the next generation of green chemical manufacturing.

[1] <https://www.gminsights.com/industry-analysis/green-ammonia-market>

[2] casale.ch

[3] Filippi and C. Pizzolitto, Catalysis Today 2022, 387, 9-11

[4] Rostrop-Nielsen, Catalysis Today 2023, 423, 113878

[5] <https://www.coherentmarketinsights.com/industry-reports/green-ammonia-market>

[6] Kong Chyong, E. Italiani and N. Kazantzis, Nature Communications 2025, 16, 766.

Acknowledgements

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Polyethylene waste hydrogenolysis over bimetallic catalysts with favorable environmental footprint and economics

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Polyolefins represent nearly two-thirds of the plastic market with no short-term alternatives, making the development of chemical recycling strategies essential. Beyond pyrolysis, hydrogenolysis is an emerging approach to support circularity, enabling the production of valuable alkanes. However, the process remains limited by modest catalytic performance and lack of clarity in the target products required to achieve environmental and economic feasibility, summarized in the ‘Plastic-to-X’ question.^[1] Integrating catalyst design with systems engineering may clarify technological prospects and guide future studies.^[2]

Our first study^[3] identified ruthenium nanoparticles supported on titania as highly active catalysts under optimized reaction conditions, although low-value gaseous products were predominantly formed. The product distribution could be controlled by incorporating nickel as a modifier to the ruthenium phase, with the supported Ru-Ni catalysts producing up to 25% liquid (C₆–C₄₅) products from high density polyethylene and plastic caps (**Fig. 1a**). The optimal composition, namely 2.5 Ru wt% and 5 Ni wt% (2.5Ru5Ni), exhibited an alloyed nature, as indicated by high resolution transmission electron microscopy and extended X-ray absorption fine structure analysis (**Fig. 1b**). Mechanistic studies with surrogate compounds and density functional theory simulations revealed facilitated internal C–C bond cleavage over the Ru-Ni catalyst and terminal C–C bond scission over the Ru catalyst, rationalizing the observed differences in selectivity. At a systems level, techno-economic and life cycle analyses predicted economically viable processing of plastic caps –even when using green H₂– with reduced CO₂ emissions compared to the alternative fossil route, presenting the first example of its kind. To generalize this, we estimate a minimum average chain length of C₁₁ in the product distribution as an effective answer to the ‘Plastic-to-X’ endeavor (**Fig. 1c**). This work highlights a practical route for valorizing polyethylene waste while emphasizing the importance of bridging analyses across scales to uncover design guidelines for future catalyst developments.

Fig. 1 a Catalytic performance of 2.5Ru5Ni and 2.5Ru for hydrogenolysis of HDPE and plastic caps. **b** Structural characterization of used 2.5Ru5Ni and 2.5Ru catalysts. **c** ‘Plastic-to-X’ analysis of the avoided CO₂ emissions and margin for profit in hydrogenolysis towards different product distributions compared to the equivalent business-as-usual operation, showing the minimum average product chain length for environmental and economic gains.

[1] A.J. Martín, S.D. Jaydev, C. Mondelli, J. Pérez-Ramírez, *Chem* **2021**, 7, 1487.

[2] S.M. Mitchell, A.J. Martín, J. Pérez-Ramírez, *Nat. Chem. Eng.* **2024**, 1, 13.

[3] S.D. Jaydev, et al., *Angew. Chem. Int. Ed.* **2024**, 63, e202317526.

Carbene-supported dinickel complexes for efficient hydroxylation of benzene to phenol

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Phenol is a valuable base chemical applied in resin and dye industry. However, it is still largely synthesized through the Hock oxidation of cumene, which suffers from harsh conditions and a mediocre atom economy.¹ Metal-catalyzed direct hydroxylation of benzene recently emerged as a more profitable synthetic approach, but only a few systems reach acceptable conversion and selectivity.² Herein, we will present a series of bimetallic hydroxo-bridged Ni^{II} complexes supported by classical and mesoionic N-heterocyclic carbene ligands³ which catalytically oxidize benzene to phenol using H₂O₂ as benign oxidant with competitive efficiency and higher TONs compared to the benchmark Ni catalysts. Spectroscopic and electrochemical studies suggest an electrophilic aromatic substitution pathway involving a [Ni^{III}(μ-O)₂Ni^{III}]²⁺ species, an elusive compound detected for the first time starting from a pre-formed dinuclear Ni catalyst.

[1] Weber, M.; Weber, M.; Weber, V. *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, **2020**; pp. 1–20.

[2] Rajeev, A.; Balamurugan, M.; Sankaralingam, M.; *ACS Catal.* **2022**, *12*, 9953–9982.

[3] Bertini, S.; Albrecht, M. *Organometallics* **2020**, *39*, 3413–3424.

Cooperative Alkene Isomerization Catalysed by a Molecular Nickel-Aluminate Complex

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Cooperative catalysis, in which two metals collaborate to facilitate a chemical reaction, is emerging as a promising strategy for replacing expensive noble metal catalysts by those based on cheaper earth abundant metals. However, only relatively few examples of heterobimetallic cooperativity in catalysis are known and understood, hampering the rational use of this strategy. In our work we synthesized a rare nickel-aluminate complex (**1**) featuring two bridging hydrides, which does not require the use of a specialized ligand for supporting the bimetallic assembly (Figure 1a). Only a handful of NiAl hydride complexes have been reported, with even fewer showing cooperative reactivity or catalysis.[1][2] Gratifyingly, we found that our complex **1** is an active catalyst for the isomerization of alkenes (Figure 1b), a reaction typically carried out with noble metal hydrides.[3] The individual LiAl-hydride, and nickel components show no or poor activity in this reaction, indicating a cooperative mechanism for **1**. By studying the stoichiometric and catalytic reactivity of **1** with alkenes and other unsaturated molecules, we provide fundamental insights into this cooperative reaction to shed light on how nickel and aluminium can cooperate in catalytic reactions.

[1] M. M. Shoshani et al., **2024**, *Dalton Trans*, 53(47), 18932–18945.

[2] M. Crimmin et al., **2025**, *ChemRxiv*. 10.26434/chemrxiv-2025-1tdn0

[3] C. Mazet, et al. **2014**, *Chem. Commun.*, 50(69), 9816.

Catalytic improvement of a metalloenzyme using hydrophobic non-canonical amino acids

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Hydrophobicity controls many aspects of protein and enzyme function.^[1-3] Although hydrophobic tuning can be achieved to a limited extent with canonical amino acids, the incorporation of non-canonical amino acids (ncAAs) has the potential to further extend this ability, enabling new and improved functionality. We engineered a robust aminoacyl-tRNA synthetase/tRNA pair for the incorporation of hydrophobic amino acids, specifically cycloalkylalanines, in *E. coli*. These ncAAs were utilized to engineer the primary coordination sphere of bacterial laccase, a prototypical metalloenzyme with T1 copper site. Laccases are high value catalysts that can perform one-electron oxidation chemistry to catalyze a variety of transformations, including lignin polymerization/depolymerization and degradation of pollutants. Our ncAA-engineered mutants revealed enhanced redox potentials and catalytic properties, particularly for the oxidation of challenging phenolic substrates. Additionally, we demonstrated that further engineering of the second coordination sphere can result in an additional increase in catalytic activity, illustrating that these new tools can be combined with traditional directed evolution techniques.

[1] D. A. Estell, T. P. Graycar, J. V. Miller, D. B. Powers, J. A. Wells, J. P. Burnier, P. G. NG, *Science* **1986**, 233, 659–663.

[2] J. A. Hunt, M. Ahmed, C. A. Fierke, *Biochemistry*, **1999**, 38, 9054-9062.

[3] D. K. Garner, M. D. Vaughan, H. J. Hwang, M. G. Savelieff, S. M. Berry, J. F. Honek, Y. Lu, *J. Am. Chem. Soc.* **2006**, 128, 15608-15617.

Organic Surface Functionalization of Transition Metal Phosphide to Enhance CatalysisY. Shen¹, M. F. Delley^{1*}¹University of Basel

Transition metal phosphides (TMPs) have emerged as promising alternatives to traditional noble metal-based catalysts because of their excellent catalytic properties for hydrogen evolution reaction, hydrotreating, and hydrogenation applications.^[1-3] While noble metal-based hydrogenation catalysts can be effectively tuned by organic ligands,^[4-5] there are only a few such organic surface modification strategies known for TMPs so far.^[6-7] The limited range of available surface functionalities for TMPs makes it very challenging to understand how the properties of the surface groups influence TMP-based catalysis. This hampers accessing the full potential of ligand-directed catalysis for the more earth-abundant TMP catalysts. Methods that allow the introduction of surface organic groups with systematically varied properties are needed for rational improvement of TMP-based catalysts.

Herein, we present a novel approach to covalently modify cobalt phosphide with organic functional groups at the surface using a sonication-assisted approach. This enabled a systematic variation of electronic and steric properties of the surface groups, as well as changing their surface coverage. Combined X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), and elemental analysis showed the successful surface modification with a range of different aryl and alkyl groups. We probed the effect of different surface groups with systematically varied properties by testing the modified materials as catalysts for the hydrogenation of α , β -unsaturated aldehydes. This analysis provided clear insight into the factors that govern catalytic properties and identified optimal electronic and steric properties and density of the surface groups for a selective C=O hydrogenation. Overall, our research significantly expands the current scope for the surface covalent functionalization of transition metal phosphides and shows the potential of these strategies for the tuning of the catalysis.

[1] S. T. Oyama, T. Gott, H. Zhao, Y.-K. Lee, *Catal. Today* **2009**, *143*, 94-107.

[2] Y. Shi, B. Zhang, *Chem. Soc. Rev.* **2016**, *45*, 1529-1541.

[3] Y. Liu, A. J. McCue, D. Li, *ACS Catalysis* **2021**, *11*, 9102-9127.

[4] L. Zhang, M. Zhou, A. Wang, T. Zhang, *Chem Rev* **2020**, *120*, 683-733.

[5] C. A. Schoenbaum, D. K. Schwartz, J. W. Medlin, *Acc. Chem. Res.* **2014**, *47*, 1438-1445.

[6] I. A. Murphy, P. S. Rice, M. Monahan, L. B. Zasada, E. M. Miller, S. Raugei, B. M. Cossairt, *Chem. Mater.* **2021**, *33*, 9652-9665.

[7] R. Gao, L. Pan, H. Wang, Y. Yao, X. Zhang, L. Wang, J. J. Zou, *Adv Sci (Weinh)* **2019**, *6*, 1900054.

Real-Time Thermal Imaging of Catalytic Hydrogen Combustion: Enhancing Stability through Operando Infrared Thermography

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Catalytic H₂ combustion (CHC) is a critical reaction for low-emission energy conversion and H₂ safety systems, yet maintaining stability under varying operating conditions remains challenging. In this study, we employ operando infrared thermography (IRT) coupled with quadrupole mass spectrometry (QMS) to monitor real-time surface temperatures and heat evolution during CHC over a Pt- γ -Al₂O₃ catalyst. Using a custom-designed, millimetre-scale reactor with an IR-transparent ZnSe window, we systematically investigate the influence of gas hourly space velocity (GHSV), H₂ concentration, and catalytic bed configuration on heat distribution, reaction front dynamics, and catalyst stability. Our findings reveal that rapid water formation at high H₂ concentrations can induce catalyst deactivation and CHC extinction by blocking active sites and restricting thermal management. However, this limitation can be mitigated through increased GHSV, which facilitates efficient water removal and preserves catalytic activity, albeit with a trade-off in overall H₂ conversion efficiency. This work highlights the critical interplay between mass transport, heat dissipation, and catalyst stability, providing valuable insights for optimising CHC systems for safer, more efficient H₂ technologies.

Influence of hydrogen and oxygen feed impurities on platinum-catalyzed acetylene hydrochlorinationA. Alkhoori¹, A. Ruiz-Ferrando^{1*}, V. Giulimondi^{1*}, J. Pérez-Ramírez^{1*}¹ETH Zurich

Platinum (Pt) nanostructuring is a powerful strategy for tuning adsorption properties and reactivity in vinyl chloride monomer (VCM) synthesis.^[1] To ensure relevance beyond ideal conditions, catalyst performance must be assessed under more realistic acetylene (C₂H₂) feeds containing unavoidable impurities such as oxygen (O₂) and hydrogen (H₂), which can impair performance through competitive adsorption and active site modification. In this study, we employed impurity concentrations as high as 5 vol% – substantially above typical industrial levels (ca. 0.075 vol%) – to rigorously test catalyst robustness under harsh conditions. We then systematically evaluated the catalytic performance of 1 wt% Pt single atoms (Pt_{SA}/AC) and their nanoparticle counterparts (Pt_{NP}/AC), both supported on activated carbon, under controlled co-feeds of H₂ and O₂. In the presence of 5 vol% H₂, Pt_{SA}/AC maintained high activity and selectivity toward VCM, with no detectable hydrogenation products due to its strong preference for HCl adsorption and limited H₂ activation (**Fig. 1**). Comparative analysis showed that Pt_{NP}/AC is more prone to undesired hydrogenation pathways forming ethylene (C₂H₄) and ethane (C₂H₆), emphasizing the importance of nuclearity in determining impurity response. In contrast, 5 vol% O₂ co-feeding on Pt_{SA}/AC catalyst led to a pronounced 80% drop in VCM yield, attributed to competitive adsorption and active site blocking. Notably, Pt_{SA}/AC catalyst demonstrated full activity recovery upon O₂ removal, indicating reversible site deactivation (**Fig. 1**).

To elucidate this behavior, we employed O₂-temperature programmed desorption (TPD) and density functional theory (DFT) simulations, which revealed that dechlorinated Pt sites exhibit enhanced O₂ affinity, thereby hindering reactivity via oxidative inhibition. These findings underscore the critical role of atomically precise catalyst design in ensuring robustness under realistic feed compositions in acetylene hydrochlorination. By establishing mechanistic links between impurity type, site structure, and catalyst resilience, this study informs the rational design of Pt-based catalysts for sustainable VCM production under non-ideal industrial conditions. The approach developed here can be extended to evaluate other noble-metal systems where impurity tolerance is a limiting factor.

Fig. 1 Time-on-stream performance of acetylene hydrochlorination over Pt_{SA}/AC and Pt_{NP}/AC catalysts under H₂ or O₂ impurity co-feeding. Pt_{SA}/AC maintained a VCM yield of ~22% in the presence of H₂ in the feed, whereas O₂ caused an 80% drop in yield. Performance recovered after O₂ co-feeding was stopped.

[1] S.K. Kaiser, I. Surin, A. Amorós-Pérez, S. Büchele, F. Krumeich, A.H. Clark, M.C. Román-Martínez, M.A. Lillo-Ródenas, J. Pérez-Ramírez, *Nat. Commun.* **2021**, *12*, 4016.

Flame-made non-stoichiometric Au-PrO_x catalyzes N₂O synthesis from NH₃G. Beshara¹, M. Agrachev^{1*}, K. Engel^{1*}, T. Heinrich^{1*}, R. Grass^{1*}, J. Pérez-Ramírez^{1*}¹ETH Zürich

Gold nanoparticles (NPs) deposited on ceria, Au/CeO₂, are highly selective for NH₃ oxidation to N₂O, offering a safer and scalable alternative to the hazardous thermal decomposition of ammonium nitrate. However, this catalyst suffers from progressive deactivation, attributed to gold NPs agglomeration, and the current systems are confined to CeO₂ as the sole reducible support enabling such initial high performance.^[1]

Herein, flame spray pyrolysis was employed as standardized approach to disperse gold (1 wt%) across a series of rare earth oxides (REO_x). The resulting Au-REO_x catalysts exhibited a trend of increasing N₂O productivity from trivalent REO_x (La > Nd > Sm > Eu) to tetravalent REO_x (Pr > Tb > Ce). Non-stoichiometric Au-PrO_x and Au-TbO_x were the most selective, achieving 86% and 88% N₂O selectivity at complete NH₃ conversion, surpassing the benchmark Au/CeO₂ (**Fig. 1a,b**). Crucially, Au-PrO_x demonstrated remarkable stability, preserving both nanostructure and performance over 80 hours on stream (**Fig. 1c**). NH₃-TPR cycles revealed the presence of weakly bound lattice oxygen species in Au-PrO_x and Au-TbO_x catalysts, facilitated by the intrinsic mixed-valence states of Pr³⁺/Pr⁴⁺ and Tb³⁺/Tb⁴⁺, enabling high N₂O evolution via a Mars-Van Krevelen-type mechanism. These findings establish Au-PrO_x as a superior catalyst for selective NH₃ oxidation to N₂O, encouraging future studies to evaluate its potential in selective catalytic oxidations at large.

Fig. 1 Performance comparison of the Au-REO_x catalysts presented in this work with the benchmark system, based on **a** the highest achieved N₂O selectivity, **b** the space-time-yield of N₂O, and **c** the deactivation constant k_d , determined by fitting the normalized rate of conversion over 40 h on stream to a power function of the form $y = ax^{-k_d}$. Conditions: T = 623-673 K; $m_{cat} = 0.2$ g; WHSV = 15,000 cm³ g_{cat}⁻¹ h⁻¹ (a, b) or 200,000 cm³ g_{cat}⁻¹ h⁻¹ (c); Feed = 8 vol% NH₃, 8 vol% O₂, 4 vol% Ar, 80 vol% He; P = 1 bar.

[1] Z. Tang, I. Surin, A. Rasmussen, F. Krumeich, E. V. Kondratenko, V. A. Kondratenko, J. Pérez-Ramírez, *Angewandte Chemie International Edition* 2022, 61, e202200772

Impact of gas diffusion electrode substrate and architecture on the electrochemical reduction of CO₂

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Electrochemical CO₂ reduction (eCO₂R) offers a promising pathway to convert CO₂ into sustainable fuels and chemicals, moving us closer to a net zero or net negative carbon economy.¹ To compete with established fuel/chemical production routes, electrodes need to be highly active, selective towards a desired product, and stable. Thanks to the use of gas diffusion electrodes (GDEs) fed by gaseous CO₂, high activities (i.e. high current densities) can generally be achieved.^{2,3} However, the performance of GDEs is affected not only by the catalyst material, but also by the structural and chemical properties of the substrate used (e.g. pore size, hydrophobicity, composition).^{4,5} Understanding the impact of these parameters is key to improve performance, but it requires a detailed knowledge of mass transport and reaction kinetics within the electrode.

In this work, we study mass transport phenomena during eCO₂R in different GDE architectures by (i) exploring different substrate pore sizes and, hydrophobicity, (ii) comparing Ag and Cu catalysts, and (iii) applying surface treatments on the catalyst. We assess GDE performance by determining the maximum carbon product current density prior to the onset of the competing hydrogen evolution reaction (HER), using this threshold as an indicator of the apparent eCO₂R reaction rate. These measurements reveal key information on the mass transport limitations in the GDE and on the activity of the different metals. Complementary experiments on CO reduction, a typical intermediate of the eCO₂R, provide further insight on gas transport and C_{≥2} product formation kinetics. Additionally, we study and compare the stability of these GDEs under commercially relevant conditions to identify potential degradation mechanisms and propose mitigation strategies. Our findings further highlight the critical role of GDE substrates and architectures in governing eCO₂R activity, selectivity, and durability, offering guidance for the future development of this technology.

[1] A. Senocrate, C. Battaglia, *J. Energy Storage* **2021**, 36, 102–373.

[2] S. Verma, Y. Hamasaki, C. Kim, W. Huang, S. Lu, H. R. M. Jhong, A. A. Gewirth, T. Fujigaya, N. Nakashima, P. Kenis, *ACS Energy Lett.* **2018**, 3, 193–198.

[3] F. P. García de Arquer, C.-T. Dinh, A. Ozden, J. Wicks, C. McCallum, A. R. Kirmani, D.-H. Nam, C. Gabardo, A. Seifitokaldani, X. Wang, Y. C. Li, F. Li, J. Edwards, L. J. Richter, S. J. Thorpe, D. Sinton, E. H. Sargent, *Science* **2020**, 367, 661–666.

[4] A. Senocrate, F. Bernasconi, D. Rentsch, K. Kraft, M. Trottmann, A. Wichser, D. Bleiner, C. Battaglia, *ACS Appl. Energy Mater.* **2022**, 5, 14504.

[5] F. Bernasconi, A. Senocrate, P. Kraus, C. Battaglia, *EES Catalysis* **2023**, 1, 1009.

The Swiss Army Knife of Electrodes: Pillar[6]arene-Modified Electrodes for Molecular Electrocatalysis Over a Wide pH Range

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Immobilising molecular catalysts on common electrode materials, including metal oxides, offer a promising strategy to merge the advantages of well-defined and oftentimes highly active molecular species with the durability and recyclability of heterogeneous catalysts.^[1] This immobilisation is often achieved through simple physisorption. However, systems that can catalyse reactions and are stable across a wide pH range are uncommon.^[2] Typically, a specifically tailored system is required for every new electrochemical transformation to ensure high activity and selectivity as well as strong catalyst binding. In aqueous environments, preventing hydrolysis is a key challenge to enable catalysis under strongly acidic and basic conditions. Conventional strategies, such as the immobilisation through carboxylic or phosphonic acids, are often limited to specific pH ranges.^[3] One method to achieve catalysis over a wider pH range is the functionalisation of mesoporous indium tin oxide electrodes with the macrocyclic host molecule pillar[6]arene (PA[6]). Such electrodes demonstrate stability within a pH range of 2.4–10.8 and can bind electrochemically active ruthenium complexes *via* host-guest interactions for various oxidation reactions. Ammonia oxidation is used as a model reaction under basic conditions, while benzyl alcohol oxidation is performed to assess the system in acidic media. When complexed with a suitable guest molecules, PA[6]-modified electrodes show catalytic activity for both reactions. Due to the relatively stable binding of PA[6] to the metal oxide support, they can be recycled after degradation of the catalyst through a simple reabsorption procedure. Additionally, the versatility of this system enables its use in sequential electrocatalytic reactions under different pH conditions, allowing a single electrode to be utilised in multiple different electrocatalytic reactions.

[1] M. Kato, K. Ogura, S. Nakagawa, S. Tokuda, K. Takashi, T. Nakamura, I. Yagi, *ACS Omega*, **2018**, 3, 9052–9059.

[2] K. L. Materna, R. H. Crabtree, G. W. Brudvig, *Chem. Soc. Rev.*, **2017**, 46, 6099–6110.

[3] M. R. Norris, J. J. Concepcion, C. R. K. Glasson, Z. Fang, A. M. Lapides, D. L. Ashford, J. L. Templeton, T. J. Meyer, *Inorg. Chem.*, **2013**, 46, 6099–6110.

Probing Pathways to Aromatics in PVC-model Pyrolysis by Operando Photoelectron Photoion Coincidence Spectroscopy (PEPICO)

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Aromatization of polyvinyl chloride (PVC) pyrolysis products has been attributed to either Diels-Alder (DA) cycloaddition reactions of light alkenes or cyclization of heavier cross-linked carbon chains. These claims, however, need experimentally supported mechanisms to validate the aromatization pathways. In this study, 1,3-dichlorobutane is utilized as a model compound for PVC, and the reaction pathways are investigated by detecting desorbed stable as well as reactive species in the HZSM-5 catalytic reaction.^[1] Photoelectron photoion coincidence (PEPICO) spectroscopy uses vacuum ultraviolet synchrotron radiation that detects and identifies elusive intermediates,^[2,3] a limitation exhibited by typical GC/MS technique. It is also a well-suited method for isomer-resolved analysis of reactive intermediates and products through a combination of product detection by mass spectrometry and product identification by threshold photoelectron spectroscopy. It was found that chlorine releases as HCl and does not chlorinate other products during its nascent stage both in catalytic (200-500 °C) and non-catalytic systems (>500 °C). The C₄ dehydrochlorinated product (1,3-butadiene), considered as primary intermediate, allows acid-catalyzed oligomerization mimicking cross-linked hydrocarbon backbone in decomposition pathways of PVC plastic pyrolysis. Dimerization to C₈ units actively plays role in aromatics formation. The mechanism however shows both contribution of DA cyclization and chain-propagated intramolecular cyclization given by the presence of both vinyl cyclohexene and trimethyl cyclopentene intermediates, respectively. It eventually undergoes ring contraction, expansion, transmethylation, dehydrogenation, and cracking reactions producing valuable aromatics such as benzene, toluene, and xylenes (BTX). Our study gives new insights into the cross-linking pathways, driven by dienes, which are relevant beyond PVC pyrolysis mechanisms, as they are also responsible for BTX formation in the methanol-to-hydrocarbons (MTH) process. Furthermore, it showcased the capability of the PEPICO technique in catalytic studies involving quantification of conversion, selectivities, identification of products/intermediates, and even mapping reaction mechanisms.

[1] J. Cabana, Z. Zhang, Z. Pan, P. Kumar, X. Wu, A. Bodi, G.A. Garcia, Y. Shen, X. Xiao, H. Ma, C. Huang, C. Liu, L. Zhao, Y. Pan, Z. Zhou, J.A. van Bokhoven, P. Hemberger, *ChemSusChem*, n/a e202500516.

[2] P. Hemberger, J.A. van Bokhoven, J. Pérez-Ramírez, A. Bodi, *Catal. Sci. Technol.*, **2020**, 10 1975-1990.

[3] P. Hemberger, Z. Pan, X. Wu, Z. Zhang, K. Kanayama, A. Bodi, *J. Phys. Chem. C*, **2023**, 127 16751-16763.

Elucidating Complex Phenomena at Electrochemical Interfaces by Surface-Enhanced Infrared Spectroscopy

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Electrocatalysis is governed by the chemistry happening at the electrified solid-solution interface. The specific binding of substrates and solution components to the catalytic surface is critical, yet this interaction is influenced by the interfacial electric fields and by the composition, structure, and electronic properties of the electrode surface. The ability to describe and disentangle these contributing factors is pivotal for the rational catalyst design. Surface-enhanced infrared spectro-electrochemical approaches have shown the potential to provide key insight at electrochemical interfaces and have for instance been employed to study interfacial electric fields.¹ However, recent research shows that the interpretation of observed vibrational shifts is often complicated by the contributions from orbital overlap and chemical binding.²⁻³ This emphasizes the need for a more quantitative assessment to disentangle these effects.

In our recent work, we present a quantitative assessment of the extent to which surface binding is determined by through-bond charge transfer that is modulated by a field or by through-space electrostatic effects. We probed the binding of thiocyanate (SCN^-) to Au and Pd as a function of applied potential (φ_{app}) using surface-enhanced infrared absorption spectroscopy (SEIRAS).⁴ By deconvoluting the observed IR patterns, we showed that the CN stretching wavenumbers (ν_{CN}) of the S- and N-bound SCN^- on Au versus Pd exhibit distinct dependencies on applied potential (φ_{app}). We showed that the simultaneous presence of two binding modes of SCN^- on the metal surfaces provided two separate interfacial probes. Therefore, their ν_{CN} shifts with φ_{app} encode different extents of through-space electric field (Stark) effects and through-bond chemical binding. This allowed us to estimate the contributions of these effects to the overall ν_{CN} versus φ_{app} slopes quantitatively. The through-bond effect for S-bound SCN^- is stronger on Pd than on Au, whereas that of N-bound SCN^- and the change of electric field with φ_{app} is similar on both metals. These conclusions are further supported by competitive adsorption experiments using SCN^- and different halides (Cl^- , Br^- , and I^-) and the study of vibrational shifts with φ_{app} using a self-assembled monolayer of 4-mercaptobenzonitrile on both metals. Our work offers a general framework for distinguishing key contributors to interfacial chemistry in an applied electric field and paves the way for the development of future electrocatalysts.

[1] S. D. Fried, S. G. Boxer, *Acc. Chem. Res.* **2015**, 48, 998–1006.

[2] W. R. Lake, J. Meng, J. M. Dawlaty, T. Lian, S. Hammes-Schiffer, *J. Am. Chem. Soc.* **2023**, 145, 22548–22554.

[3] A. Maitra, P. Das, B. C. Thompson, J. M. Dawlaty, *J Phys Chem. B* **2023**, 127, 2511–2520.

[4] T.-C. Chang Chien, M. F. Delley, *J. Phys. Chem. C* **2025**, 129, 1, 999–1012.

Tailoring iron speciation in zeolites through controlled one-pot synthesis for dual pollutant abatement

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Iron-exchanged zeolites have proven suitable catalysts for the abatement of nitrogen-based polluting gases, such as N₂O and NO_x (NO, NO₂). The activation and decomposition of N₂O over iron-zeolites have been established to occur via specific monomeric iron active sites in different zeolite topologies, namely the iron in a six-membered ring in chabazite (CHA) [1], corresponding to an iron in β -cationic position in ZSM5 (MFI) [2]. The selective catalytic reduction of NO on iron-zeolites is considered to occur on the iron in γ -cationic position in FER [3] and MFI [4]. However, the main challenge of iron-zeolites remains the heterogeneous distribution of iron species arising from synthesis. This work aims at elucidating the influence of the different preparation methods on the iron speciation and distribution, while targeting the maximization of active sites for NO-assisted N₂O decomposition.

We have prepared iron-zeolites by two classic exchange methods, wet ion-exchange and incipient wetness impregnation, as well as by one-pot hydrothermal synthesis. The one-pot synthesized iron-zeolites have been further exposed to high-temperature Ar-activation treatment. Diffuse reflectance UV-Visible (DR-UV-Vis) and infrared (DRIFT) spectroscopy have been used to investigate the iron speciation and coordination. The catalytic activity in NO-assisted N₂O decomposition was determined at 200-500 °C in a fixed-bed powder reactor.

DR-UV-Vis spectroscopy revealed that the traditional exchange methods deliver samples with large distribution of iron species, with significant spectral contribution from oligomeric iron species and iron oxide particles. This phenomenon can be partially solved by dealuminating the zeolite before iron addition. Differently, the materials synthesized by one-pot synthesis exhibited a narrower distribution of iron species, showing mostly isolated Fe³⁺ in tetrahedral position in the zeolite framework. The high-temperature Ar-activation caused a redistribution of the iron species with partial extraction of the isolated Fe³⁺ to extra-framework positions. Furthermore, a broad IR signal of NO adsorbed on Fe²⁺ suggested heterogeneity among the monomeric Fe²⁺ species throughout the different materials. The samples synthesized by exchange methods and the ones activated in Ar displayed the IR signal of N₂O adsorbed on Fe²⁺ sites, emphasizing the successful extraction of iron to extra-framework positions. Catalytic tests were in line with the spectroscopic observations, as the Ar-activated samples showed higher activity compared to untreated ones. These results, coupled with other advanced spectroscopic tools, such as extended X-ray absorption fine structure (EXAFS) and electron paramagnetic resonance (EPR) spectroscopy, can provide a holistic understanding of the effect of the synthesis over the iron speciation.

[1] 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*, **2021**, 143, 16243-16255.

[2] G.I. Panov, V.I. Sobolev, A.S. Kharitonov, *Journal of Molecular Catalysis*, **1990**, 61, 85-97.

[3] F. Buttignol, J.W.A. Fischer, A.H. Clark, M. Elsener, A. Garbujo, P. Biasi, I. Czekaj, M. Nachtegaal, G. Jeschke, O. Kröcher, D. Ferri, *Nature Catalysis*, **2024**, 7, 1305–1315.

[4] F. Buttignol, A. Garbujo, P. Biasi, O. Kröcher, D. Ferri, *Journal of the American Chemical Society*, **2025**, 147, 8978–8990.

Active Sites of Titania-Supported Rhenium-Based Catalysts for CO₂ Hydrogenation

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The mitigation of anthropogenic CO₂ emission experiences a rapid growing interest in the industry to tackle global warming and climate change as one of the biggest environmental issues of the near future. The conversion of CO₂ into renewable fuels and value-added chemicals is an auspicious way to transition from fossil fuels to more sustainable energy and material sources while ideally yielding a closed carbon cycle.^{[1],[2]} The conversion of CO₂ and the yield of methanol are a function of temperature, pressure, and reaction gas mixture, which is competing with an array of possible processes and products, such as reverse water gas shift (rWGS) and methanation.^{[3],[4]} Besides Cu and most transition metals, Re, which is known to adopt a broad range of oxidation states, also shows activity in CO₂ hydrogenation catalysts.^[5]

In this work, titania-supported Re-based catalysts were synthesised, characterised, and evaluated for CO₂ hydrogenation activity. Following the generation of surface sites via Surface Organometallic Chemistry, different metal loading and treatment conditions yielded a wide range of catalyst types according to HAADF-STEM from highly dispersed Re sites over Re clusters to small Re nanoparticles, and their associated reactivity showing either methanation or rWGS/methanol synthesis activity. The material-reactivity relationship, as well as unique, well-defined carbonyl species, will be discussed.

- [1] X. D. Xu, J. A. Moulijn, *Energ Fuel* **1996**, *10*, 305-325.
- [2] R.-P. Ye, J. Ding, W. Gong, M. D. Argyle, Q. Zhong, Y. Wang, C. K. Russell, Z. Xu, A. G. Russell, Q. Li, *Nat Commun* **2019**, *10*, 5698.
- [3] X. Jiang, X. W. Nie, X. W. Guo, C. S. Song, J. G. G. Chen, *Chemical Reviews* **2020**, *120*, 7984-8034.
- [4] K. W. Ting, T. Toyao, S. M. A. H. Siddiki, K. Shimizu, *Acs Catal* **2019**, *9*, 3685-3693.
- [5] M. L. Gothe, K. L. C. Silva, A. L. Figueredo, J. L. Fiorio, J. Rozendo, B. Manduca, V. Simizu, R. S. Freire, M. A. S. Garcia, P. Vidinha, *Eur J Inorg Chem* **2021**, *2021*, 4043-4065.

Photocatalysis with Cu₂O particles for water splittingY. Gan¹, S. Bae^{1*}, D. Tilley^{1*}¹Department of Chemistry, University of Zurich, 8057 Zurich, Switzerland

The growing demand for sustainable energy and the environmental impact of fossil fuel consumption have intensified the pursuit of clean alternatives¹. Hydrogen is considered a promising energy carrier due to its high energy density and zero carbon emissions when produced from renewable sources. Among various production technologies, photoelectrochemical and photochemical water splitting offer a direct and sustainable route for solar-to-hydrogen conversion. Cuprous oxide (Cu₂O), an earth-abundant p-type semiconductor, exhibits favorable optoelectronic properties for photocatalysis, including a suitable bandgap and strong visible light absorption². Herein, this study investigates the application of Cu₂O powder for photocatalytic water splitting. Synthesis routes for Cu₂O powder were explored and the protection layer was applied to enhance the stability. The Cu₂O powders were then used to fabricate particulate sheets, offering a scalable and cost-effective alternative to conventional thin films. The performance was evaluated, followed by further optimization to enhance photocatalytic efficiency. This work provides insights into the design of efficient Cu₂O-based systems for sustainable energy production.

[1] Peters, G. P., Peregon, A., Carbon dioxide emissions continue to grow amidst slowly emerging climate policies. *Nature Climate Change*, 2020,10(1), 3-6.

[2] Bagal, I. V.; Ryu, S.-W., Cu₂O as an emerging photocathode for solar water splitting - A status review. *International Journal of Hydrogen Energy*, 2019, 44 (39), 21351-21378.

Descriptors toward higher alcohols and olefins formation in CO₂ hydrogenation on promoted iron catalysts

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Developing efficient catalysts for CO₂ hydrogenation to higher alcohols (HA) or olefins remains a long-standing challenge. Iron-based catalysts, with single or multiple promoters, show promise for both product families.^[1] However, prior studies often isolate the effects of a few promoters under varied conditions, resulting in fragmented insights. Advancing high-performance catalysts requires a unified framework for understanding promoter effects under standardized conditions.^[2]

In this work, through a systematic study involving nine alkali/alkaline-earth metals, thirteen metal oxides, and copper, we identified the surface Fe₅C₂:(Fe₃O₄+Cu) ratio as a key performance descriptor for HA and olefin formation, revealing that productivity to both product families can be simultaneously optimized for 1.0-2.5 values. By optimizing it in the Na₁Fe₅₉Cu₃₀Zn₁₀ catalyst, we doubled reported productivities, namely 0.5 g h⁻¹ g_{cat}⁻¹ for HA and simultaneously 1.1 g h⁻¹ g_{cat}⁻¹ for olefins alongside a combined selectivity of 75% (**Fig. 1**). Deep characterization, including operando XRD and XAS, revealed how different promoters influence the Fe₅C₂:(Fe₃O₄+Cu) ratio and its impact on the reaction mechanisms. Alkali metals were found to drive carbide formation, whose amount can be fine-tuned by metal oxides. Additionally, operando DRIFTS studies monitored how copper drives the building up of oxygenated intermediates and their subsequent transformation into HA. Data science was finally used to identify for each type of promoter interpretable descriptors accounting for these effects. This approach may facilitate future multicomponent catalyst design efforts in CO₂ valorization.

Fig. 1 Platform for the design of promoted iron catalysts toward alcohols and olefins production from CO₂. A matrix of 65 Fe-based materials with stepwise increase in compositional complexity was evaluated and characterized to identify a general performance descriptor and elucidate individual roles of each promoter. Data science enabled the subsequent association of roles with physically interpretable magnitudes. A: alkali/alkali-earth metals, MO_x: metal oxide.

[1] J. Artz, T. E. Muller, K. Thenert, J. Kleinekorte, R. Meys, A. Sternberg, A. Bardow, W. Leitner, *Chem. Rev.* **2018**, *118*, 434-504.

[2] D. Xu, Y. Wang, M. Ding, X. Hong, G. Liu, S. C. E. Tsang, *Chem* **2021**, *7*, 849-881.

Structure-Activity Relationship for PtSn Propane Dehydrogenation Catalysts from Surface Organometallic Chemistry

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The emergence of shale gas reserves as feedstock has necessitated the development of active and stable dehydrogenation catalysts for the production of light olefins through alkane dehydrogenation, mainly *via* the PtSn-based Oleflex process^{1,2}. Herein, we apply surface organometallic chemistry (SOMC) combined with a thermolytic molecular precursor (TMP) to prepare a family of bimetallic PtSn catalysts supported on SiO₂³. First, we develop a new precursor to prepare Sn^(IV) doped SiO₂ and fully characterize the material. Next, we prepare a family of PtSn/SiO₂ propane dehydrogenation (PDH) catalysts with decreasing Pt:Sn ratio *via* a second grafting of a Pt precursor and subsequent H₂ treatment⁴. The resulting nanoparticles were found to be alloyed as judged from a combination of high-resolution scanning transmission electron microscopy (STEM), energy dispersive x-ray (EDX) spectroscopy mapping, CO-adsorption Fourier transform infrared (FTIR) spectroscopy, as well as x-ray absorption spectroscopy (XAS) measurements. Furthermore, synchrotron x-ray diffraction (SXRD) confirms the presence of ordered alloyed Pt_nSn_m phases. The diffraction patterns for the materials show Pt₃Sn₁ and Pt₁Sn₁ for the highest Pt:Sn ratio of 1.17. At a Pt:Sn ratio of 0.68 we observe only Pt₁Sn₁ in the diffraction pattern, while at a low Pt:Sn ratio of 0.34 an additional monometallic β-Sn phase was found. All prepared PtSn catalysts show remarkable PDH activity, with the most active and stable catalyst stabilizing at a Pt productivity of 265 g_{C₃H₆}/g_{Pt}/h after 30 h on stream, while exhibiting an extremely low deactivation rate ($k_d = 0.008 \text{ h}^{-1}$). Our findings show that the formation of an alloyed Pt₁Sn₁ phase is key to producing highly active and stable PtSn PDH catalysts, thereby shedding light on the promotional effect of Sn in PDH catalysts.

[1] Bruijninx, P. C. A.; Weckhuysen, B. M. *Angew Chem Int Ed* **2013**, 52 (46), 11980–11987.

[2] Hayes, J. Multicomponent Dehydrogenation Catalyst. US3878131A.

[3] Copéret, C.; Comas-Vives, A.; Conley, M. P.; Estes, D. P.; Fedorov, A.; Mougél, V.; Nagae, H.; Núñez-Zarur, F.; Zhizhko, P. A. *Chem. Rev.* **2016**, 116 (2), 323–421.

[4] Ehinger, C.; Zhou, X.; Candrian, M.; Docherty, S. R.; Pollitt, S.; Copéret, C. *JACS Au* **2023**, 3 (8), 2314–2322.

Enhancing Photocatalytic Hydrogen Production via Molybdenum Carbide-Modified Graphitic Carbon Nitride (g-C₃N₄)

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Graphitic carbon nitride (g-C₃N₄) is a layered organic semiconductor composed of tri-s-triazine units forming a graphitic π -conjugated framework. With a suitable band gap and responsiveness to visible light, g-C₃N₄ serves as a promising photocatalyst for water-splitting applications. However, achieving optimal performance requires structural and chemical modifications.^[1,2]

This study explores the enhancement of g-C₃N₄'s photocatalytic properties through incorporation of molybdenum carbide (Mo₂C), a material recognized for its excellent electrical conductivity, catalytic activity, and platinum-like electronic structure - offering a cost-effective alternative to noble metals. The high thermal stability of Mo₂C minimizes oxide formation during synthesis, allowing for the formation of a well-defined heterojunction with g-C₃N₄.^[3]

Incorporation of Mo₂C introduces additional active sites, significantly improving the hydrogen evolution reaction (HER) efficiency. The influence of temperature on photocatalytic performance is also examined, with Mo₂C's high thermal conductivity expected to play a key role in optimizing hydrogen production. To ensure real-time HER measurements, a novel experimental setup featuring a gas chromatograph with continuous argon flow enables precise data collection.

These findings advance the current understanding of g-C₃N₄-based photocatalysis and support the development of efficient, sustainable hydrogen production methods.

[1] Grayson Zhi Sheng Ling, Valerie Bei-Yuan Oh, Choon Yian Haw, Lling-Lling Tan, Wee-Jun Ong, *Energy Mater. Adv.*, 2023, 4:Article 0038.

[2] Yonggui Zhao, Devi Prasad Adiyeri Saseendran, Chong Huang, Carlos A. Triana, Walker R. Marks, Hang Chen, Han Zhao, Greta R. Patzke, *Chem. Rev.*, 2023, 6257–6358.

[3] Jin Zhang, Mao Wu, Beibei He, Rui Wang, Huanwen Wang, Yansheng Gong, *Appl. Surface Science*, 2019, 470, 565–572.

Roadmap towards standardization of electrocatalytic CO₂ reduction

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Electrocatalytic CO₂ reduction (eCO₂R) is a promising technology for sustainably converting harmful CO₂ emissions into valuable chemicals and fuels. Significant research efforts have been devoted to advancing catalyst development, leading to rapid growth in the field. However, the lack of standardized testing protocols and data reporting has hindered objective evaluation of catalysts, as eCO₂R performance is highly influenced by a number of operational parameters and conditions that are not consistently controlled or reported.^[1] Furthermore, the absence of integrated life cycle assessment (LCA) and techno-economic analysis (TEA) causes uncertainty on which performance metrics should be prioritized and what threshold values are required for the technology to be environmentally and economically viable in real-world applications.^[2] Collectively, these issues create barriers to scaling and implementation of emerging eCO₂R technologies.

To address this, we present a roadmap on standardizing testing protocols, data management, and performance reporting in eCO₂R (**Fig. 1**). This initiative is the result of a collaborative effort within the National Centre of Competence in Research (NCCR) Catalysis, a hub that brings together expertise for driving the transition to a carbon-neutral society. The roadmap includes identification of main operating parameters affecting performance, leading to establishment of a checklist that provides standardized guidelines for data reporting. LCA and TEA will be employed to define performance metrics that are most relevant from an industrial perspective, and to establish corresponding figures of merit. Based on these findings, testing protocols will be standardized to enable more accurate performance benchmarking. For high-throughput testing under variable operating parameters to find the optimized protocols, automatized parallel reactor setups, that are capable of precise control across a wide range of industry-relevant conditions, will be utilized to accelerate the process. The proposed standards are expected to serve as a benchmark and guideline for future eCO₂R studies, facilitating advancement toward higher technology readiness levels.

Fig. 1 Schematic diagram for the standardization strategy for electrocatalytic CO₂ reduction.

[1] A. Senocrate, F. Bernasconi, P. Kraus, N. Plainpan, J. Trafkowski, F. Tolle, T. Weber, U. Sauter, C. Battaglia, *Nature Catalysis*, 2024, 7, 742–752.

[2] A.W. Zimmermann, T. Langhorst, S. Moni, J.A. Schaidle, F. Bensebaa, A. Bardow, *Frontier in Climate*. 2022, 4, 841907–841918.

Value-Added Photocatalytic Oxidation of Biomass-Derived Platform ChemicalsH. Le¹, P. Adams^{1*}, T. Moehl^{1*}, D. Tilley^{1*}¹Department of Chemistry, University of Zurich, CH-8057 Zurich, Switzerland

In response to the growing threats posed by rising global temperatures, such as an increase in deadly natural disasters, declining food security, and widespread biodiversity loss, the European Green Deal was introduced with the ambitious goal of making Europe the first climate-neutral continent by 2050¹. An important step towards this goal is to lower the dependence of the energy and chemical sector on fossil fuels by developing green and carbon-neutral alternatives. The coupling of photocatalytic value-added oxidation of biomass-derived platform chemicals with the hydrogen evolution reaction (HER) is a strategy to address both problems as it provides a source for carbon-neutral chemical feedstock and green hydrogen. In this project, we aim to design an electrocatalyst for the oxidation of 5-(hydroxymethyl)furfural (HMF) and levulinic acid into value-added platform chemicals that can serve as precursors for sustainable polymers, potentially replacing fossil fuel-derived single-use plastics and acrylate polymers. Nickel oxide shows a poor ability to adsorb HMF reactant and OH⁻ oxidant at the beta-nickel oxy hydroxide active sites². The addition of cobalt oxide addresses this limitation by enhancing the adsorption of the reactants to the surface of the catalyst². We also aim to show that this catalyst can improve the efficacy of the HMF oxidation reaction (HMFOR) and the selectivity for 2,5-furandicarboxylic acid (FDCA) as well as oxidize levulinic acid. Following this, attempts at pairing the catalyst with bismuth vanadate (BVO) to form a photocatalyst before coupling the oxidative half-reaction with a HER photocatalyst will be carried out to prepare a tandem photoelectrochemical cell.

[1] European Commission: The European Green Deal. https://commission.europa.eu/strategy-and-policy/priorities-2019-2024/european-green-deal_en (accessed Mar 11, 2025).

[2] Z. Cheng, J. Hu, W. Zhou, W. Deng, M. Ma, Y. Tan, *Journal of Materials Chemistry A*, 2024, 12, 13400-13408.

{Co₄O₄} Cubanes in a conducting polymer matrix as bio-inspired molecular oxygen evolution catalysts

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The development of efficient and durable water oxidation catalysts based on polynuclear metal-oxo clusters remains a significant challenge and opportunity in the context of converting renewable energy into chemical fuels. Among these, cubic {Co₄O₄} clusters have garnered considerable attention as molecular water oxidation catalysts, owing to their unique combination of heterogeneous and homogeneous catalytic properties, as well as their structural resemblance to biological systems.¹⁻³ However, their practical application in the oxygen evolution reaction (OER) is limited by stability concerns, necessitating the development of effective stabilization strategies.

Inspired by the architecture of the oxygen-evolving complex in photosystem II (PSII), we report a polymer-hybrid approach for immobilizing {Co₄O₄} cubane oxo clusters to enhance their performance as OER catalysts. This strategy involves the design of asymmetric cubane structures and their incorporation into a conjugated polypyrrole matrix, aiming to improve catalytic activity while suppressing intermolecular aggregation during operation. The asymmetric architecture contributes to improved stability by mitigating decomposition pathways and enhances catalytic efficiency through the presentation of a directed cofacial dihydroxide motif at the active site.

Beyond providing structural stabilization, polypyrrole functions as a p-type conducting polymer, facilitating hole transport during the OER and resulting in significantly increased turnover frequencies (TOFs) compared to both unmodified {Co₄O₄} clusters and conventional heterogeneous cobalt oxide catalysts. Combined experimental and computational analyses suggest the presence of multiple oxygen evolution pathways, modulated by intramolecular hydrogen bonding interactions.

Overall, this work presents a rational design strategy for enhancing the efficiency and durability of {Co₄O₄} cubane oxo clusters, demonstrating their potential as accessible and highly adaptable catalysts for water oxidation.

[1] S. Li, Z. Zhang, W. R. Marks, X. Huang, H. Chen, D. C. Stoian, R. Erni, C. A. Triana and G. R. Patzke, —, 2024, , 8432.

[2] F. Song, K. Al-Ameed, M. Schilling, T. Fox, S. Lubner and G. R. Patzke, *J. Am. Chem. Soc.*, 2019, **141**, 8846–8857.

[3] F. Song, R. Moré, M. Schilling, G. Smolentsev, N. Azzaroli, T. Fox, S. Lubner and G. R. Patzke, *J. Am. Chem. Soc.*, 2017, **139**, 14198–14208.

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

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Heterocyclic amines are a key structural motif in the backbone of medicinal natural products, as well as pesticides and flavors. For this reason, and due to the lack of general synthetic routes to access these molecules, many efforts are still ongoing towards producing more efficient alternatives [1].

Imine reductases (IREDs) have recently emerged as highly selective and sustainable biocatalysts for asymmetric reductive aminations [2]. Herein, we have tested 4 known IREDs and 2 newly characterized IREDs for the reduction of heterocyclic imines containing S, O, or N. Most of the IREDs showed the highest catalytic activity towards the newly reported sulfur-containing heterocyclic amine. Since IREDs are NADPH-dependent enzymes, a cofactor-regenerating enzyme was added to the catalytic system with the glucose dehydrogenase from *Bacillus megaterium* (BmGDH). The bi-enzymatic system achieved full conversion at a 10 mM scale of the S-containing heterocyclic imine in less than 2 h and using only 2% w/v of biocatalyst.

To further improve the efficiency and sustainability of the system, we carried out enzyme immobilization on porous microparticles (inSEIT technology). In fact, immobilization of IREDs is very challenging due to the decrease of enzyme activity upon immobilization, thus it has barely been explored until now [3]. By using CapiPy bioinformatic tools [4], we quickly developed an immobilized biocatalyst that retains up to 90% of its initial activity. This enables the integration of the biocatalytic system into a continuous-flow reactor for process intensification. Moreover, the multidisciplinary synergy between academia and industry allowed the development of a synthetic technology platform that gives access to new molecules in a green and efficient manner.

[1] Jonathan Barrios-Rivera *et al.* *Organic Chemistry Frontiers*, **2020**, 7, 3312-3342.

[2] Amelia K. Gilio *et al.* *Chemical Science*, **2022**, 13, 4697-4713.

[3] David Roura Padrosa *et al.* *Green Chemistry*, **2020**, 22, 5310- 5316.

[4] David Roura Padrosa *et al.* *Bioinformatics*, **2021**, 37, 2761-2762.

Steam-induced decoking of MTO catalysts

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Light olefins—such as ethene, propene, and butene—are key precursors in the production of a wide range of polymers and chemicals, which are currently derived mainly from crude oil. The methanol-to-olefins (MTO) process, which is catalyzed by SAPO-34 zeotype as well as by various other small pore zeolites, offers a sustainable alternative by enabling the production of these valuable molecules from non-petroleum-based resources. The MTO has become a well-established and industrially relevant technology, representing a significant advancement in C1 chemistry. However, during the reaction, hydrocarbon species can undergo chain growth and condensation, forming larger molecules that accumulate within the micropores and on the external surface of the catalyst as coke. Catalyst coking is a major challenge in hydrocarbon processing, as it leads to deactivation and limit process efficiency. Here, we investigate regeneration strategies for small pore zeolites like SAPO-34 using steam treatments under controlled conditions to remove coke while preserving catalytic structure and functionality. Our study systematically examines different stages of the regeneration process. We identified regeneration conditions capable of removing up to 40% of the coke deposited on MTO catalysts and enhance olefin selectivity, particularly toward ethylene. Steam regeneration also promotes the in situ conversion of coke into CO and H₂ transforming coke into useful syngas ^[1]. This regeneration strategy of MTO catalyst offers a promising approach to extend catalyst lifetime and enhance process performance.

[1] Zhou, J., Gao, M., Zhang, J. *et al. Nat Commun* 12, 17 (2021)

^{Ir}PYE⁺ as versatile and biocompatible organometallic NAD(P)H regeneration systemL. Monte¹, R. Keller^{1*}, F. Paradisi^{1*}, M. Albrecht^{1*}¹Department of Chemistry, Biochemistry and Pharmaceutical Sciences, University of Bern, Freiestrasse 3, CH-3012 Bern (Switzerland)

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

We recently developed an iridium complex bearing a pyridylidene-amine (PYE) ligand that exhibits unique functional ligand-type reactivity, storing the hydride on the heterocycle ring and mimicking NADH-type reactivity (Fig. 1b). This complex also catalyzes NAD(P)H reduction.^[5] Herein, we focused on the application of our optimized ligand for efficient NAD(P)H regeneration under biocompatible conditions (Fig. 1c) and explore ways to prevent the mutual inhibition between the two systems. We will discuss two solutions that successfully solve these issues.

[1] L. Sellés Vidal, C.L. Kelly, P. M. Mordaka and J. T. Heap, *Biochim Biophys Acta Proteins Proteom*, **2018**, 1866(2), 327–347

[2] C. E. Paul, F. Hollmann, *Appl Microbiol Biotechnol.*, **2016**, 100(11), 4773-4778

[3] H. Wu, C. Tian, X. Song, C. Liu, D. Yanga, Z. Jiang, *Green Chemistry*, **2013**, 15, 1773–1789

[4] T. Quinto, V. Köhler, and T.R. Ward, *Topics in Catalysis*, **2014**, 57, 321–331

[5] N. Lentz, S. Reuge and M. Albrecht, *ACS Catalysis*, **2023**, 13(14), 9839-9844

Genetic incorporation of non-canonical amino acids for histidine substitution

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Among proteinogenic amino acids, histidine has the highest catalytic propensity and is often found in the active site of enzymes¹. Its substitution with other proteinogenic acids is typically not a viable strategy to study or tune its role in catalysis. Alternatively, a given histidine residue can be substituted by a histidine-like non-canonical amino acids (ncAA). Genetic code expansion endows researchers with the ability to introduce ncAAs into proteins site-specifically by hijacking ribosomal protein synthesis². Despite the importance of histidine in catalysis, the scope of histidine-like ncAAs that can be incorporated by genetic code expansions remains limited. We report the genetic encoding of a panel of diverse histidine-like ncAAs in *Escherichia coli*. Through directed evolution, we identify eight novel aminoacyl-tRNA synthetase (aaRS)/tRNA pairs for the site-specific genetic incorporation of a panel of ten new-to-nature histidine-like ncAAs. The encoded ncAAs feature broadly tuned nitrogen pKaH, alternative heterocycles and substitution patterns. We investigate the substrate scope of each aaRS and identify mutually orthogonal substrate-aaRS combinations that enable dual histidine-like ncAA incorporation. We apply a subset of the new ncAAs to tune the biochemical properties of model proteins. We expect that the tools presented herein will be broadly applicable to study histidine catalysis and to tune the properties of histidine residues for enzyme engineering applications and enzyme design.

[1] Bartlett, GJ. et al. *Journal of Molecular Biology*, 2002, 324, 105–121.

[2] Natter Perdiguero, A. & Deliz Liang, A. *CHIMIA*, 2024, 78, 22–31.

Genetic incorporation of non-canonical amino acids for histidine substitution

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[1] Bartlett, GJ. et al. *Journal of Molecular Biology*, 2002, 324, 105–121.

[2] Natter Perdiguero, A. & Deliz Liang, A. *CHIMIA*, 2024, 78, 22–31.

Small Ru clusters stabilized by Ti single sites on silica for the hydrogenation of CO₂ to methane

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In order to understand the interaction between Ti and Ru in the highly active methanation catalyst Ru/TiO₂, [1] the well-designed catalyst RuNP/Ti@SiO₂ has been made using a Surface organometallic approach (SOMC). [2] The catalyst of interest was investigated under methanation conditions, exhibiting a 2.6-fold increase in activity compared to the benchmark RuNP/SiO₂. Both transmission electron microscopy (TEM) and CO chemisorption reveal a higher Ru dispersion after the addition of Ti atoms on the support surface. [3] Extended X-ray absorption fine structure (EXAFS) analysis is consistent with the previous results as the mean (Ru–Ru) coordination number is decreased from the benchmark to the RuNP/Ti@SiO₂. The analysis also points towards direct Ru-Ti interface sites. [4] Additional X-ray photoelectron spectroscopy (XPS) analysis are also pointing towards lower average particle size. It also shows that some Ru species are in contact with Ti atoms.

To understand further the impact of Ti on Ru, CO adsorption monitored via IR is used. [5] The Ru-Ti catalyst reveals spectral features resembling those of supported Ru₃(CO)₁₂ on the corresponding support, implying the stabilization of similar clusters on the bimetallic catalyst surface. Such clusters are shown to be active during methanation conditions as shown by the blue-shifted CO bands detected in the *in-situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiment.

Microscopic and different spectroscopic tools have shown that Ti stabilize small Ru clusters on the support and that they are active under methanation conditions, explaining the higher activity towards methane of the catalyst. Further identification of such supported cluster using ¹³CO NMR is pending.

[1] Kim, A. *et al.*, *ACS Appl. Nano Mater.* **2**, 3220–3230 (2019)

[2] Copéret, C. *Chem. Rev.* **116**, 2, 323–421 (2016)

A new method for the simulation of catalyst deactivation in fluidized bed reactors

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A fluidized bed methanation reactor with a throughput of ca. 50 Nm³/h of reactive gases was used to measure concentration and bubble rise profiles. These data were used to validate a fluidized bed reactor model, developed on the base of the two phase assumption [1]. This assumption considers the reactor as composed of a bubble phase with no catalyst and plug flow characteristics, and a dense phase with perfect mixing where the catalyst is present and the reaction occurs. Based on the experimental results, we calibrated a model of the particle movement, based on the work of Mostoufi et al. [2]. The result is a complete description of the fluidization in terms of reactivity and flow patterns. In this model, we plugged a kinetic model of deactivation obtained by regression from experimental results. The result is a model which predicts the performances of the reactor over a long time on stream including the effect of deactivation.

The figure shows the concentration profiles recorded in the pilot plant, when performing CO₂ methanation. The reactor is substantially isothermal, with a maximum hotspot of 5 °C. We derived a model for the consumption of CO in the fluidized-bed reactor, describing the results in the figure. In addition to this, the model for the particle circulation was implemented, showing that most of the particles slowly rise in the reactor under the influence of rising bubbles and then fall by gravity, when they drop inside the bubbles. Deactivation experiments showed that the deactivation is favored in the presence of CO and hindered by that of water [3], which also causes reactivation, though slow at the reactor temperature. Hence, it is necessary to minimize the permanence of the particles in the zones of the reactor rich in CO and maximize the residence time in those with a high water content.

To conclude, we developed a new methodology for the characterization of deactivation in fluidized bed reactors. We applied it to CO methanation to have a simple, but significant case study. We defined the number of experimental results required to build a reliable model and we showed how these models can be used to suggest measures to minimize the influence of catalyst deactivation. We showed how the bubble size and steam addition can be used to control the optimization process and to increase the effective time-on-stream for this relevant class of reactors.

[1] D. Kunii, O. Levenspiel, *Fluidization Engineering* **1991**. [2] H. R. Norouzi, N. Mostoufi, et al., *Chem. Eng. Res. Des.* **2011**, 89 (6), 817–826. [3] J. Kopyscinski, et al., *Appl. Catal. A Gen.* **2013**, 462–463, 150–156.

Impact of Offretite Dealumination on Methanol-to-Hydrocarbon Performance

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The need for transition toward sustainable energy sources makes methanol to hydrocarbon conversion (MTH) a promising alternative to current petroleum-based processes. MTH process undergoes the dual cycle hydrocarbon pool mechanism and is catalyzed by zeolites (ZSM-5) and zeotypes (SAPO-34), where framework topology and acidity influence catalyst stability and product selectivity. Zeolites with 3D channels provide effective micropore confinement, promoting both olefins and aromatic product formation [1]. Offretite (OFF) comprising of 12 and 8 membered ring offers a distinct 3D pore topology suitable for MTH application. However, the high acid site density in OFF accelerates coking, limiting the catalyst lifetime [2]. To address this, post synthetic modification like dealumination techniques offer a facile strategy to regulate acidity in zeolites [3]. We investigate acid dealumination strategies in presence of different co-cations (Na^+ , NH_4^+ and H^+) using oxalic and nitric acid in addition to the conventional steaming methods. The treatment conditions were optimized to prevent the structural degradation. Although the oxalic acid treated OFF extracted more framework aluminum, the catalytic stability was low. In contrast, nitric acid dealumination resulted in more controlled regulation of acidity and outperforming other dealuminated OFF. At high conversion levels the selectivity of ethene and propylene achieved is 40 and 35% respectively, with 4-5% of aromatic products. This study demonstrates how co-cation assisted acid dealumination in OFF can effectively improve the catalyst stability in MTH application.

Figure 1: Plot of **a)** Methanol conversion vs time-on-stream (TOS) of various OFF post dealumination, **b)** Product distribution and selectivity, and **c)** Coke quantification by thermal gravimetric analysis of spent catalysts. Samples labelled are denoted as follows: the subscript refers to the co-cations (Na^+ , NH_4^+ and H^+), followed by treatment method (S-steaming, NA-nitric acid, OA-oxalic acid) and the numbers 4 and 16 represent the treatment time.

- [1] I. Yarulina, A.D. Chowdhury, F. Meirer, B.M. Weckhuysen, J. Gascon, *Nat Catal* **2018**, 1, 398.
- [2] C. Fernandez, J. Grosmangin, G. Szabo, J.C. Viedrine, *Appl Catal* **1986**, 27, 335.
- [3] C. Fernandez, J.C. Viedrine, J. Grosmangin, G. Szabo, *Zeolites* **1986**, 6, 484.

Integrating In Silico and Experimental Approaches to Enhance Functionality of L-Tryptophan Decarboxylase for Sustainable Production of 5-Methoxytryptamines

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5-methoxy-tryptamine analogues have emerged as promising therapeutic molecules: melatonin is widely used for the treatment of insomnia¹, while 5-MeO-DMT derivatives are being investigated for their potential to reduce depression and anxiety symptoms². These compounds are usually obtained from indoles through multi-step synthetic paths^{3,4}.

In this study, exploiting a range of *in silico* tools, we rationally designed a variant of *Ruminococcus gnavus* L-tryptophan decarboxylase (RgTDC)⁵ able to efficiently convert the non-natural amino acid 5-methoxy-L-tryptophan to 5-methoxytryptamine. This enzyme variant, RgTDC W349Y, exhibits a specific activity of 0.3 U/mg towards 5-methoxy-L-tryptophan, corresponding to a 30-fold increase relative to the wild-type enzyme. Interestingly, RgTDC W349Y also retains very good specific activity towards its natural substrate. By using computational techniques, we investigated the dynamic behaviour of this novel enzyme variant in complex with various ligands, providing insights into catalytic pocket environment and ligand stability.

The sustainable production of 5-methoxy-tryptamine represents a key biocatalytic step that can be integrated into greener chemoenzymatic strategies for the synthesis of pharmacologically active compounds relevant to the treatment of neuropsychiatric disorders.

[1] Adattini, J. A.; Wills, C.; Martin, J. H. *Pharmacol Res Perspect* **2025**, *13* (1).

[2] Warren, A. L.; Lankri, D.; Cunningham, M. J.; Serrano, I. C.; Parise, L. F.; Kruegel, A. C.; Duggan, P.; Zilberg, G.; Capper, M. J.; Havel, V.; Russo, S. J.; Sames, D.; Wacker, D. *Nature* **2024**, *630* (8015), 237–246.

[3] Wang, S. Y.; Shi, X. C.; Laborda, P. *European Journal of Medicinal Chemistry*. Elsevier Masson s.r.l. January 1, **2020**.

[4] McDonald, A. D.; Perkins, L. J.; Buller, A. R. *ChemBioChem* **2019**, *20* (15), 1939–1944.

[5] Williams, B. B.; Van Benschoten, A. H.; Cimermanic, P.; Donia, M. S.; Zimmermann, M.; Taketani, M.; Ishihara, A.; Kashyap, P. C.; Fraser, J. S.; Fischbach, M. A. *Cell Host Microbe* **2014**, *16* (4), 495–503.

Base-free highly active transfer hydrogenation catalysts based on Ru complex with acyclic diamino carbene ligands

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N-heterocyclic carbenes (NHCs) are key ligands in homogeneous catalysis due to their strong donor ability and thermal/oxidative stability.^[1] Typically, bulky R-groups (e.g., mesityl, adamantyl) stabilize the metal complex and offer steric protection, though lack a proximal proton source for assisting hydrogen transfer.^[1] To address these issues, acyclic diamino carbene (ADC) analogues have been developed. These ligands exhibit increased flexibility due to their open-chain geometry, exceptional donor strength, and localized steric bulk around the metal centre.^[1–3]

Our design of a transfer hydrogenation catalyst thus involved the use of a protic ADC. We therefore synthesized Ru-ADC analogues such as Ru-Pyr from a Ru□ isocyanide precursor and an amine source.

We will present the synthesis as well as the excellent catalytic activity of these Ru-ADC variants in the transfer hydrogenation (TH) of ketones under base-free conditions, which is still fairly rare despite the many Ru-based catalysts known for this reaction.^[4] Our studies show excellent reactivity across a diverse range of substrates with high catalyst stability and attractively low catalyst loading.

- [1] L. M. Slaughter, *ACS Catal.* **2012**, 2, 1802–1816.
- [2] J. Ruiz, L. García, M. Vivanco, D. Sol, S. García-Granda, *Dalton Trans.* **2017**, 46, 10387–10398.
- [3] A. S. K. Hashmi, T. Hengst, C. Lothschütz, F. Rominger, *Adv. Synth. Catal.* **2010**, 352, 1315–1337.
- [4] A. Ruff, C. Kirby, B. C. Chan, A. R. O'Connor, *Organometallics* **2016**, 35, 327–335.

Controlled Oxygen-Vacancy Formation for Improved Catalytic Activity

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Discovering and optimizing routes to carefully craft catalyst surfaces is essential for efficient catalyst design. To introduce defects in to a heterogeneous catalyst is often thought to enhance the catalytic performance. Especially vacancy defect are considered to serve as active sites or to tune the electronic structure.^[1-2] State-of-the-art methods to generate vacancy defects apply harsh conditions such as H₂-reduction, plasma treatments and elevated temperatures.^[3-4] The methods lead to a variety of defects that could each have different catalytic activities. Analysis of the number and nature of defects in such materials is extremely challenging. Spectroscopic signatures for defect sites can be ambiguous and are often controversially discussed.^[5-6] To elucidate quantitative defect-activity relationships is hence extremely difficult and has only been achieved in specific cases, for instance with *in-situ* EPR spectroscopy.^[7] Precise methods to introduce and probe defects on heterogeneous catalysts are needed to understand their catalytic function and design the catalyst surface accordingly.

Herein, we describe a mild method to introduce vacancy defects into metal oxides. The method allows a quantitative tracking of the defects introduced into the material by simple spectroscopic means. Comparison of the performance of vacancy-enriched materials were probed in epoxidation catalysis versus a defect-free analogue and showed enhanced epoxidation activities in presence of defects. Our approach offers new avenues to novel quantitative structure-reactivity relationships for defects in metal-oxide based catalysis. This may accelerate the rational design of vacancy-containing catalysts for future applications.

[1] C. Xie, D. Yan, H. Li, S. Du, W. Chen, Y. Wang, Y. Zou, R. Chen and S. Wang, *ACS Catal.*, **2020**, 10, 11082-11098.

[2] P. L. Gai-Boyes, *Catal. Rev. - Sci. Eng.*, **1992**, 34, 1-54.

[3] L. Xu, Q. Jiang, Z. Xiao, X. Li, J. Huo, S. Wang, L. Dai, *Angew. Chem. Int. Ed.*, **2016**, 55, 5277-5281.

[4] Y. Kuwahara, Y. Yoshimura, K. Haematsu, H. Yamashita, *J. Am. Chem. Soc.*, **2018**, 140, 29, 9203-9210.

[5] T. J. Frankcombe, Y. Liu, *Chem. Mater.*, **2023**, 35, 5468-5474.

[6] K. Ye, K. Li, Y. Lu, Z. Guo, N. Ni, H. Liu, Y. Huang, H. Ji, P. Wang, *Trend Anal. Chem.*, **2019**, 116, 102-108.

[7] T. P. Araújo, C. Mondelli, M. Agrachev, T. Zou, P. O. Willi, K. M. Engel, R. N. Grass, W. J. Stark, O. V. Safonova, G. Jeschke, S. Mitchell, J. Pérez-Ramírez, *Nat. Commun.*, **2022**, 13, 5610.

From Chemical Shift to Olefin Metathesis Catalysis: Orbital Origins of ^{95}Mo NMR Trends in Mo(VI) Precatalyst

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Understanding the formation of molybdenum oxo alkylidene species from supported Mo^{VI} dioxo precursors is critical for improving heterogeneous olefin metathesis catalysts. These active species form via reduction of Mo^{VI} to Mo^{IV} under reaction conditions, followed by reoxidation to the catalytically active Mo^{VI} state. Previous studies have linked higher olefin conversion rates to increased populations of deshielded Mo^{VI} species, as detected by ^{95}Mo NMR [1]. To investigate the molecular basis of this observation, studies using model complexes of the type $\text{Mo}^{\text{VI}}(\text{O})\text{Cl}_2(\text{OR})_2(\text{Et}_2\text{O})$ have been carried out. These investigations demonstrated that more electron-withdrawing alkoxide ligands lead to increased ^{95}Mo deshielding, which in turn correlates with enhanced reducibility and improved catalytic activity [2]—thereby reinforcing the central role of first-sphere ligand electronics in governing both the spectroscopic and functional behavior of these catalysts

To expand on this understanding, we studied a series of $\text{Mo}^{\text{VI}}(\text{E})(\text{Cl})_2(\text{OC}(\text{CF}_3)_3)_2(\text{THF})$ complexes, varying the E ligand to examine its influence on spectroscopic and catalytic properties. This work combined geometry optimizations with Natural Chemical Shift (NCS) analysis, alongside parallel synthesis, ^{95}Mo NMR measurements, and catalytic testing. Interestingly, and in contrast to the alkoxide trend, more electron-withdrawing E ligands led to increased ^{95}Mo shielding while still promoting higher catalytic activity. This behavior was rationalized by frontier orbital analysis: whereas alkoxide substitution primarily affects the LUMO, E-ligand variation predominantly modulates the HOMO. As a result, electron-withdrawing E ligands increase the HOMO–LUMO gap and shift the ^{95}Mo chemical shift upfield. Despite this shielding, their positive impact on reactivity highlights the continued importance of LUMO in the catalyst activation. These findings offer new insight into the interplay between electronic structure, ^{95}Mo NMR signatures, and catalytic function in molybdenum-based olefin metathesis systems.

[1] Berkson, Z. J.; Zhu, R.; Ehinger, C.; Lätsch, L.; Schmid, S. P.; Nater, D.; Pollitt, S.; Safonova, O. V.; Björgvinsdóttir, S.; Barnes, A. B.; et al. *Journal of the American Chemical Society* **2023**, *145* (23), 12651-12662.

[2] D. F. Nater, C. J. Kaul, L. Lätsch, H. Tsurugi, K. Mashima, C. Copéret, *Chem. Eur. J.* **2022**, *28*.

Characterization of two novel tryptophanase A from *Ardenticatena maritima* and *Haloarcula japonica*

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L-Tryptophan is a key amino acid with significant roles in both biological systems and industrial industries. Beyond its natural role in cellular metabolism, L-tryptophan derivatives and other non-canonical amino acids (ncAAs) are increasingly valued in medicinal chemistry and synthetic biology, contributing to the design of chemical probes and pharmaceutical scaffolds ¹. The biosynthesis of L-tryptophan is classically mediated by the heterodimeric tryptophan synthase (TrpS) ²; however, in *Escherichia coli* strains, it has also been well-documented that L-tryptophan can be synthesized under high concentrations of L-serine via tryptophanase A (*Ec-TnaA*), an enzyme typically involved in L-tryptophan catabolism (Figure 1) ³.

Figure 1. Biosynthesis of L-tryptophan from indole and L-serine.

A major limitation in such reactions is the low solubility of indole in aqueous media, which makes the use of high substrate concentrations challenging. However, this issue can be partially mitigated by increasing the reaction temperature, thereby improving indole solubility ². In the case of *Ec-TnaA*, which originates from a mesophilic source, exposure to elevated temperatures may compromise enzyme stability. Furthermore, *Ec-TnaA* is known for its cold lability, a reversible loss of activity at low temperatures correlated with the dissociation of its active tetrameric structure ⁴. This research focuses on the characterization of two novel TnaA enzymes: *Am-TnaA* from the thermophilic organism *Ardenticatena maritima* and *Hj-TnaA* from the halophilic organism *Haloarcula japonica*. Due to their resilience to harsh physicochemical conditions, these enzymes offer promising biocatalytic tools for overcoming existing challenges. In this study, we also evaluate the use of these enzymes for L-tryptophan synthesis and investigate their potential application in the production of L-tryptophan derivatives, aiming to expand their utility in biocatalysis.

1 D. K. Romney, J. Murciano-Calles, J. E. Wehrmüller and F. H. Arnold, *J. Am. Chem. Soc.*, 2017, **139**, 10769–10776.

2 A. R. Buller, S. Brinkmann-Chen, D. K. Romney, M. Herger, J. Murciano-Calles and F. H. Arnold, *Proc. Natl. Acad. Sci. U. S. A.*, 2015, **112**, 14599–14604.

3 W. A. NEWTON and E. E. SNELL, *Proc. Natl. Acad. Sci. United States*, 1964, **51**, 382–389.

4 K. Green, N. Qasim, G. Gdraelvsky, A. Kogan, Y. Goldgur, A. H. Parola, O. Lotan and O. Almog, *urn:issn:1399-0047*, 2015, **71**, 2364–2371.

Deploying an Interactive, Collaborative, and FAIR-oriented Data Processing Pipeline for Data Driven High-Throughput Catalysis Research

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SwissCAT+ East is a state-of-the-art technology platform at ETH Zürich, launched by the ETH domain, and focused on automated high-throughput and data-driven experimentation in heterogeneous catalysis. Equipped with advanced robotic systems and high-throughput tools, the Hub enables the synthesis, characterization, and evaluation of catalysts, aided by artificial intelligence and machine learning algorithms to optimize data analysis and workflows [1].

Given the wide array of catalysis related instruments and methods in use at SwissCAT+ East, a robust and user-friendly data management pipeline is needed to streamline data analysis involving large data sets from a diverse set of instruments and enhance collaborations. Recently through a collaboration with the Swiss Data Science Center (SDSC), SwissCAT+ East has adopted Renku [2], an open-source platform aimed to connect data, code, and compute ecosystems, into its data management pipeline. In this contribution, we present the integrated data processing pipeline of SwissCAT+ East, and how it utilizes Renku to make data analysis, data visualization and collaboration in the field of catalysis easier in a manner compliant with the FAIR guidelines. A general overview is given in figure 1 where scientists use Renku to interact with the data processing tools from SwissCAT+ East, and use them on the data that is produced by the high-throughput laboratory. The pipeline uses mainly open-source services and can be adopted to a wide array of chemistry and catalysis related projects (e.g. catalyst synthesis/testing, gas adsorption, TGA/DSC-MS) to share and visualize data collaboratively.

Figure 1: General workflow of SwissCAT+’s integrated pipeline. Renku can access lab results that are automatically uploaded to openBIS and pass them to SwissCAT+’s software where the users can see, interact with, and analyze the data.

[1] Paco Laveille, Pascal Miéville, Sourav Chatterjee, Elisa Clerc, Jean-Charles Cousty, Florian de Nanteuil, Erwin Lam, Edy Mariano, Adrian Ramirez, Urielle Randrianarisoa, Keyan Villat, Christophe Copéret, and Nicolai Cramer, CHIMIA, 2023, 77(3), 154–158.

[2] Rok Roškar, Chandrasekhar Ramakrishnan, Michele Volpi, Fernando Perez-Cruz, Lilian Gasser, Firat Ozdemir, Patrick Paitz, Mohammad Alisafaei, Philipp Fischer, Ralf Grubenmann, Eliza Harris, Tasko Olevski, Carl Remlinger, Luis Salamanca, Elisabet Capon Garcia, Lorenzo Cavazzi, Jakub Chrobosik, Darlin Cordoba Osnas, Alessandro Degano, Jimena Dupre, Wesley Johnson, Eike Kettner, Laura Kinkead, Sean D. Murphy, Flora Thiebaud, and Olivier Verscheure, Advances in Neural Information Processing Systems, 2023, 35, 42161–42173.

Engineering a High Conversion System for CO₂ Electroreduction to Formic Acid

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It is of the utmost importance that anthropogenic CO₂ emissions are reduced in order to decelerate climate change and its harmful effects. Using CO₂ as a chemical feedstock is a promising solution that could simultaneously produce valuable chemicals and fuels without fossil or biomass resources. Electrochemical CO₂ reduction (CO₂RR) uses protons and electrons supplied by water oxidation to transform CO₂ without the use of H₂ gas. Most studies have applied neutral or alkaline media to boost selectivity for CO₂RR, however this is conjoined with the formation of carbonate ions, lowering carbon utilization. The use of acidic media is therefore highly favorable but requires novel strategies to suppress the dominant side-reaction, hydrogen evolution.

We implemented a three-pronged approach to boost CO₂ conversion: a) electrolyzer optimization, ensuring effective mass transport of CO₂ to the catalyst; b) catalyst design, developing a high-surface-area dendritic tin electrocatalyst; and c) microenvironment engineering, applying different binders to modify the electrode surface. The optimized system (Figure 1) demonstrated high selectivity for formic acid (>85%) at a low pH (<1.5) and at high current densities (>200 mA/cm²). Notably, by reducing the CO₂ flow rate, exceptional single-pass conversion efficiencies of over 85% could be reached.

Figure 1. Schematic of the hybrid flow-electrolyzer, optimized for high-conversion of CO₂ to formic acid using a dendritic tin electrocatalyst.

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Making Carbon-Carbon Bonds from CO₂: Alkalimetal doping of Cobalt-based Hydrogenation 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] While these transformations are well established for syngas in the Fischer-Tropsch (FT) process, the analogous reaction with CO₂ as feedstock remains relatively underdeveloped. Cobalt is well known for its versatile CO_x hydrogenation properties and thus an interesting candidate to consider in the selective transformation of CO₂.^[3, 4] In the framework of these challenges, we have studied alkalimetal (Li, Na, K) doping of supported cobalt nanoparticles for CO₂ hydrogenation. Herein, we found that doping of Co/SiO₂ with Na and K leads to a significant increase in the C₂₊ product formation. 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.

- [1] M. Aresta, A. Dibenedetto, A. Angelini, *Chemical Reviews* **2014**, *114*, 1709-1742.
- [2] W. Li, H. Wang, X. Jiang, J. Zhu, Z. Liu, X. Guo, C. Song, *RSC Advances* **2018**, *8*, 7651-7669.
- [3] X. Pan, F. Jiao, D. Miao, X. Bao, *Chemical Reviews* **2021**, *121*, 6588-6609.
- [4] T. Fan, H. Liu, S. Shao, Y. Gong, G. Li, Z. Tang, *The Journal of Physical Chemistry Letters* **2021**, *12*, 10486-10496.

Acidity of zeolites determined by in situ spectroscopy in the presence of solvents

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The acid sites in solid catalysts are commonly quantified by adsorption of a base molecule on the catalyst surface, followed by its desorption in a temperature ramp. Spectroscopic methods can be applied to identify the nature of the acid sites, i.e. Lewis vs Brønsted acid sites. Infrared (IR) spectroscopy is the most used technique for characterization of acid sites in solid catalysts, where the shift of characteristic vibrational modes of the adsorbed base probe molecule with respect to the free molecule is observed. As a fundamental property of solid catalysts, characterization of acidity is well studied in gas phase experiments. However, it is poorly investigated in the liquid phase, where many catalytic reactions take place. There is thus a clear need in the development of acidity determination in liquid environments.

In this work, we studied the effect of wet environment on the acidity of selected zeolites. By using probe molecules, the acidity of zeolites was studied by Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) and Attenuated Total Reflection Infrared (ATR-IR) spectroscopy in both gas and liquid environments, respectively. A consistent pulsing method was developed, where small doses of the probe molecule was admitted into the *in situ* cell, thus slowly titrating the acid sites and revealing key information on the presence and distribution of acid sites.

[1] William E. Farneth, Raymond J. Gorte, *Chemical Reviews*, **1995**, 95, 615-635.

[2] Silvia Bordiga, Carlo Lamberti, Francesca Bonino, Arnaud Travert, Frédéric Thibault-Starzyk, *Chemical Society Reviews*, **2015**, 44, 7262-7341.

Impact of Acidity on Reaction Intermediates and Catalytic Performance in Methanol-to-Hydrocarbons Conversion over ZSM-22 Zeolite

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Decarbonizing the chemical industry requires retrofitting existing infrastructure to operate with renewable feedstocks. In this context, the conversion of green methanol to hydrocarbons (MTH) over zeolites represents a promising technology to sustainable fuels production.[1] One-dimensional 10-membered ring zeolites such as ZSM-22 (TON topology), characterized by non-intersecting straight pores and needle-shaped crystallites, have attracted considerable attention. Owing to their shape-selectivity, these materials yield hydrocarbon fractions rich in C₃-C₅ olefins, suitable for further processing into sustainable kerosene via oligomerization.[2] However, the one-dimensionality of pore channels in ZSM-22 leads to hindered molecular diffusion and rapid catalyst deactivation due to pore blockage (*i.e.* coke formation). The nature of coke species within the straight pores, and the influence of the zeolite texture and acid site distribution on their evolution, remains poorly understood. We synthesized a series of ZSM-22 catalysts with well-defined acidity and varying acid site distribution, thoroughly characterized by FTIR of adsorbed pyridine, as well as ²⁷Al and ²⁹Si MAS NMR. The kinetic evaluation of this comprehensive series of catalysts in MTH conversion, complemented by *in situ* FTIR, *operando* UV-VIS spectroscopy, and ¹³C MAS NMR measurements of the coked material, allowed us to analyze the structure of active sites and their conversion into coke species under reaction conditions. By establishing structure-deactivation relationships, our study provides insights for the rational design of future ZSM-22 catalysts with superior stability.

Figure 1. Methanol conversion as a function of time-on-stream over ZSM-22 zeolites with different acidity, prepared tuning the aluminum source and synthesis-gel composition.

[1] I. Yarulina, A. Dutta Chowdhury, F. Meirer, B. M. Weckhuysen, J. Gascon, *Nat. Catal.*, **2018**, *1*, 398-411.

[2] S. Teketel, W. Skistad, S. Benard, U. Olsbye, K. P. Lillerud, P. Beato, S. Svelle, *ACS Catal.*, **2012**, *2*, 26-37.

Efficient photoelectrochemical water oxidation of bimetallic phthalocyanine decorated BiVO₄ photoanode

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Photoelectrochemical (PEC) water splitting process is mainly divided into three steps, including adequate light harvesting, effective charge separation, and a fast surface reaction. Unfortunately, many photocatalysts suffer from severe surface recombination at the photoanode/electrolyte junction, which significantly hampers their application in photocatalytic and photoelectrocatalytic systems.

Recently, by loading oxygen evolution cocatalysts (OECs) on the photoanodes, the PEC performance could be enhanced. This enhancement could be due to improvement of the sluggish surface reaction kinetics of the oxygen evolution reaction (OER) at the semiconductor/electrolyte (S-E)

interface. Even though the above approach has clearly enhanced PEC performance, improvement of the PEC water oxidation efficiency to the

required level remains challenging owing to high recombination at the semiconductor/electrocatalyst interface.

Interface charge modulation has been proven as an effective strategy to boost photogenerated charge separation by injection or extraction of charge carriers in optical devices. Phthalocyanine can be chosen as a mediator to maximize charge utilization as compared to previously reported photosensitizers, since they show relatively high hole mobility and it is possible to adjust their optical and electronic properties by modifying the peripheral and nonperipheral substituents and metal center

Enhanced Photocatalytic Hydrogen Evolution Over Pt-loaded S-doped g-C₃N₄: Effects of Deposition Methods and Pt Distribution

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Optimizing synthetic techniques for the loading of co-catalyst materials on carbon-based substrates is important for efficient photocatalytic hydrogen production. In this study, sulfur-doped graphitic carbon nitride (S-g-C₃N₄) was modified with platinum nanoparticles (Pt-NPs) through two different deposition methods: in-situ photoreduction and solvothermal reduction. By systematically varying the amount of Pt-loading, we explored the relationships between the synthesis method and the distribution of Pt-NPs with the performance for photocatalytic hydrogen production. Our results indicate that the solvothermal reduction approach leads to a more uniform distribution of dispersed Pt-NPs on the surface of the S-g-C₃N₄ substrate when compared to the in-situ photoreduction method. Consequently, the Pt/S-g-C₃N₄ composites prepared via solvothermal reduction exhibited significantly higher photocatalytic hydrogen evolution activity. Moreover, the optimized catalysts revealed remarkable stability, maintaining an efficient hydrogen evolution performance for over 150 hours, which is attributed to the uniform distribution and stability of the loading Pt-NPs. The enhancement of the catalytic efficiency is attributed to the improved charge transfer kinetics and reduced recombination rates resulting from the optimized dispersion of Pt-NPs. This work highlights the critical role of deposition methods in co-catalyst performance and provides valuable insight into the design of highly efficient and stable photocatalytic systems for sustainable hydrogen production.

Interface-engineered WO_x/ZrO₂ Catalysts for Highly Effective Hydrogen-Free Polypropylene Upgrading to Gasoline

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The catalytic transformation of polyolefin plastics into liquid fuels under hydrogen-free and noble-metal-free conditions represents a significant scientific challenge^[1]. Owing to the inherent complexity of the reaction network and the difficulty in narrowing product selectivity, the fundamental catalytic mechanisms for low-temperature, hydrogen-free polyolefin conversion remain elusive. To date, most studies in this emerging field have focused on model polyethylene (PE) systems and have primarily employed zeolite-based catalysts with limited tunability and moderate activity. However, the WO_x/ZrO₂ catalysts reported in this study—featuring tunable interfacial structures and highly dispersed atomic clusters—represent a previously unexplored catalytic platform that enables efficient hydrogen-free transformation of polypropylene (PP), including commercial-grade plastics, under mild conditions.^[2-3] In this study, WO_x/ZrO₂ catalysts with tailored surface structures were synthesized via flame spray pyrolysis (FSP) for efficient hydrogen-free transformation of polypropylene (PP) under mild conditions (240 °C, 4 h, **Fig. 1a**). Catalytic tests and characterizations revealed diverse W/Zr configurations. Catalysts with monolayer dispersed WO_x nano-islands on ZrO₂ surface showed superior activity due to abundant W–O–Zr interfacial sites (**Fig. 1b**), achieving 94% conversion and ~90% selectivity to gasoline-range hydrocarbons (C₄–C₁₂) for PP12K. This performance remained consistently across a wide range of PP molecular weights and for a variety of consumer goods. The optimal catalyst, W₁₀Zr₉₀, performed over five cycles without performance loss nor structural changes, as confirmed by STEM analysis. In contrast, W₆₀Zr₄₀ catalysts with nanoparticulated crystalline WO₃ on ZrO₂, were less active (**Fig. 1c**). EXAFS, Raman, NH₃-TPD, and FTIR analyses confirmed that catalytic performance correlates with WO_x dispersion and W–O–Zr interface density. Raman and FTIR suggest Brønsted acidity, modulated by WO_x dispersion, governs depolymerization (**Fig. 1d**). In situ DRIFTS and TPSR provided further mechanistic insights. This study highlights that precise interface engineering and the stabilization of catalytically active structures are central to the rational design of efficient, hydrogen-free polyolefin upcycling systems, offering a foundational strategy for developing future low-carbon catalytic technologies.

Fig.1 (a) Catalytic performance of WO_x/ZrO₂ catalysts with different metal ratios for PP ($M_w = 12$ kDa) (240°C, 4 h, 4 bar N₂). (b) STEM-HAADF and EDS characterization of W₁₀Zr₉₀ catalyst. (c) STEM-HAADF and EDS characterization of W₆₀Zr₄₀ catalyst. Pyridine desorption IR spectra under different temperatures on (d) W₁₀Zr₉₀ and (e) W₆₀Zr₄₀ catalysts.

[1] Cen, Z., Han, X., Lin, L. et al., *Nat. Chem.* **2024**,16, 871–880

[2] W. Han, et al, *Chem*, **2025**, 11(2), 102340

[3] S.D. Jaydev et al., *Angew. Chem. Int. Ed.* **2024**, 63, e202317526.