The 21st Nordic Symposium on Catalysis

June 8-10 2026

Göteborg, Sweden

Welcome!

The Nordic Symposium on Catalysis is a biannual event, which in 2026 is organized by the Competence Centre for Catalysis at Chalmers, within the framework of the Nordic Catalysis Society. The conference is an important event for dissemination of new findings and techniques as well as for networking between researchers and catalysts developers from academia and industry.

Good to know

Conference venue: The street address to the conference venue is Lindholmspiren 5, 417 56 Göteborg. The closest tram stop is Lindholmen and the closest ferry stop is Lindholmspiren.
Oral presentations: Plenary presentations are 60 minutes, including 10 minutes of questions. Nordic keynote presentations are 40 minutes, including 10 minutes of questions. Contributed oral presentations are 20 minutes, including 5 minutes of questions.
Poster presentations: The conference has a poster session starting at 18.00 on Monday, June 8. Please put up your posters during the coffee break on Monday. The posters can be displayed during the entire conference but please remove them at the latest during lunch on Wednesday, June 10.
Lunches and coffee breaks: Lunches and coffee are included in the conference fee and will be served in the Candela foyer.
Conference Dinner: The conference takes place at the City council hall (Börsen) located at Östra Hamngatan 21. The dinner starts at 18.30. A ticket is needed to attend the dinner.

Organization

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Monday, June 8th

12:30 – Registration

13:50 – Welcome

14:00 – **Plenary**

Location: Main Hall, Chair: Magnus Skoglundh

Optical spectroscopy as a “Swiss army knife” in understanding catalysts
P1 Silvia Bordiga

15:00 – Coffee

15:30 – **Nordic Keynote**

Location: Main Hall, Chair: Magnus Skoglundh

Dynamic electrochemical interfaces: From understanding to controlling reactivity
K1 Antonia Herzog

16:10

Electrocatalysis *Pascal, Chair: B. Wickman*	**Emission Control** *Tesla, Chair: T. Maunula*	**New methods and concepts** *Main Hall, Chair: P-A. Carlsson*
16:20 O1 Reza Khaleghi Abasabadi *In-situ studies revealing the synthesis mechanism of platinum-yttrium nanoalloy catalysts*	O4 Susanne Mossin *In-situ EPR applied for speciation of active metal sites in zeolites*	O7 Jessi van der Hoeven *Nanoscale strain-engineering controls the reactivity of nanoparticle catalysts*
16:40 O2 Mailde S. Ozório *Coupled effects governing stability and ORR activity in AuPd and AuCu binary alloy catalysts*	O5 Patrick Lott *Catalyst design through pathway synergy: NH_3-SCR-driven enhancement of H_2-SCR activity and selectivity*	O8 Florian Maurer *From single atoms to clusters and back: Evolution of noble metals on CeO_2 for oxidation catalysis*
17:00 O3 Nils Rieger *In-situ investigation of PEMFC catalyst-ionomer interactions with electrochemical quartz crystal microbalance* 17:20	O6 Audrey Dannar *Revisiting pressure modulation as a method to increase reaction rates*	O9 Jan Knudsen *Capabilities and analysis methodologies for dynamic operando spectroscopy vision of catalyst surfaces at the MAX IV laboratory*

17:30 – **Berzelius lecture**

Location: Main Hall, Chair: Hanna Härelind

TBA

18:10

18:20 – **Poster session**

21:00

Tuesday, June 9th

9:00	**Plenary** *Location: Main Hall, Chair: Anders Hellman* Spin-mediated promotion of magnetic metal catalysts P2 Jens K. Nørskov		
10:00	Coffee		
10:30	**Nordic Keynote** *Location: Main Hall, Chair: Anders Hellman* Transient (spectro-)kinetics as a generous source of knowledge about reaction-diffusion systems in catalysis K2 Evgeniy Redekop		
11:10	**CO_2 hydrogenation and C-C coupling** *Pascal, Chair: U. Olsbye*	**Biomass, plastic and rubber valorization** *Tesla, Chair: L. Olsson*	**New methods and concepts** *Main Hall, Chair: O. Deutschmann*
11:20	O10 Aqsa Batool *Gallium promotes Ni/Al_2O_3 from methanation to methanol synthesis catalysts in CO_2 hydrogenation*	O14 Anker Jensen *Effect of sulfur on noble metal catalysts for stabilization of biomass pyrolysis oil model compounds*	O18 Hjalte Ambjørner *Advances in operando electron microscopy in heterogeneous catalysis*
11:40	O11 Leonardo Sousa *Identification of transient intermediates and active species in $CuZnZrO_2$ catalysts for CO_2 hydrogenation to methanol*	O15 Karina Valihura *Design of hydrotalcite-derived Mg-Al oxide catalysts for the selective valorisation of bioethanol into higher alcohols*	O19 Luca Carnevale *Multi-stimulus in situ TEM for catalysis using a mems-based environmental nano-reactor*
12:00	O12 Nasir Shezad *Hierarchical zeolite 13X-supported Ni catalysts for carbon dioxide conversion into methane*	O16 Duangamol Tungasmita *Integrated valorization of agricultural residues to ethyl levulinate and sustainable bio-based applications*	O20 Christian Reece *Determining the state of a $Pd/\gamma\text{-}Al_2O_3$ catalyst using pulsed flow and transient spectroscopy*
12:20	O13 Raffaele Cheula *Graph models and fine-tuned machine learning potentials for microkinetic analyses in heterogeneous catalysis*	O17 Jiaqi Wang *Intrinsic metal effects govern methoxy retention versus demethoxylation in the electrochemical upgrading of guaiacol*	O21 Silvia Mauri *CO oxidation on $NiFe_2O_4$ under an applied magnetic field: Elucidating the relation between catalytic mechanism and magnetic properties*
12:40	Lunch		
	CO_2 hydrogenation and C-C coupling *Pascal, Chair: L. Castoldi*	**Biomass, plastic and rubber valorization** *Tesla, Chair: A. Jensen*	**New methods and concepts** *Main Hall, Chair: J. Halldin Stenlid*
13:40	O22 Sahra Ahmed *Structural and catalytic insights into Pd@UiO-66 for C-C coupling reactions*	O26 Päivi Mäki-Arvela *Solventless hydrodeoxygenation of dihydroeugenol in a continuous reactor over Ni catalysts modified with Fe and Ce*	O30 Aksel Violle *AI-driven automated synthesis for zeolite-based catalyst discovery*
14:00	O23 George Marnellos *K-doped $LaFeO_3$ perovskites for CO_2 hydrogenation to light olefins*	O27 David Serrano *Coupling low-temperature lignocellulose pyrolysis with vegetable oil catalytic co-processing over ZSM-5 zeolite: Enhanced aromatic hydrocarbon production and extended catalyst lifetime*	O31 Luis Antonio Cipriano Marcos *Computational robustness of the spin effects in chemisorption and catalysis*
14:20	O24 Adeem Ghaffar Rana *Impact of hydrothermal treatment on the physicochemical properties and MTO activity of H-ZSM-5 catalysts*	O28 Meline Parent *Influence of hexagonal MoO_3 tunnel structure on HDO performance*	O32 Marius Juul Nielsen *Adsorption energy calculation on inverse catalysts with machine learning interatomic potentials*
14:40	O25 Felix Herold *On the anchoring mechanism of metal nanoparticles on carbon supports*	O29 Muhammad Abdus Salam *Catalytic valorization of sugarcane bagasse: effect of cu loading to Ni in Y-Zeolite*	O33 Alvaro Posada-Borbón *Reaction kinetics of liquid organic hydrogen carriers from first-principles: Conversion of methylcyclohexane/ toluene on Pt(111)*
15:00			

Tuesday, June 9th

15:00 — Coffee

15:30 — **Nordic Keynote**

Location: Main Hall, Chair: Henrik Grönbeck

On DFT-based multiscale modelling in heterogeneous catalysis
K3 Minttu M. Smith

16:10

	H_2 production and storage *Pascal, Chair: M. Rønning*	**Biomass, plastic and rubber valorization** *Tesla, Chair: D. Creaser*	**Ammonia synthesis and utilization** *Main Hall, Chair: S. Mossin*
16:20	O34 Lidia Castoldi *Impact of Fe-Fe_3C-C phase evolution on methane pyrolysis kinetics: From catalyst structure to reactor scale*	O38 Filippo Ravasio *Selective reduction of α-pinene by transfer hydrogenation with noble metals on carbon*	O42 Olaf Deutschmann *Electro-catalytic ammonia synthesis in proton-conducting ceramic cells*
16:40	O35 Auden Ti *Electro-oxidation of Au(111) studied by operando EC-qXRR*	O39 Rui Pedro da Cruz *Catalytic hydrodeoxygenation of biomass pyrolysis oil model compounds in a continuous slurry reactor*	O43 Vasyl Marchuk *Highly dispersed pt for low-temperature ammonia oxidation: Insight into ligand environment with HERFD XAS*
17:00	O36 Jakob Munkholt Christensen *Insights into methane reforming from oscillations in the reaction*	O40 Jonas Elmroth Nordlander *Active phase of a Cu-Mo catalyst supported on alumina for HDO of biomass*	O44 Alexander Gunnarson *Water tolerance as a key challenge for ammonia decomposition catalysts*
17:20	O37 Zouhair El Assal *Improvement of the performance of Fe-based catalysts by Ni in CO_2-free H_2 production by thermocatalytic decomposition of CH_4*	O41 Xuan-Huy Le *Activity of NiMo/Al2O3 catalyst in waste tire pyrolysis oil upgrading: The effect of sulfidation degree*	O45 Clemens Wöllhaf *Inductively heatable catalysts for ammonia synthesis*

17:40 — Free time

18:30 — Conference Dinner

21.00

Wednesday, June 10th

9:00 — **Plenary**
Location: Main Hall, Chair: Edvin Lundgren
Electrolyte effects on electrocatalytic hydrogen and oxygen evolution
P3 Marc T.M. Koper

10:00 — Coffee

10:30 — **Nordic Keynote**
Location: Main Hall, Chair: Edvin Lundgren
Shedding synchrotron light on catalyst surfaces at work
K4 Uta Hejral
11:10

	Selectivity in complex synthesis *Pascal, Chair: H. Grönbeck*	**New catalytic materials** *Tesla, Chair: A. Holm*	**Ammonia synthesis and utilization** *Main Hall, Chair: M. Luneau*
11:20	O46 Tapio Salmi *Synthesis of hydrogen peroxide and epoxides: catalysts, kinetics, mechanism and reactor modelling*	O50 Paula Sebastián Pascual *Pulse-mediated electrodeposition of shaped structures for HMF electrocatalysis*	O54 Sašo Gyergyek *Electrified hydrogen storage and on-demand release via ammonia using magnetically heatable Ru–CoNi nanocomposite catalysts*
11:40	O47 Ananya Mohanty *Size-dependent bulk hydride diffusion in Pd nanoparticles and its impact on H_2O_2 synthesis*	O51 Yang Hu *In operando studies of the synthesis and structural evolution of supported electrocatalysts*	O55 Alicia San Martin Rueda *Structural and chemical stability of $LaSrCoFeO_3$ perovskite thin films for ammonia oxidation*
12:00	O48 Martin Høj *Methanol-to-jet fuel (MTJ) pathway and catalysts*	O52 Martina Zava *Ni-Cu alloy-decorated TiO_2 nanotubes for photocatalytic degradation of pharmaceuticals*	O56 Miha Grilc *Magnetically-heated Ru/C hydrotreatment of levulinic acid in cold fluid by electrified slurry reactor*
12:20	O49 Matej Hus *Size and shape effect of silver nanoparticles on ethylene epoxidation: A multiscale simulation*	O53 Henrik Eliasson *Automated 3D characterization of small nanoparticles for high-throughput screening with transmission electron microscopy*	O57 Marcin Makosa-Szczygie *Ammonia oxidation on perovskites for ammonia SOFCs*

12:40 — Lunch

	Electrocatalysis *Pascal, Chair: S. Sunde*	**Emission Control** *Tesla, Chair: R. Villamaina*	**Ammonia synthesis and utilization** *Main Hall, Chair: S. Blomberg*
13:40	O58 Elias Diesen *Entropy-enthalpy compensation in electrocatalytic rates*	O61 Tim Delrieux *Scale-bridging characterization of Pd/Al_2O_3 methane oxidation catalysts during sulfur poisoning*	O64 Sam Taylor *Operando AP-XPS on plasma catalysis for ammonia production: A temperature study*
14:00	O59 María Paula Salinas-Quezada *Lab-scale operando X-ray diffraction reveals temperature-accelerated coalescence-dominated growth of Pt nanoparticles*	O62 Willow Dew *Influence of support on alloying and segregation behavior in palladium-silver alloy catalysts during methane oxidation*	O65 David Degerman *Effect of potassium promotion of the Haber-Bosch process, investigated by in-situ X-ray photoelectron spectroscopy*
14.20	O60 Anna Panagiota Souri *Exploiting the tunability of dilute alloys for sustainable electrocatalytic reactions*	O63 Ulrike Küst *Carbon subsurface traffic jam as driver for methane oxidation activity and selectivity on palladium surfaces*	O66 Christian Marinelli Johansen *Photodriven reduction of N_2-to-NH_3 and mechanistic lessons learned along the way*

14.40 — Conclusion

15.00 — Coffee

Plenary lectures

Optical spectroscopy as a "Swiss army knife" in understanding catalysts

Silvia Bordiga

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Introduction

The study of heterogeneous catalysis is crucial for advancing industrial processes in energy, chemicals, and environmental applications. Spectroscopic techniques have emerged as powerful tools to investigate the complex phenomena occurring at the catalyst surface during reaction processes. These methods provide detailed insights into the structural and electronic properties of catalyst materials, as well as their dynamic behavior under reaction conditions. Techniques such as infrared (IR), Raman, ultraviolet-visible (UV-Vis) and X-ray Absorption (XAS) spectroscopies, just to mention some of them, enable the observation of key intermediates, reaction mechanisms, and changes in the active sites of catalysts. However, though some spectroscopic tools (e.g. IR or UV-vis) are nowadays broadly available, their fundamentals are often not fully handled by the final user, sometime leading to gross errors in their application and reporting of results. Moreover, operando spectroscopies, which allow measurements under actual catalytic reaction conditions, have greatly enhanced our understanding of catalyst behavior in real-time. However, to be properly applied, they need devoted advanced experimental tools to measure and to analyze the results. The combination of these spectroscopic and molecular modelling approaches has been instrumental in unraveling the molecular-level interactions between catalysts and reactants, identifying reaction pathways, and guiding the design of more efficient, selective, and durable catalytic systems. The present contribution aims to illustrate potentialities and limits of spectroscopies, in characterizing zeolites and Metal organic Frameworks, selecting a few case studies.

References

Carlo Lamberti et al., Chem. Soc. Rev., **39**, 4951(2010)

Silvia Bordiga et al., Chem. Soc. Rev., **39**, 4885 (2010)

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Spin-mediated promotion of magnetic metal catalysts

Jens K. Nørskov

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The lecture will give a detailed explanation of the spin-mediated promotion mechanism**,** and illustrate the effect for three different reactions: ammonia synthesis, ammonia decomposition, and CO methanation. I will conclude by discussing how spin-mediated promotion can be utilized for other reactions and classes of catalysts, and how it can guide new catalyst development.

Cao, V. J. Bukas, V. Shadravan, Z. Wang, H. Li, J. Kibsgaard, I. Chorkendorff and J. K. Nørskov, *Nat. Commun.*, 2022, **13**, 2382

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K. Zhang, A. Cao, L. H. Wandall, J. Vernieres, J. Kibsgaard, J. K. Nørskov and I. Chorkendorff, *Science*, 2024, **383**, 1357–1363

A. Gunnarson, A. Cao, O. F. Sloth, M. Varón, R. B. Villoro, T. Veile, C. D. Damsgaard, C. Frandsen, J. K. Nørskov and I. Chorkendorff, *Energy Environ. Sci.*, 2024, **17**, 9313–9322.

A. Gunnarson, O. Christensen, A. Frisina, M. Varón, E. R. Billeter, C. D. Damsgaard, C. Frandsen, J. K. Nørskov and I. Chorkendorff, *ACS Energy Lett.*, 2025, **10**, 3383–3387

Electrolyte effects on electrocatalytic hydrogen and oxygen evolution

Marc T.M. Koper
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The electrocatalytic hydrogen and oxygen evolution reactions are the cornerstone reactions of water electrolysis. I will discuss recent advances from my group in how the electrolyte composition determines the rate of these reactions. This complex interplay between electrode and electrolyte is currently still far from being completely understood. For the hydrogen evolution reaction (HER), cations play a key role in alkaline media in promoting or inhibiting the rate-determining step of HER. For the oxygen evolution reaction (OER) on NiFe-oxyhydroxide catalysts, cations have a strong effect on the non-kinetic contribution to the OER rate, suggesting that cations influence the accessibility of the active sites inside the layered oxyhydroxide. Finally, the electrolyte composition can have a major influence on bubble dynamics at high current densities, for both reactions.

Nordic keynote lectures

Dynamic Electrochemical Interfaces: From Understanding to Controlling Reactivity

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The urgent need for sustainable chemical processes is critical to combating climate change, particularly by reducing the carbon footprint of essential chemicals and materials. Electrochemical methods powered by renewable energy offer a transformative approach to converting simple molecules like carbon dioxide and nitrogen into high-value chemical products. The electrochemical reduction of CO_2 (CO_2RR) has the potential to produce multicarbon chemicals and fuels such as ethanol and ethylene [1], while nitrogen reduction (NRR) provides a sustainable alternative to the energy-intensive Haber-Bosch process for ammonia synthesis [2]. Despite their promise, both processes face significant challenges in achieving high selectivity, activity, and stability under industrially relevant conditions.

This study utilizes advanced operando spectroscopic techniques to probe the dynamic behavior of the catalyst-electrolyte interface, a critical factor in optimizing these processes [3]. For CO_2RR, time-resolved operando surface-enhanced Raman spectroscopy (SERS) and X-ray absorption spectroscopy (XAS) were employed to monitor the evolution of adsorbed intermediates and catalyst composition during reaction conditions on Cu-based catalysts. Pulsed electrochemical techniques enhanced ethanol selectivity by modulating the surface coverage of Cu/Cu(I) sites [4,5]. The findings also highlight the crucial roles of co-adsorbed hydroxide and CO in driving C-C coupling and suppressing undesired C_1 products. Additionally, the incorporation of ZnO_x into Cu catalysts improved stability and selectivity by influencing the dynamic adsorption behavior of CO and hydroxide [6]. Key observations include the interplay between oxidative Cu species, hydroxide coverage, and CO adsorption kinetics, which govern reaction pathways and product distributions.

The lithium-mediated nitrogen reduction reaction (LiNRR) offers a promising approach to ammonia synthesis under ambient conditions. In this process, metallic lithium is electrochemically deposited in an organic electrolyte, where it reacts with nitrogen molecules to produce ammonia. The efficiency and stability of this reaction are critically influenced by the structure and composition of the solid electrolyte interphase (SEI) known from lithium battery research. Modifying the electrolyte composition, such as transitioning from $LiClO_4$ to LiFSI in tetrahydrofuran/ethanol-based solvents, significantly reduces the lithium plating potential and enhances overall reaction performance [7]. Operando Raman spectroscopy was employed to monitor the formation and evolution of SEI species, including lithium ethoxide and lithium nitride, under reaction conditions. These investigations revealed key insights into the interplay between nitrogen activation and the competing hydrogen evolution reaction (HER), which remains a major drawback to improve the selectivity of the LiNRR process [8].

By integrating operando insights with strategic catalyst and electrolyte design, this work advances the understanding of dynamic interactions at the catalyst-electrolyte interface for both CO_2RR and NRR. These findings address fundamental challenges in selectivity and stability, offering a pathway to scalable, renewable energy-driven chemical synthesis and contributing to a more sustainable future.

References

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[2] Iriawan, Chorkendorff, Shao-Horn et al. Nat. Rev. Methods Primers 1, 56 (2021).
[3] Herzog, Bergmann, Roldan Cuenya et al. Angew. Chem. Int. Ed. 60, 74264 (2021).
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Transient (spectro-)kinetics as a generous source of knowledge about reaction-diffusion systems in catalysis

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The non-steady-state response of a catalytic system to a well-defined external perturbation, e.g., of gas composition, contains valuable information about the inner workings of the molecular transport and/or chemical reaction networks which govern the overall process at the molecular scale. The key challenge for an experimentalist employing transient kinetic methods, then, is to assess the window of measurable rates under given conditions and to identify characteristic behaviors of time-dependent kinetics that can serve as “fingerprints” for the underlying chemistry. In this lecture, I will highlight the potential of transient analysis for mechanistic research in catalysis, drawing on two recent case studies: (1) Modulation-Excitation X-Ray Adsorption Spectroscopy (MES-XAS) investigation of PdAu bimetallic nanoparticles and (2) Temporal Analysis of Products (TAP) characterization of alkene adsorption and diffusion in acidic microporous materials (zeolites and zeotypes). Lastly, I will outline several research avenues in both, experiments and data analysis, that our team is currently pursuing to advance the frontier of catalytic kinetics.

On DFT-Based Multiscale Modelling in Heterogeneous Catalysis

Minttu M. Smith

Department of Chemistry, Nanoscience Center, University of Jyväskylä, Finland
Nordic Symposium on Catalysis, Göteborg, Sweden, 8-10 June 2026

Computational heterogeneous catalysis has matured considerably over the past three decades, yet a gap persists between what individual methods can tell us and what a complete, quantitative description of a catalytic system actually requires. This Nordic keynote lecture outlines the chain of computational methods that connects quantum mechanical calculations to observable reaction rates. The lecture offers a practitioner's perspective on what these tools can reveal about catalysis as a phenomenon, and what remains out of reach.

At the foundation, density functional theory (DFT) provides atomic-scale access to the energetics of adsorption and bond activation at the active site that experiments cannot directly resolve. Realistic represenations of the active site are a prerequisite for a physically meaningful kinetic model. Over the past decade, the scope of tractable DFT problems has expanded substantially: catalyst-support interfaces, multi-component surfaces, and electrochemical interfaces are now routinely studied. Machine learning interatomic potentials (MLIPs) have emerged as a practical surrogate for DFT calculations, though as an accelerator rather than replacement, at least for now. The lecture will discuss how these tools fit into the broader modeling workflow and what is required to use them reliably.

The second part of the lecture addresses microkinetic modeling: how DFT-computed energetics are translated into reaction rates and other kinetic observables, what choices are made along the way, and how those choices affect the conclusions that can be drawn. Simple model systems will be used to make the consequences of these choices concrete and visible, and illustrate how they can produce substantially different predicted outcomes.

The third part addresses error propagation and uncertainty. Inaccuracies at the DFT level are amplified as they pass through rate constants into predicted turnover frequencies and selectivities. Simple illustrative examples will be used to show how sensitive kinetic predictions are to uncertainties in the input energetics, and to make the case that quantifying this sensitivity is a practical and necessary step rather than an optional refinement.

Connecting microkinetic models to reactor-scale descriptions remains challenging. Intrinsic surface kinetics derived from DFT must ultimately be embedded in mass and heat transport models to produce predictions that are comparable to laboratory or industrial experiments. Direct coupling is computationally demanding, and the microkinetic component can become a bottleneck. Neural network surrogates trained on microkinetic output offer an attractive route to coupling the scales.

The overarching message is that the tools available to the community are powerful and increasingly mature, but that realising their potential depends on how carefully they are applied and connected. Rigour in model construction, transparency about assumptions, and honest treatment of uncertainty are as important as the underlying level of theory.

Shedding synchrotron light on catalyst surfaces at work

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Introduction

Surfaces are vital in heterogenous catalysis since they provide the active, physical space for chemical reactions to occur. To improve catalyst performance it is essential to be able to correlate the catalyst surface structures to the catalytic activity and selectivity under realistic reaction conditions. As the latter are typically characterized by high pressures/temperatures in gas phase catalysis and by corrosive electrolytes in electrocatalysis, accessing the surface structures of catalysts at work remains a challenge.

Results and Discussion

In recent years we have shown how synchrotron-based Surface X-Ray Diffraction provides atomic-scale information on the model catalyst surface structure under operando conditions, where the use of different photon energies allows to investigate various aspects (Fig. 1). While High Energy Surface X-Ray Diffraction (HESXRD, E=70-80 keV) allows a fast probing of reciprocal space and the catalyst surface structure [1,2], conventional photon energies (E=10-20 keV) facilitate to resolve the nanoparticle facet structure under operando conditions [3].

Using examples from our latest experiments in thermo- and electrocatalysis, I will illustrate the advantages and applications of the different photon energy ranges. Thus, HESXRD allowed us to track the potential-dependent restructuring of 2D (oxy)hydroxides at the solid/liquid interface of Ni-based model electrocatalysts during the oxygen evolution reaction [4]. The use of conventional photon energies, in turn, facilitated to correlate Rh nanoparticle facet surface structures to the catalytic selectivity under thermocatalytic ammonia oxidation conditions.

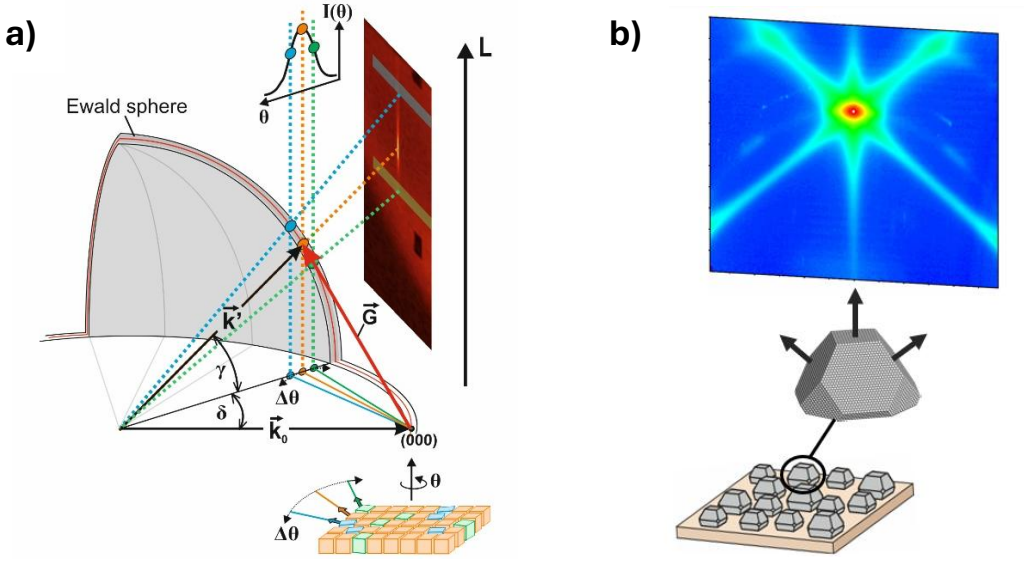

Fig. 1: a) Working principle of HESXRD [2], b) Diffraction pattern of Rh particle facets using conventional photon energies.

References

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Oral presentations

In-situ Studies Revealing the Synthesis Mechanism of Platinum-Yttrium Nanoalloy Catalysts

Reza Khaleghi Abasabadi[1*], Cornelia Constance Buan[1], Yang Hu[2], and Susanne Mossin[1]

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Introduction

Platinum Yttrium (Pt_xY) nanoalloy catalysts are attractive for the oxidation reduction reaction (ORR) due to their good activity with lower platinum usage. The stability of Pt_xY catalysts is a challenge; however, better control over the formation and structure of nanoalloys is required.[1] We have recently developed a solid-state chemical approach for synthesizing Pt_xY nanoalloys on a carbon support, Pt-Y-NC. In this synthesis method, Pt and Y precursors, a nitrogen-rich compound (CN_2H_2), and carbon black were mixed with a mortar and pestle and then calcined in an inert atmosphere. The last synthesis step, H_2 reduction to form Pt-Y nanoalloys, is a critical step that is not fully understood.[2] In this study, we have performed H_2 temperature-programmed reduction (H_2-TPR) connected to a mass spectrometer and *in situ* XRD measurements to better understand the reduction and formation pathways of Pt_xY nanoalloy catalysts.

Results and Discussion

In Figure 1a, H_2-TPR results show a reduction at 585 °C for the Pt-NC sample and two reduction peaks at 575 and 625 °C for Pt-Y-NC sample. For both samples, HCN and NH_3 were detected as byproducts of the reduction at the same temperatures as H_2 consumption. The calculated H_2/Pt molar ratios are 10.5 and 15 for Pt-NC (11 wt% Pt) and Pt-Y-NC (13 wt% Pt and 6 wt% Y), respectively. These relatively high ratios indicate that H_2 is not only consumed in the reduction of Pt but also in the reduction of the nitrogen containing matrix. The *in situ* XRD results indicate the formation of Pt particles at 650 °C during the initial stage of measurements. Then, a peak corresponding to Pt_3Y nanoalloys appears while the intensity of the Pt peak gradually decreases (Figure 1b). These results suggest that Pt nuclei form first, promoting H_2 spillover on the catalyst. This process facilitates the simultaneous reduction of Y and the remaining Pt species, leading to the formation of Pt_3Y nanoalloys.

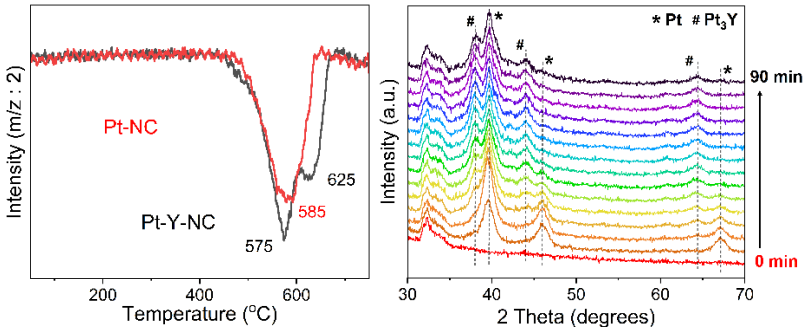

Figure 1. a) H_2-TPR profiles in 5% H_2/Ar flow with a ramp of of 5°C/min and b) in situ XRD of Pt-Y-NC taken at 650 °C in 5% H_2/N_2 over 90 min.

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Coupled Effects Governing Stability and ORR Activity in AuPd and AuCu Binary Alloy Catalysts

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Introduction

Understanding how alloy structure governs both catalytic activity and stability remains a central challenge in the design of oxygen reduction reaction (ORR) catalysts. In Au-based binary alloys, atomic arrangement, ligand effects, and elastic strain are strongly coupled, making it difficult to extract general design principles. Here, we use density functional theory and atomistic modeling to investigate AuPd and AuCu binary alloys on fcc(111) surfaces. Our goal is to establish a common, physically grounded descriptor that links surface structure to thermodynamic stability and ORR activity.

Results and Discussion

Our results show that catalytic activity and structural stability are both governed by the net surface strain established by Au partitioning between surface and subsurface layers. Surface segregation of Au lowers the surface energy and simultaneously generates self-induced compressive strain, stabilizing flat, alloy-rich surface configurations. ORR energetics, however, emerge from the interplay of short-range ligand effects and longer-range elastic interactions. In the local environment, increasing the number of neighboring Au atoms weakens intermediate binding through ligand perturbations, whereas more distant Au atoms impose strain fields that further tune adsorption energetics at active sites. In mixed surface alloys, this combined ligand-strain response shifts adsorption energies toward the Sabatier optimum. This picture is consistent with recent studies on Pt-based surface alloys,[1,2] where long-range self-induced strain and competitive strain effects were likewise found to modulate ORR activity, highlighting the broader importance of strain-mediated activity tuning in binary alloy monolayers. Overall, these findings establish net surface strain as a key descriptor linking atomic arrangement, thermodynamic stability, and ORR performance in AuPd and AuCu catalysts.

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In-Situ Investigation of PEMFC Catalyst-Ionomer Interactions with Electrochemical Quartz Crystal Microbalance

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Introduction

The performance degradation of proton exchange membrane fuel cells (PEMFCs) over extended usage is a critical challenge that hinders long-term viability of fuel cell technology (*1*). Therefore, it is crucial to explore the underlying mechanisms of the degradation processes in order to improve the lifetime and efficiency of this type of fuel cell. In this sense, this study investigates the interaction of catalyst and ionomer during cyclic potential changes using an electrochemical quartz crystal microbalance with integrated dissipation monitoring (EQCM-D). This in-situ method allows for highly precise analysis of mass and viscoelastic changes at electrode surfaces (*2*). By employing this technique, important insights can be gained into the interaction between the catalyst and ionomer during electrochemical reactions.

Results and Discussion

For the investigations, model platinum electrodes were deposited on quartz sensors by thermal evaporation. The mass and dissipation change behavior during cyclic voltammetry (CV) measurements between 0 and 1.2 V vs. RHE in 0.5 M H_2SO_4 was compared with that of sensors where the platinum electrode was coated with a thin Nafion layer. The Nafion coated electrodes exhibit a pronounced and partially irreversible increase in both Sauerbrey mass and dissipation during the initial CV cycles, indicative of substantial hydration and structural rearrangement of the ionomer matrix (*3*). Comparative measurements using quartz sensors with both carbon and gold electrodes suggest that this effect is primarily triggered by the repeated oxidation and reduction of the platinum surface. To assess the relevance of these findings with respect to practical PEMFC systems, additional EQCM-D measurements were conducted on a PEMFC catalyst layer (CL) spray-coated on a quartz crystal with a cabon electrode. The measurements exhibit behavior very similar to that observed for Nafion-coated platinum electrodes. Specifically, redox transitions induce periodic modulation of the viscoelastic properties of the ionomer, and repeated cycling results in a cumulative, irreversible increase in ionomer hydration. These results suggest that the response during the measurement of a CL is dominated by interactions involving Nafion and the catalyst, and that the ionomer structure undergoes substantial reconfiguration in response to the oxidation–reduction cycling of the active catalyst phase. These insights provide important contributions to the understanding of interactions between the various components of a PEMFC electrode and are highly relevant for the development of activation protocols aimed at conditioning electrodes and optimizing their performance.

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In-situ EPR applied for speciation of active metal sites in zeolites

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Introduction

Electron paramagnetic resonance (EPR) is a powerful quantitative spectroscopic method for following catalytic processes at realistic reaction conditions. The method requires the presence of paramagnetic centers and therefore it is especially relevant for transition metal catalysis when the metal center is paramagnetic in some stage during the catalysis.
Copper centers in zeolites are active catalysts in the selective catalytic reduction (SCR) of NO(g) and NO_2(g) with NH_3. When exposed to catalytic poisons such as SO_2, the catalyst deactivates due to a decrease in the number of redox-active sites. The catalytic activity partially recovers after thermal regeneration, but some of the initial reactivity is irreversibly lost.

Results and discussion

In-situ EPR protocols are applied to copper chabazite catalyst materials (Cu-CHA) with different amounts of copper. Firstly, we show how the alumina distribution in the zeolite affect the copper speciation and reconcile the quantifications performed by hydrogen temperature programmed reduction and by in-situ EPR on the same material series.[1]
Secondly, we show the EPR can be used to reveal the mechanism of catalyst deactivation by gas phase SO_2 exposure. The differences between fresh, sulfated and regenerated catalyst are revealed by identifying and quantifying the copper sites and the time resolved speciation of Cu sites during reduction and oxidation half cycles (Fig. 1).[2] Finally, we present the results of controlled dosing of NO(g) on other metal exchanged zeolite materials.

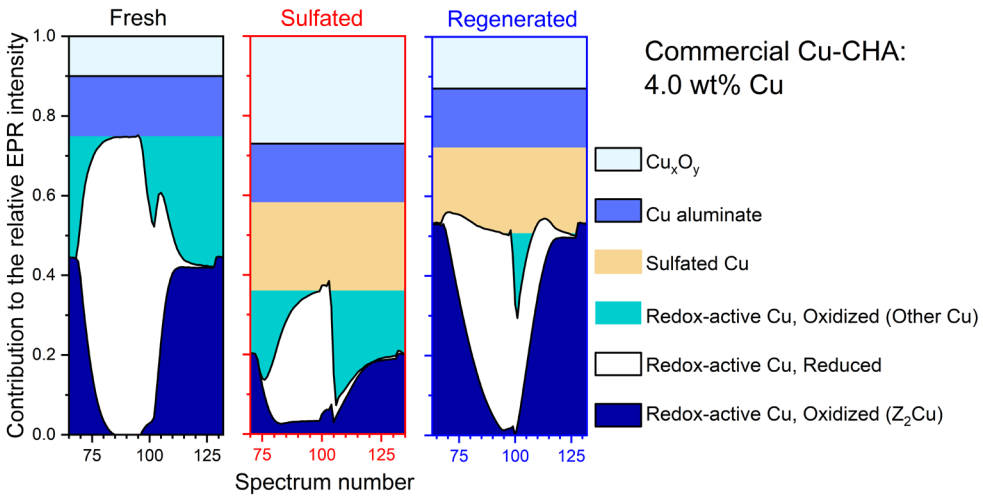

Figure 1. Cu species detected by in-situ EPR protocols at 200°C during first reduction (1000 ppm of NO+NH_3) and then oxidation (1000 ppm NO + 10 % O_2) of Fresh, SO_2-poisoned and Regenerated Cu-CHA (Si/Al = 7, 4.0 wt.% Cu).

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Catalyst design through pathway synergy: NH_3-SCR-driven enhancement of H_2-SCR activity and selectivity

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Introduction

Carbon-free energy carriers are central to global decarbonization efforts, with hydrogen (H_2) gaining particular attention due to its broad applicability. For off-road sectors, such as agricultural machinery, retrofitting lean-operated diesel engines for H_2 combustion enables rapid and large-scale carbon emission reduction, yielding water vapor (H_2O) as the primary exhaust component. Nevertheless, small quantities of nitrogen oxides (NO_x) are still formed and require effective aftertreatment. While conventional ammonia-based selective catalytic reduction (NH_3-SCR) is readily deployable, direct use of H_2 as the reductant (H_2-SCR) presents a more streamlined alternative. Noble-metal catalysts are typically preferred for their high low-temperature activity,[1] with palladium (Pd) showing particularly high selectivity across broad operating conditions.[2] Zeolite-supported Pd catalysts further enhance performance.[3]

Results and Discussion

A bifunctional monolithic catalyst was prepared whose washcoat consisted of a 2:1 mass ratio mixture of 1%Pd/TiO_2/HY, serving as the H_2-SCR component, and Fe-BEA, a conventional NH_3-SCR formulation selected because nitrates and NH_x species have been identified as key intermediates in Pd-catalyzed NO_x reduction.[4] This material combination outperformed the standalone H_2-SCR catalyst with respect to both activity and selectivity, achieving >80% N_2 selectivity between 180 and 300 °C, even under highly humid feed conditions, and maintained stable performance over 12 h. Capillary-based spatial profiling provided axially resolved concentration profiles that enabled detailed mechanistic interpretation. NH_3 formation near the catalyst inlet was attributed to Brønsted acid sites of the β-zeolite, while downstream consumption of these NH_3 species via Fe-mediated NH_3-SCR pathways contributed to enhanced NO_x conversion and relevant mitigation of N_2O formation. Overall, the strong synergy observed in the Pd/TiO_2-HY + Fe-BEA bifunctional system underscore its potential to advance H_2-SCR toward practical implementation in H_2-ICE emission control.

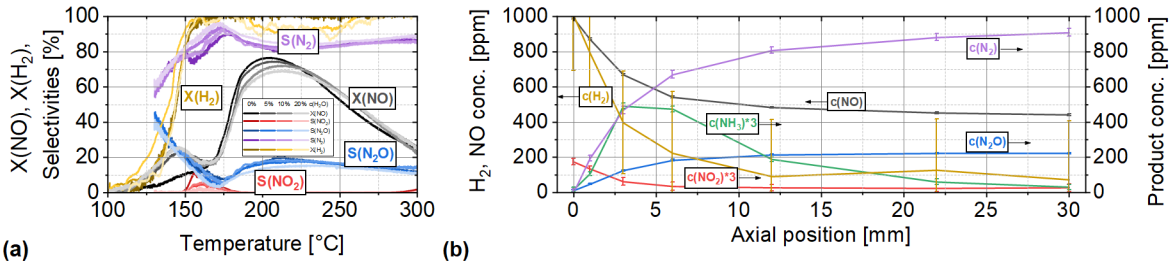

Figure 1: (a) Performance of 1%Pd/TiO_2/HY + Fe-BEA (1000 ppm NO, 5000 ppm H_2, 10 vol% O_2, 0 – 20 vol% H_2O, in N_2; GHSV = 75 000 h^{-1}); (b) axially resolved performance data at T = 200 °C (5 vol% H_2O).

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Revisiting pressure modulation as a method to increase reaction rates

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Introduction

Catalysts enable the production of fuels, chemicals, and materials indispensable to modern society. As global demands for resources increase, further improvements in catalytic performance are required. However, many conceptual and technical challenges in optimising catalytic processes remain. A significant number of industrial chemical processes operate under steady-state conditions, yet catalysts in industrial reactors restructure and deactivate indicating that they are not static entities and respond to their environment. Given the intimate relationship between catalyst structure and catalyst activity, we propose an alternative approach that exploits this dynamic nature by using oscillations in reactant feed compositions to enhance reaction rates.

Results and Discussion

Herein we revisit a more direct and industrially accessible form of dynamic operation: oscillation of reactant partial pressures. Using CO oxidation over a Pd/Al_2O_3 catalyst, we demonstrate that the periodic oscillation of CO and O_2 partial pressures in the reactant feed can enhance catalytic activity up to three-fold relative to the steady-state maximum under otherwise identical conditions (Fig. 1). Additionally, measurable activity can be induced under conditions where no steady-state conversion is observed. Numerical simulations of the experiments find a rate enhancement under oscillatory conditions, demonstrating that solely kinetic effects can enhance rates. However, the simulations consistently underpredict the degree of rate enhancement implying more complex phenomena is involved.

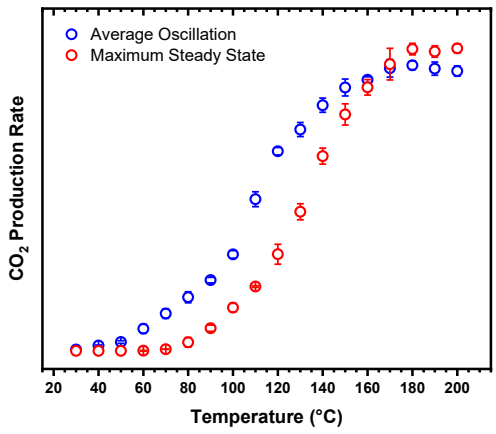

Fig. 1. Maximum steady-state (red) and average oscillatory (blue) rates measured for CO oxidation over Pd/Al_2O_3 as a function of temperature.

The numerical model and experimental in situ diffuse reflectance IR spectroscopy demonstrate that CO surface coverages oscillate with external modulation. We rationalise that the observed rate enhancement is partially caused by a decoupling between gas-phase composition and surface coverage. However, we also conclude that more complex phenomena such as surface reconstructions or metastable surface states that are inaccessible under steady-state conditions are at play. By demonstrating that the oscillation of a pre-existing process variable can bypass steady-state maxima without changing catalyst formulation or reactor design, this work reframes non-steady-state operation as a practical strategy for enhancing catalytic performance in mature industrial systems.

Nanoscale Strain-Engineering Controls the Reactivity of Nanoparticle Catalysts

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Introduction

Nanoparticle catalysts are key enablers of the energy transition, accelerating chemical transformations while making them cleaner and more energy-efficient. Traditionally, the catalytic performance of these nanocatalysts is tuned through nanoparticle size, composition, and support interactions. Lattice strain has emerged as an additional handle to control catalytic reactivity, where local deformation at the nanoparticle surface significantly alters the adsorption/desorption equilibria of reactants and intermediates, giving rise to distinctly different catalytic reactivities in metals compared to their unstrained counterparts [1]. However, synthetically controlling lattice strain in nanocatalysts and locally characterizing strain at the nanoparticle surface is difficult, and the lack of robust materials that are stable under operating conditions has hampered the experimental implementation of strain-engineering in thermal catalysis.

Results and Discussion

In this talk, I will demonstrate the power of strain-engineering in nanoparticle catalysts for thermally-driven hydrogenation and oxidation catalysis combining experiment and theory. Using a novel material system of Pt-shell AuCu-core nanoparticles, we can systematically tune surface lattice strain from −3.5% compressive to +2.1% tensile through varying the Au:Cu ratio in the metal core [2]. Next, we show that 4D STEM is a powerful and unique tool to assess the local deformation of the crystal lattice within these nanoparticles for a large amount of nanoparticles of several compositions [3]. This enabled determining the intra- and interparticle strain distribution for the different core-shell catalysts. Catalytic evaluation in the hydrogen–deuterium exchange reaction and in the CO oxidation reaction revealed direct relationships between lattice strain and the hydrogenation and oxidation activity. Interestingly, we find that the dependence of the catalytic activity on lattice strain is opposite in hydrogenation and oxidation catalysis. Increasing tensile strain enhances the hydrogenation activity by a factor 6 due more facile hydrogen displacement at the nanoparticle surface. Contrarily, compressive strain is needed to strongly enhance the CO oxidation rate facilitated through weaker binding of CO on compressively strained Pt surfaces allowing higher oxygen dissociation rates. All in all, our results establish lattice strain as a powerful and experimentally accessible design parameter for performance control of nanoparticle catalysts in thermal catalysis.

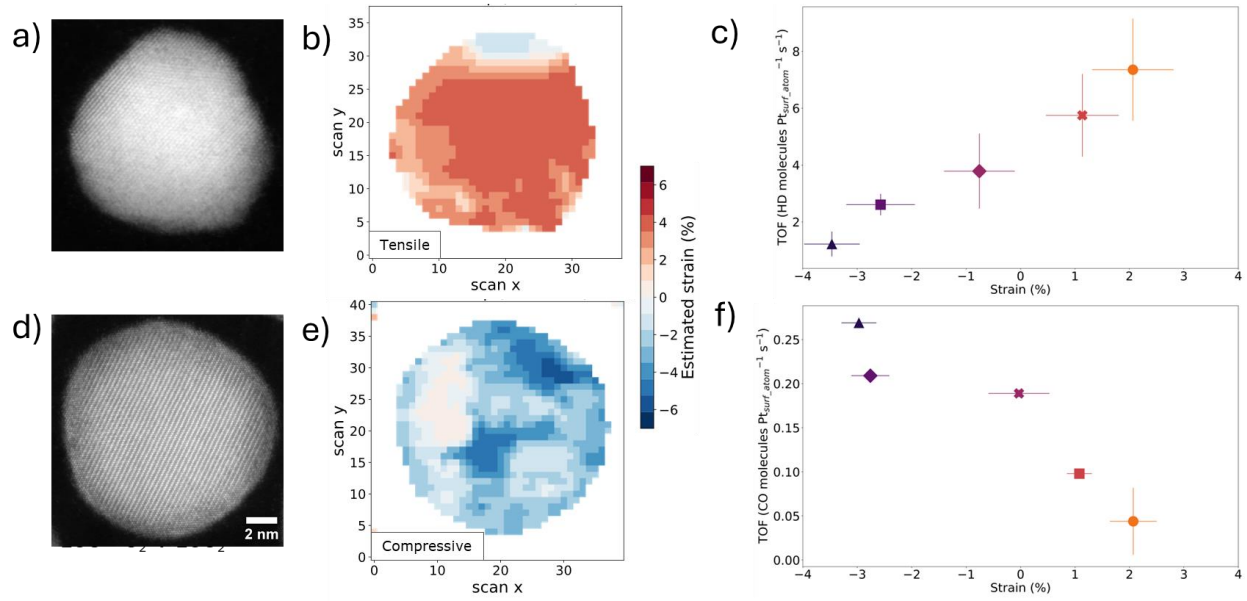

Figure 1: Influence of strain on catalytic performance in hydrogenation and oxidation catalysis. *a) High-resolution scanning transmission electron microscopy (HRSTEM) image of a tensile strained polycrystalline Pt-shell AuCu-core nanoparticle. Spots correspond to atomic columns. b) Distribution of tensile strain in a polycrystalline Pt-shell AuCu-core nanoparticle. c) HD exchange rate as a function of lattice strain of Pt-shell $Au_{1-x}Cu_x$-core nanoparticle catalysts. d) HRSTEM image of a compressive strained polycrystalline Pt-shell AuCu-core nanoparticle. e) Distribution of compressive strain across a polycrystalline Pt-shell AuCu-core nanoparticle. f) CO oxidation rate as a function of lattice strain for Pt-shell $Au_{1-x}Cu_x$-core catalysts.*

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From Single Atoms to Clusters and Back: Evolution of Noble Metals on CeO_2 for Oxidation Catalysis

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Introduction

Catalytic properties are dictated by the atomic structure of active centers, which is far more dynamic under operating conditions than previously assumed. Understanding these structural changes is essential for explaining activity and selectivity. Unlike many catalysts that deactivate mainly through sintering, noble metals on ceria behave differently due to their strong metal-support interaction. This interaction enhances low-temperature oxidation activity[1] and enables Pt redispersion under oxidizing conditions at high temperatures, offering an alternative to classical sintering-driven degradation.[2] The key challenge is to define the balance between dispersion and stability and to identify particle sizes and structural motifs with optimal performance. Using X-ray absorption spectroscopy (XANES, EXAFS), environmental transmission electron microscopy (ETEM), theoretical calculations (DFT), and catalytic testing, we followed the complete structural life cycle of Pt and Pd on CeO_2 in oxidation catalysis.

Results and Discussion

A high-temperature treatment of Pt/CeO_2 at 800 °C generated isolated Pt^{2+} species stabilized in CeO_2 "nanopockets," proven by EXAFS, FTIR, and DFT.[3] These pockets arise from local ceria restructuring, such as Ce substitution in the {110} lattice, providing a well-defined platform to study highly dispersed noble-metal species. Despite their high dispersion, these single-atom sites showed lower CO, C_3H_6, and CH_4 oxidation activity than Pt nanoparticles. *Operando* HERFD-XAS revealed that the Pt single atoms respond dynamically to gas-phase changes, especially to strongly adsorbing species like CO. MCR-ALS analysis combined with DFT indicated that, at the onset of CO oxidation, single Pt atoms agglomerate, and only after forming small clusters does significant CO conversion occur.[3] Therefore, designing catalysts that resist redispersion on the atomic level, while preserving the beneficial noble-metal/ceria interface, is essential. One strategy, increasing the surface noble-metal concentration, successfully stabilizes catalytic activity but requires a relatively high total metal loading.[4] A more elegant solution employs ceria islands dispersed on an inert support, which locally increases the Pd concentration.[5] Finally, using Pt doped CeO_2 cubes, we quantified the redispersion rate using ETEM.[6] The number of exposed surface atoms correlates directly with the reaction rate. With this understanding, predicting the structural evolution and associated catalytic performance of NM/CeO_2 nanomaterials becomes feasible, which can ultimately facilitate the rational design of redispersion-resistant catalytic materials.

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Capabilities and analysis methodologies for Dynamic Operando Spectroscopy Vision of Catalyst Surfaces at the MAX IV laboratory

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Introduction

In catalysis research, it is common to establish structure–function relationships from observations of static majority phases observed on the active catalyst surface in operando experiments. Catalyst surfaces are, however, highly dynamic entities that respond rapidly to changes in their local gas environment, and the dynamics of their response is a decisive factor for the catalysts' action and activity. Until recently, ambient pressure X-ray photoelectron spectroscopy - one of the few techniques capable of simultaneously probing catalyst activity/selectivity and surface chemistry – been unable to follow this dynamic when a chemical reaction is running. Further, the technique has been unable to selectively detect catalytic active minority phases which might govern the catalytic function.

Results and Discussion

In this talk, I will give an overview of the time-resolved APXPS methodology we recently developed at the MAX IV laboratory to tackle these limitations of APXPS [1-8]. First, I will discuss how event-averaging and the use of gas composition or temperature pulses can be used to drive the surface back and forth between different surface structures in a periodic pattern to achieve sub-second to µs time-resolution. I will discuss how software-based image recognition of spectral features [5] or synchronization to the pulsing [1,6] can be used to perform the event-averaging. Secondly, I will demonstrate how the analysis of time-resolved data in frequency space by Fourier transformations can be used to selectively detect and correlate surface and gas-phase minority oscillations, which are completely buried in the noise of the raw data [2,3]. Finally, I will discuss how grain specific studies can be performed on poly-crystals hosting entire libraries of crystallographic oriented surfaces [7] and how hysteresis can be performed with gas composition pulses [8].

After introducing the new time-resolved methods I will give a few examples of what we scientifically can learn from spectral vision of dynamic catalyst surfaces. I will demonstrate that a CO covered metallic Pd(100) surface with vacancies is as active as the oxide surface [5] and how it exists for a few seconds prior to the formation of a surface oxide [5]. Extending the studies to a polycrystal I will illustrate how the structure-function relationship breaks down for a Pd-polycrystal when the pressure is raised to the mbar regime and dynamic changes are considered [7]. Studying the same reaction on Pt(111) with tr-APXPS with µs time-resolution reveal that chemisorbed oxygen, rather than Pt surface oxide, is the main species reacting with CO to form CO_2, supporting a primary Langmuir-Hinshelwood mechanism [1].

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Gallium Promotes Ni/Al_2O_3 from Methanation to Methanol Synthesis Catalysts in CO_2 Hydrogenation

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Introduction

Nickel-based catalysts are widely employed for CO_2 hydrogenation but intrinsically favor methanation. In this work, gallium is investigated as a promoter to modify the surface chemistry of Ni/Al_2O_3 and redirect the reaction pathway toward methanol formation. A series of monometallic catalysts, including 15 wt% Ni/Al_2O_3, 5 wt% Ga/Al_2O_3, and bimetallic 15 wt%Ni–Ga/Al_2O_3 with different Ni:Ga ratios (3:1, 2:1, and 1:1), were prepared by wet impregnation and evaluated for CO_2 hydrogenation at 40 bar over 230–320 °C.

Results and Discussion

Catalytic performance was evaluated at 260 °C and 40 bar (H_2/CO_2 = 3). As shown in **Figure 1**, monometallic Ni exhibits high CO_2 conversion with nearly 99% CH_4 selectivity, confirming its intrinsic methanation activity. In contrast, Ga incorporation significantly modified product distribution. Ni–Ga (3:1) suppresses methane formation and enables methanol production alongside CO, while higher Ga content progressively shifts selectivity toward CO and reduces methanol formation. Although CO_2 conversion decreases with the addition of Ga, and Ga/Al_2O_3 alone is inactive, the selectivity change indicates that Ga alters the nature of active Ni surface sites.

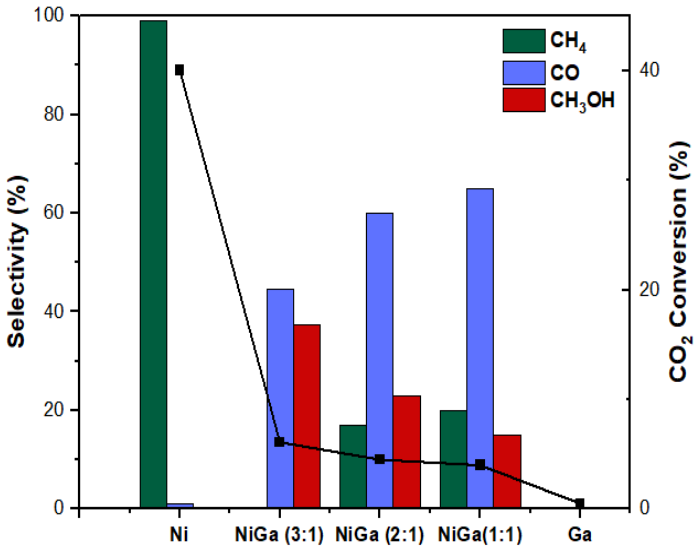

Figure 1. CO_2 conversion (line, left axis) and product selectivities (bars, right axis) over 15 wt% Ni/Al_2O_3, 15 wt% Ni–Ga/Al_2O_3 (Ni:Ga = 3:1, 2:1, 1:1), and 5 wt% Ga/Al_2O_3 at 260 °C and 40 bar (H_2/CO_2 = 3).

Catalysts characterization (BET, XRD, TEM, SEM–EDX, and H_2-TPR) indicates that gallium enhances Ni dispersion and modifies Ni reducibility without formation of bulk Ni–Ga intermetallic phases. The shift toward methanol selectivity is attributed to Ga-induced modification of Ni surface sites, which suppresses CO dissociation and subsequent deep hydrogenation to CH_4, while promoting hydrogenation of surface oxygenated intermediates associated with methanol formation. These results demonstrate that Ga promotion effectively tunes the reaction pathway of Ni/Al_2O_3 in CO_2 hydrogenation.

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Identification of Transient Intermediates and Active Species in $CuZnZrO_2$ Catalysts for CO_2 Hydrogenation to Methanol

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Introduction

Direct CO_2 hydrogenation to methanol presents a promising form of Carbon Capture Utilization (CCU) in the near and longer term. New classes of catalysts, such as those based on ZrO_2, are a potential way to enhance the system's activity, selectivity and stability.[1] However, due to the high structural complexity, establishing a direct structure-activity relationship is challenging. To solve this problem, we combined advanced characterization and signal processing techniques, *i.e.* High Energy Resolution Fluoresce Detected (HERFD) XANES and Modulation Excitation Phase Sensitive Detection (ME-PSD) DRIFTS to untangle the different active sites and reactional intermediates under *operando* conditions.[2]

Results and Discussion

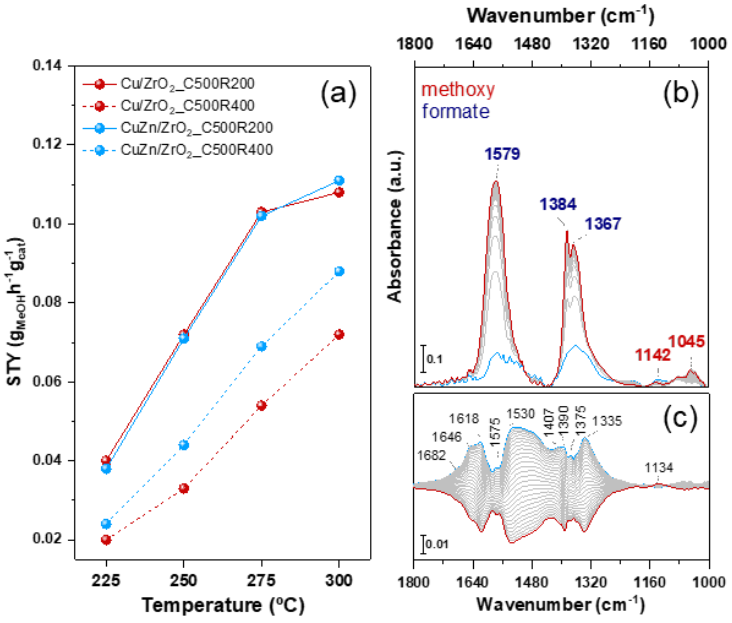

Figure 1. (a) CO_2 hydrogenation to methanol on $CuZn/ZrO_2$ catalysts (b) ME-PSD-DRIFTS time and (c) phase domain.

A set of binary (1 wt.% Cu/ZrO_2) or ternary (1 wt.% $CuZn/ZrO_2$) catalysts either activated under mild or harsh conditions (reduction at 200 and 400 ºC, respectively) were tested under CO_2 hydrogenation to methanol (225 – 300 ºC, 30 bar, 1:3 CO_2:H_2), as seen in Figure 1a. The mildly reduced catalysts outperformed the harshly reduced counterparts, and the presence of Zn promoted the catalytic outcome. *In situ* HERFD XANES points at the formation of highly mobile Cu clusters for the mildly reduced samples, and larger nanoparticles for the harshly reduced ones. Meanwhile, the use of ME-PSD-DRIFTS (Figure 1b,c) helped to filter out spectator species, such as the formate at 1579 cm^{-1}, and draw attention to other important intermediates, such as monodentate formate 1618 cm^{-1}, and carbonate in the 1500 cm^{-1} region. We also show that the presence of Zn influences the reaction kinetics, facilitating the formate intermediates hydrogenation. These are important contributions to the mechanistic debates which often rely solely on DRIFTS results. This work employes different signal processing techniques to make the most of *in situ* and *operando* datasets. We show how their combination can be a powerful tool to elucidate structural and mechanistic features of catalysts.

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Hierarchical zeolite 13X-supported Ni catalysts for carbon dioxide conversion into methane

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Introduction

The catalytic conversion of carbon dioxide (CO_2) into methane (CH_4) is a promising strategy due to the extensive global infrastructure for CH_4 storage and distribution[1]. However, conventional nickel (Ni)-based catalysts often deactivate due to sintering and coke formation[2]. Strategies to enhance the catalyst resistance to deactivation typically focus on controlling nanoparticle size, strengthening metal–support interactions, and optimizing spatial distribution on porous supports such as zeolites[3–5]. The zeolites as a support material offer several advantages, including high surface area, tunable pore structures, thermal stability, and strong metal–support interactions[6]. In addition, their chemical composition can be readily modified through approaches such as dealumination and surface functionalization[7]. However, zeolites with high Al/Si ratios exhibit stronger acidity, making them more susceptible to coking. Increasing the Si content by adjusting the Al/Si ratio can reduce hydrophilicity and improve resistance to coke formation[8]. Additionally, the abundance of hydroxyl groups in zeolites can serve as anchoring sites for metal nanoparticles, promoting the formation of stable, highly dispersed catalysts[9]. Furthermore, incorporating co-catalysts and promoters can significantly enhance catalyst stability, conversion efficiency, and selectivity toward CH_4 during CO_2 hydrogenation[10]. In view of these considerations, this study reports highly stable Ni-based catalysts for CO_2 hydrogenation, developed by simultaneously tuning catalyst dispersion and hydrophilicity through amine and silanol functionalization, together with the incorporation of Co as a co-catalyst.

Results and Discussion

We engineered the metal–support interaction by immobilizing silane molecules bearing silanol and amine functional groups onto the hierarchical 13X framework (h13X), enabling the successful grafting of Ni and Co nanolayers along the edges and boundaries of the h13X crystals. The synthesized catalysts were characterized using STEM, EELS, XPS, and H_2-TPR. Catalytic performance was evaluated for CO_2 conversion to CH_4 under different reaction conditions. The optimized catalyst (AF-7.5Ni3Co/h13X) achieved a maximum CO_2 conversion of ~75% at 20 bar and 400 °C with a GHSV of 60,000 ml g_{cat}^{-1} h^{-1}. Notably, the catalyst demonstrated excellent stability for more than one month with no observable loss in CO_2 conversion. EELS, XPS, and TPR analyses revealed strong metal–support interactions between Ni and h13X, as well as electronic interactions between Ni and Co, which contribute to sustained catalytic performance. These results demonstrate that hierarchical 13X-supported Ni catalysts exhibit robust catalytic activity and stability, highlighting their potential for large-scale CO_2 methanation and broader heterogeneous catalysis applications.

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Graph models and fine-tuned machine learning potentials for microkinetic analyses in heterogeneous catalysis

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Introduction

Heterogeneous catalysis is nowadays expected to solve the challenges of our society related to the diversification of energy sources and the reduction of greenhouse gases. The processes of CO_2 hydrogenation have the potential to sustainably produce chemicals and fuels from green hydrogen and waste CO_2. To make such processes economically advantageous, R&D in catalysis relies on the discovery and optimization of catalytic materials based on experimental testing and computational analyses. The *in-silico* modeling and design of catalyst materials must tackle the extreme complexity of chemical reactions at catalytic surfaces. This makes the direct application of density-functional theory (DFT) computationally prohibitive, especially when targeting a wide combinatory space of elements of the periodic table. This problem can be addressed with machine learning (ML) techniques, which can significantly reduce the number of DFT calculations required.

Results and Discussion

In this contribution, we combine DFT and ML models to investigate CO_2 hydrogenation reactions across a broad range of catalyst materials, including metals, single-atom alloys [1], and doped ZrO_2 surfaces [2]. As illustrated in Figure 1, we explore different levels of modeling, from accurate but computationally demanding DFT calculations to increasingly efficient ML-based strategies. These include descriptor-based models such as WWL-GPR (a graph-based Gaussian Process Regression framework [3]), as well as universal ML potentials (MLPs), which we apply to predict energies of reaction intermediates and transition states (TS) of reaction mechanisms. Beyond predicting energies with ML models, we also apply active learning strategies to efficiently achieve DFT accuracy. For example, we combine single-ended TS-search methods with MLPs fine-tuning to estimate DFT activation barriers at a fraction of the usual computational cost [4]. Finally, we apply mean field microkinetic modeling to calculate the catalytic performances (i.e., activity and selectivity) of the catalyst materials, accounting for the contribution of the different active sites of the catalyst surfaces. The application of our frameworks to CO_2 hydrogenation reactions allows us to rationalize how reaction mechanisms and catalytic performances change with the catalyst composition, paving the way toward the design and nano-engineering of catalyst materials [1, 2].

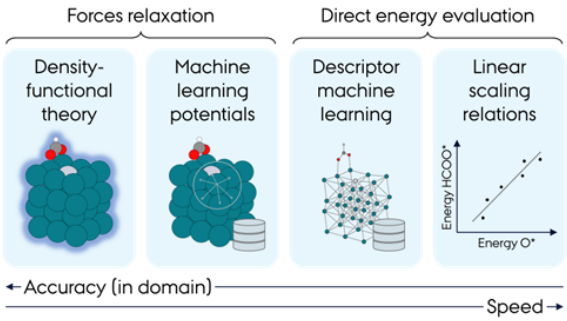

Figure 1: Schematic overview of the computational strategies employed in this work

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Effect of sulfur on noble metal catalysts for stabilization of biomass pyrolysis oil model compounds

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Introduction

Biomass pyrolysis oil (PO) must be hydrotreated to produce a fuel that can be used in the present infrastructure[1]. However, the oil has a high oxygen content making it highly reactive, causing catalyst coking and reactor plugging. Therefore, a two-step upgrading process involving stabilization followed by deoxygenation is required[2]. In this contribution, we studied the activity and sulfur tolerance of noble metal catalysts for stabilization of pyrolysis oils using model compounds. Experiments were carried out in a continuous trickle-bed reactor with Pd/C and Pt/C catalysts. A model compound mixture (furfural, acetophenone, diacetone alcohol, guaiacol, octanoic acid, and ethyl hexanol) designed to mimic a diluted woody PO (40 %) was used to investigate these potential stabilization catalysts. Experiments were run at 100 bar H_2, in the temperature range 120-180 °C with a liquid flow of 0.2 mL/min and a H_2/liquid feed ratio of 2500 V/V. The catalysts were tested as follows: 24 h without sulfur, 48 h with 500 ppm sulfur (thiophene) in the feed, and finally 24 h without sulfur.

Results and Discussion

The study revealed the effect of sulfur on the catalysts' activities towards converting the model compounds to more stable molecules. The plots for furfural, acetophenone and diacetone alcohol displayed in Figure 1 show a decrease in conversion of all three compounds during the period with sulfur in the feed. However, after switching to sulfur-free feed some of the initial activity was regained, although not completely. Thus, the deactivation of the catalysts due to sulfur poisoning is partly reversible. The loss of activity for conversion of acetophenone and diacetone alcohol apparent by the end of the experiments in Figure 1B and C may either be due irreversible deactivation, or that the catalyst did not have had enough time to recover.

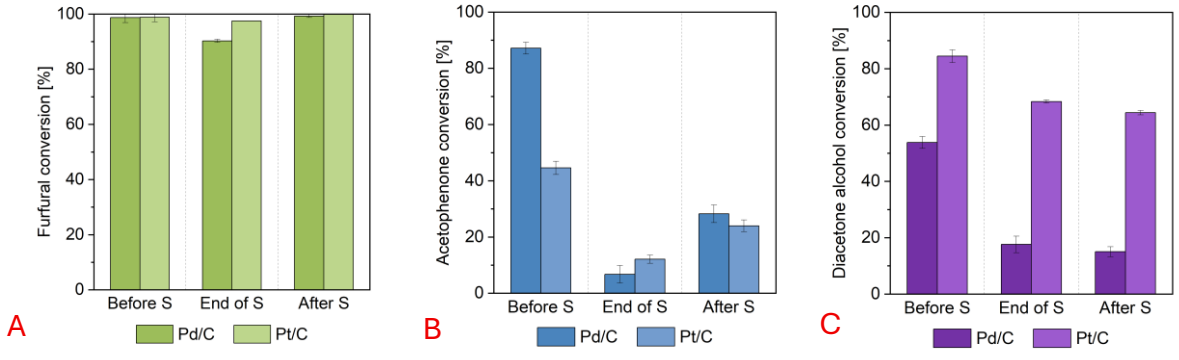

Figure 1: Conversion of A) furfural, B) acetophenone, and C) diacetone alcohol for experiments with sulfur addition (before sulfur, end of time with sulfur, and after sulfur addition).

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Design of hydrotalcite-derived Mg-Al oxide catalysts for the selective valorisation of bioethanol into higher alcohols

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Introduction

The catalytic upgrading of bioethanol into higher-value chemicals is a promising route for replacing fossil-derived feedstocks. Ethanol is an efficient platform molecule for producing oxygenates such as 1-butanol through the Guerbet condensation, which relies on a balanced sequence of dehydrogenation, aldol condensation, hydrogen transfer, and dehydration steps. Hydrotalcite-derived Mg-Al mixed oxides are particularly effective in this transformation due to their bifunctional acid-base properties, high surface area, and thermal stability. Systematic studies at the L.V. Pisarzhevskii Institute of Physical Chemistry (NASU) demonstrated the strong potential of these materials and highlighted the importance of composition, textural optimisation, and promoter incorporation for enhancing ethanol valorisation.

Results and Discussion

Hydrotalcite-derived Mg-Al oxides exhibit superior activity and selectivity in the Guerbet condensation compared with single oxides of MgO and Al_2O_3, achieving up to 18% 1-butanol yield with 65% selectivity at Mg/Al=2 [1]. Increasing the aluminium content beyond the stoichiometric hydrotalcite composition enhances surface area and optimises the distribution of acid-base sites [2]. Reducing hydrotalcite ageing time increases mesoporosity, external surface area, and the concentration of weak and moderately weak basic sites, which correlates with higher ethanol conversion and improved BuOH selectivity [3]. Incorporation of Y via coprecipitation increases the total concentration of acidic and basic surface sites and provides higher selectivity to 1-butanol (~75%) [4]. Further optimisation through Cu impregnation increases ethanol conversion up to 90% by enhancing dehydrogenation capacity; however, BuOH yield decreases due to blockage of Mg-O-Al condensation sites. This limitation is overcome by introducing Cu and Ni during hydrotalcite synthesis via coprecipitation, preventing site blockage and enabling simultaneous enhancement of dehydrogenation and aldol-condensation steps. The resulting Ni-Cu-Mg-Al-Y catalysts show a drastic increase in ethanol conversion (from 31% to 60% at 250 °C) and maintain stable performance even at 150 °C, achieving 60% total selectivity to higher alcohols (40% BuOH, 20% $C_{6\text{-}8}$ alcohols) [5]. Thus, optimisation of hydrotalcite-derived Mg-Al catalysts and their modification with Y, Cu, and Ni significantly improves the efficiency of bioethanol valorisation into 1-butanol and higher alcohols, offering selective, thermally stable, and lower-temperature catalytic routes aligned with sustainable industrial processes based on renewable feedstocks.

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Integrated Valorization of Agricultural Residues to Ethyl Levulinate and Sustainable Bio-Based Applications

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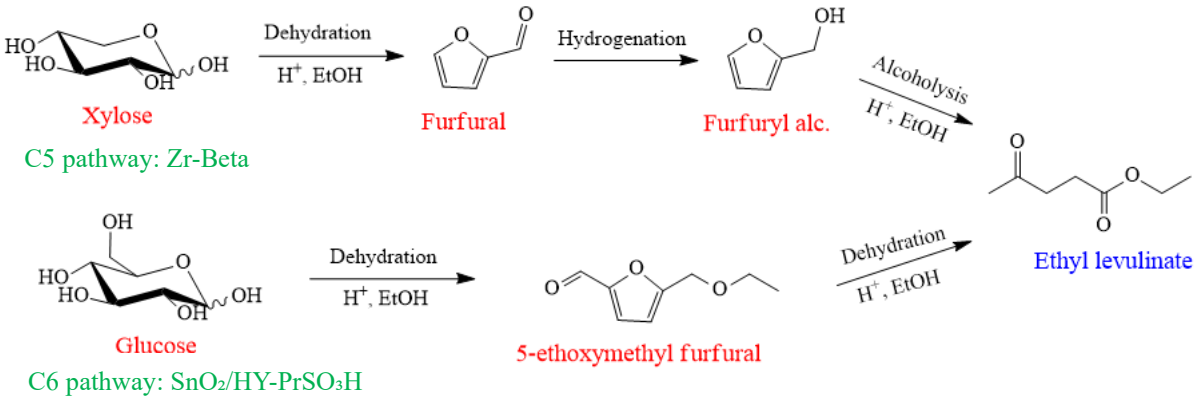
Introduction

Advancing a sustainable bio-circular economy requires efficient conversion of agricultural residues into high-value chemicals and functional products. Empty palm fruit bunch (EFB), a major by-product of the palm oil industry, is often underutilized or incinerated, leading to environmental concerns. Developing effective heterogeneous catalytic systems for direct lignocellulosic biomass conversion into platform chemicals is therefore of significant importance. Ethyl levulinate (EL) is a promising bio-based compound with applications as a fuel additive and green solvent.

Results and Discussion

An integrated catalytic approach employing synergistic Brønsted/Lewis acidic heterogeneous catalysts Zr-Beta and SnO_2/HY-$PrSO_3H$ was developed for EL production from C5 and C6 carbohydrates (Scheme 1) and real EFB biomass. The system achieved EL yields of 34–43 wt.% from EFB under optimized one-pot conditions, demonstrating efficient direct biomass valorization while overcoming limitations of homogeneous acid processes.



Scheme 1. The reaction pathway of C5 and C6 carbohydrates lead to EL.

Furthermore, the produced EL was evaluated as a bio-based solvent in color applications. After one-year, minimal color changes were observed compared to commercial oil media. These results highlight the dual role of EL as both a valuable platform chemical and a sustainable solvent alternative, supporting circular bioeconomy development.

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Intrinsic Metal Effects Govern Methoxy Retention versus Demethoxylation in the Electrochemical Upgrading of Guaiacol

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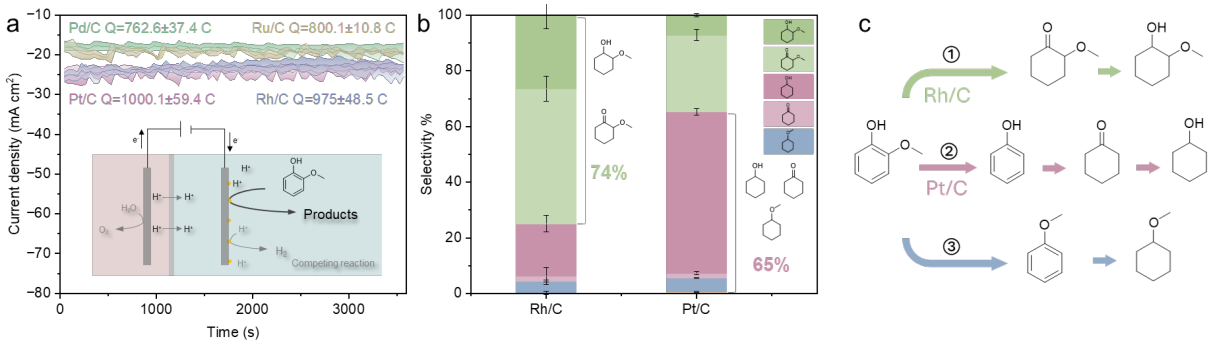
Introduction

Electrochemical upgrading of lignin-derived aromatics offers a pathway for storing renewable electricity in chemical bonds while simultaneously generating value-added products[1-3]. In electrochemical hydrogenation (ECH) of methoxylated aromatics, however, controlling selectivity between hydrogenation and C-O bond cleavage remains a central challenge that directly influences hydrogen content, oxygen functionality, and physicochemical properties relevant to downstream fuel and chemical applications. Guaiacol, a representative lignin-derived platform molecule, is particularly attractive due to its structural similarity to functional components in biofuels and energy-relevant aromatic intermediates.

Here, we demonstrate that the type of metal catalyst intrinsically governs divergent reaction pathways in guaiacol ECH. A systematic comparison of carbon-supported noble metal electrocatalysts (Rh/C, Pt/C, Ru/C, and Pd/C) under identical operating conditions reveals substantially different selectivity: Rh/C selectively produces methoxy-retaining hydrogenation products, whereas Pt/C promotes demethoxylation via C-OCH_3 bond cleavage. This selectivity divergence is preserved across variations in applied potential, temperature, electrolyte composition, and substrate scope, indicating that fundamental catalyst-substrate interactions control reaction outcomes rather than external reaction parameters. Integrating electrochemical characterization with density functional theory (DFT) calculations, we attribute this behaviour to differences in adsorption energetics, interfacial electronic structure, and hydrogen-transfer mechanisms that govern the competition between hydrogenation and demethoxylation. These findings establish a composition-selectivity relationship for electrocatalytic transformations of lignin-derived molecules and highlight how catalyst identity controls the formation of products relevant to renewable fuels and electricity-driven chemical energy storage. This work advances mechanistic understanding of selective ECH and provides guiding principles for designing electrocatalysts that tailor biomass-derived feedstocks into energy-relevant chemicals.



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Advances in operando electron microscopy in heterogeneous catalysis

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Introduction

Understanding structure-activity relationships in heterogeneous catalysis calls for methods capable of resolving both the atomic structure and catalytic function of individual nanoparticles [1,2]. While *operando* electron microscopy has recently enabled direct imaging of nanoparticle structures reaching an ultimate ~ 0.5 Å resolution [3], the intrinsic activity of single nanoparticles remains inaccessible due to their size and shape distributions and assembly into cooperating networks [2,3]. Overcoming this limitation requires an improvement of the chemical sensitivity by a factor of ~ 10^6 as compared to conventional catalysis measurement techniques.

Results and Discussion

Here, we present a novel nanoreactor platform designed to enable *operando* electron microscopy of individual 1-10 nm nanoparticles under thermal reaction conditions [4-6]. The nanoreactor consists of micrometre-scale circular recesses etched into a silicon chip bounded by an electron-transparent SiO_2 bottom and a lid of a 2D material, forming ~ 20 μm^3 batch reactors. Prior to sealing, single nanoparticles are loaded into the reactors through exposure to a nanoparticle beam [7], and gas mixtures are subsequently introduced through diffusion along the SiO_2–2D material interface [4-5].

Advances in electron energy loss spectroscopy (EELS) methods allow quantification of both total and partial gas pressures inside the confined volumes, providing access to catalytic conversion of single nanoparticles. Simultaneously, the electron-transparent reactor lid and bottom allow atomic-resolution TEM imaging, reaching ~ 0.5 Å at pressures far beyond ambient, enabling single-atom sensitivity and three-dimensional structural analysis during reaction conditions. Thus, this nanoreactor concept offers a pathway to correlating the atomic-scale structure and catalytic behavior of individual nanoparticles, opening new opportunities for *operando* studies of heterogeneous catalysis with orders-of-magnitude improved sensitivity [6].

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Multi-Stimulus In Situ TEM for Catalysis Using a MEMS-Based Environmental Nano-Reactor

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Introduction

Understanding catalytic processes under realistic reaction conditions remains a central challenge in heterogeneous catalysis. Key phenomena such as catalyst activation, deactivation, redox dynamics, and metal–support interactions occur under complex gas environments and elevated temperatures that are difficult to replicate using conventional ex situ techniques. In situ transmission electron microscopy (TEM) enables direct visualization of catalysts at the nanoscale; however, achieving simultaneous control over gas composition, pressure, temperature, and electrical stimuli, while maintaining atomic resolution and chemical sensitivity, remains non-trivial. Here, we present a MEMS-based System for operando in situ TEM catalysis studies, combining a dedicated gas supply system (GSS), a MEMS Nano-Reactor with integrated heating and electrical biasing, and an inline residual gas analyzer (RGA) to enable comprehensive multi-stimulus experiments under dynamically adjustable reaction conditions.

Results and Discussion

The System enables precise on-the-fly gas mixing**,** allowing arbitrary gas compositions to be generated and modified during experiments. Due to the extremely small internal reactor volumes, operation at pressures up to 2 bar is possible, including controlled mixtures of otherwise explosive gases such as H_2 and O_2. Rapid switching between dry and wet environments can be achieved through controlled introduction of water vapor, without overnight pumping or baking, ensuring a clean gas manifold and stable baseline conditions. The MEMS-based Nano-Reactor provides eight independent electrical contacts, enabling simultaneous heating and electrical biasing under flowing gas environments. The integrated microheater delivers millikelvin-level temperature accuracy and stability directly at the sample location, with demonstrated reliability up to 1000 °C. In addition, the MEMS architecture enables micro-calorimetric measurements, allowing detection of heat dissipation or absorption during catalytic reactions and distinguishing endothermic from exothermic processes. While maintaining full control over gas composition, pressure, flow rate, temperature, and biasing, the system allows atomic-resolution imaging of catalytic processes. Correlative analytical capabilities include in situ electron diffraction (single-particle analogue to XRD), in situ EELS (comparable to XPS), and in situ EDS, complemented by real-time product analysis via the integrated mass spectrometer. The modular system design further enables cross-platform correlative research, allowing the same Nano-Reactor to be transferred from TEM to SEM and synchrotron facilities. Representative application examples will be presented, including the dynamic interplay between metal nanoparticles and oxide supports under redox conditions, catalytic activation and deactivation mechanisms, in situ carbon nanotube growth, the redox dynamics of Cu/CuO_x nanoparticles, and solid oxide fuel cells.

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Determining the State of a Pd/γ-Al_2O_3 Catalyst Using Pulsed Flow and Transient Spectroscopy

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Introduction

A precise understanding of heterogeneous catalyst structure and activity is required to design more efficient, greener, industrial chemical processes. While it is possible to resolve both the structure and activity of a catalyst, their innate complexity means it is nontrivial to unambiguously assign one to the other. Given the intimate relationship between structure and activity, we propose that if catalytic activity could be measured with sufficient precision over a broad enough range of steady state and transient conditions, it should be possible to assign a structure to a specific "active site" using the measured kinetics.

Results and Discussion

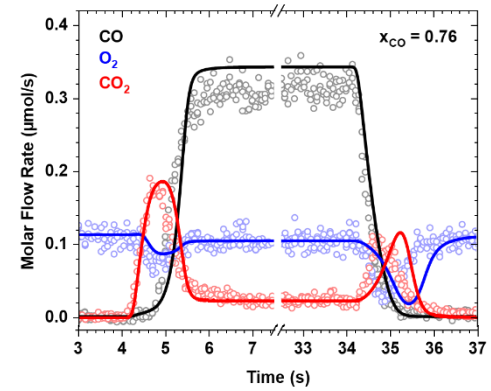

Fig. 1 Transient CO oxidation switching experiment over a Pd/Al_2O_3 catalyst, circles are experimental data, solid lines are numerical simulation.

Herein, we demonstrate how transient measurements, coupled with kinetic modelling (Fig. 1), can be used to resolve kinetics with sufficient precision such that it is possible to resolve the identity of an "active site" over technical catalysts.[1] We find that under CO rich conditions the transient activity and coverage dependencies measured over a Pd/γ-Al_2O_3 catalyst during pulsed flow and transient spectroscopy CO oxidation experiments can be quantitatively predicted using a kinetic model derived from ultrahigh vacuum surface science experiments over Pd(111) single crystals. Thus, we conclude that the state (i.e., structure and composition of the active site) of the Pd/γ-Al_2O_3 catalyst under reaction conditions is equivalent to that of a Pd(111) surface. Instead of determining a catalyst's structure and assigning it to activity, we instead propose a new approach: using precise kinetic measurements to infer the catalyst's state. This approach enables the identification of active sites that have been challenging to resolve using traditional spectroscopic or microscopic methods, offering a powerful and complementary tool for designing new catalysts.

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CO oxidation on $NiFe_2O_4$ under an applied magnetic field: elucidating the relation between catalytic mechanism and magnetic properties

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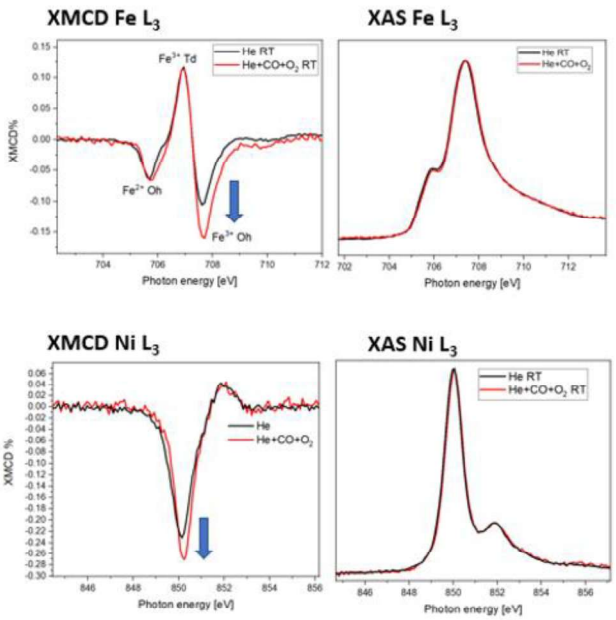
Introduction

Magnetocatalysis has emerged in recent years as a highly promising field, with several studies showing enhanced electrocatalytic performance in ferromagnetic materials [1,2]. Most of these studies, however, remain empirical, and the mechanisms behind spin related effects are still unclear due to the lack of suitable experimental techniques. For thermocatalytic oxidation reactions, investigations on the influence of external magnetic fields or intrinsic magnetic order on activity and selectivity are almost entirely absent. In this work, we synthesized $NiFe_2O_4$ magnetic nanoparticles via sol-gel autocombustion method and characterized them *ex-situ* (XRD, SEM, XPS, VSM). We then spectroscopically investigated the catalytic CO oxidation mechanism on the NPs surface under an applied magnetic field, exploting a unique setup [3] at SPECIES beamline (MAX IV Laboratory, Sweden). By using the *operando* X ray Magnetic Circular Dichroism (XMCD) technique at 1 bar of total pressure, for the first time we characterized simultaneously the magnetic and electronic properties of the single chemical species constituting $NiFe_2O_4$ during the reaction at different temperatures.

Results and Discussion

The *operando* 1 bar XMCD experiment started by exposing the sample to CO + O_2 at 25°C. As shown in the figure, the Ni and Fe XAS spectra remain unchanged after exposure, whereas the XMCD signal is selectively altered at the octahedral (spin aligned) sites. This indicates that reactant adsorption (most likely CO) modifies the magnetic properties of the surface while preserving the electronic structure, and that this perturbation is confined to octahedral Ni and Fe sites. Upon heating the sample to 300 °C, the XMCD data reveal that CO adsorption shifts from Fe octahedral to tetrahedral sites, while the XAS spectra remain unchanged. Above the reaction activation temperature (T > 150 °C), the trend reverses and the overall XMCD intensity progressively decreases. This advanced *operando* experiment provides two key insights: *(i)* CO adsorption modifies the spin properties of Ni and Fe with minimal alterations of the electronic structure, offering a foundation to explore the relationship between magnetic properties and catalysis; *(ii)* XMCD is demonstrated, for the first time, as a chemically and site selective probe for monitoring the CO + O_2 reaction mechanism.



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Structural and Catalytic Insights into Pd@UiO-66 for C-C coupling reactions

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Introduction

Palladium, renowned for its versatile catalytic properties, has been well-established as a central metal in many chemical transformations due to its ability to facilitate hydrogenation reactions and carbon-carbon cross-couplings. In our previous works, we demonstrated the catalytic performance of immobilized Pd nanoparticles in functionalized MIL-101[1], UiO-66[2], and UiO-67[3] metal-organic frameworks for butadiene and CO_2 hydrogenation reactions. Here, we report the first instance of immobilized neutral Pd single atoms within the pores of functionalized UiO-66. Combined experimental, spectroscopic, and computational studies elucidate the nature and speciation of these well-defined Pd moieties and reveal the role of Pd speciation in Pd-catalyzed reactions.

Results and Discussion

Comprehensive structural characterization was conducted, and Pd speciation and local environment was probed using X-ray absorption spectroscopy (XAS), transition electron microscopy (TEM), inelastic neutron scattering (INS), thermal desorption spectroscopy (TDS), and X-ray atomic pair distribution function analysis (PDF). Studies of hydrogen interactions with the Pd@MOF materials reveal distinct behavior, as interstitial hydride formation is observed for Pd nanoclusters in INS and TDS, whereas Pd single atoms do not form hydrides and instead show stronger Pd-H interactions and desorption at higher *T* (**Fig 1a**). These differences can be directly correlated with their observed catalytic reactivity.

Previously, we found that the supported Pd NPs were able to promote the hydrogenation step in the CO_2-to-methanol conversion. In contrast, we link the activity of these Pd@UiO-66 material in the Stille cross-coupling (C-H activation and C-C bond formation) to the presence of Pd single atoms Pd speciationis thus crucial for the catalytic performance of the material, as both synthesized Pd-loaded MOFS containg single atoms show high activity in the Stille coupling, whilst samples bearing only Pd NPs in UiO-66 are inactive under identical conditions (**Fig. 1b**). Post-reaction structural analysis of the spent catalysts indicates that Pd speciation evolves under the reaction conditions, underscoring the intrinsic link between Pd speciation and catalytic performance.

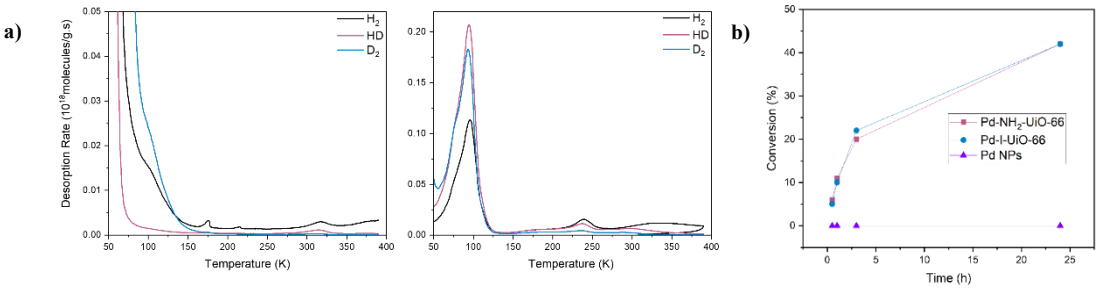

Fig 1. a) TDS spectrum of Pd@UiO-66 demonstrating desorption peaks characteristic of Pd NPs (240 K) or single atoms (315 K). b) Product conversion for the Stille coupling to yield biphenyl catalyzed by Pd@UiO-66 (0.03 mmol). No product detected for Pd NPs in control experiment.

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K-doped $LaFeO_3$ perovskites for CO_2 hydrogenation to light olefins

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Introduction

CO_2 valorization through thermocatalytic hydrogenation represents a promising pathway for the production of green value-added chemicals such as light olefins. In this study, $LaFeO_3$ perovskite (LFO) and its potassium-promoted derivatives (K/LFO, with a nominal K:Fe=1.7) are synthesized using three synthesis routes, namely sol-gel (sg), hydrothermal (ht) and mechanochemical method (m). The catalysts were systematically characterized (via XRD, Raman, FTIR, SEM and XPS analysis) to determine their phase composition, surface chemistry, morphology, and oxidation state distribution of the iron active sites, and evaluated at 340 - 400 ºC, 20 bar, WHSV= 5.5 $L \cdot gcat^{-1} \cdot h^{-1}$ and a feed ratio of H_2:CO_2=3:1 with the aim to reveal structure-performance relationships.

Results and Discussion

Structural and spectroscopic analyses revealed that the mechanochemical route produced a defect-rich perovskite with enhanced Fe^{2+}/Fe^{3+} redox flexibility and oxygen vacancies, whereas the sol-gel and hydrothermal routes yielded more stoichiometric, less reducible lattices. Upon K incorporation, the structural reconstruction was pronounced, accompanied by the appearance of Fe_3O_4 and FeC_x phases. Catalytic evaluation studies demonstrated a strong dependence on both synthesis and potassium promotion. The mechanochemical K/LFO-m catalyst exhibited the highest CO_2 conversion (50%) and light-olefin selectivity (17%) at 340 ºC , outperforming the sol-gel and hydrothermal counterparts (Fig 1). This superior activity was associated with sustained oxygen-vacancy contribution, stabilized reduced iron species, homogeneous K dispersion, and the formation of iron carbide phases which facilitated CO_2 activation and C-C coupling. Moreover, the effect of reaction temperature demonstrated that CO_2 conversion increases with an increase in temperature, while C_2-$C_4^=$ selectivity reaches a plateau over 370 ºC, and further temperature increase hinders paraffin formation. Overall, the findings highlight the critical interplay between defect chemistry and alkali promotion in tuning perovskite-derived Fe active sites for efficient CO_2-to-olefins conversion.

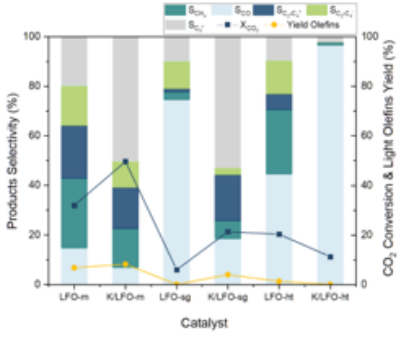

Figure 1: Catalytic activity and product distribution over LFO and K/LFO catalytic systems.

Acknowledgements: This research has received funding from the European Union under grant agreement No 101099717 - ECOLEFINS project and UK Research and Innovation (UKRI) under the UK governments Horizon Europe funding Guarantee (10079292).

Impact of hydrothermal Treatment on the physicochemical Properties and MTO Activity of H-ZSM-5 Catalysts

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Introduction

The methanol-to-olefins (MTO) process converts methanol into light olefins such as ethylene and propylene using H-ZSM-5 zeolite catalysts. However, rapid deactivation due to coke deposition limits catalyst lifetime and process efficiency. Hydrothermal treatment (steaming) modifies the structural and acidic properties of H-ZSM-5, thereby influencing its catalytic behavior. This study investigates the relationship between controlled steaming, physicochemical properties, and MTO performance.

Results and Discussion

Hydrothermal treatment of H-ZSM-5 was analyzed by NH_3-TPD, pyridine-DRIFTS, and IPA-TPD. The steamed sample (ZPS-180) showed reduced total acidity, Brønsted/Lewis site intensity, and acid strength compared to ZP-180, indicating partial dealumination and redistribution of acid sites; EDX and XRF confirmed the framework composition prior to steaming. This moderated acidity suppressed secondary reactions such as aromatization and hydrogen transfer, favoring light olefins. The decrease in strong Brønsted sites suggests selective removal of framework Al species. Overall, steaming tailored both acid density and strength without collapsing the zeolitic structure [1].

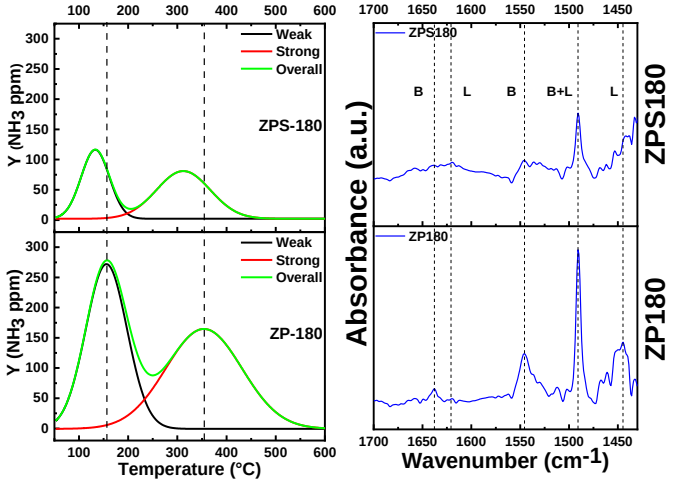

Figure 1 NH3-TPD and pyridine-DRIFTS of steamed and unsteamed catalyst

MTO performance was evaluated at 475 °C, 3 bar, and WHSV = 1.5 h^{-1} after steaming at 500 °C. Olefin yield increased from 66.8 % to 77.5 % (Si/Al = 90) and from 75.9 % to 84 % (Si/Al = 200), while methanol conversion remained 100 % for all samples. Steaming reduced C_6^+ and aromatic fractions, confirming that controlled dealumination optimizes acid site density and enhances light olefin selectivity. The improvement was more pronounced at higher Si/Al ratio, indicating a synergistic effect between intrinsic acidity and post-treatment. These findings demonstrate that moderate hydrothermal treatment enhances selectivity without compromising catalytic activity [2].

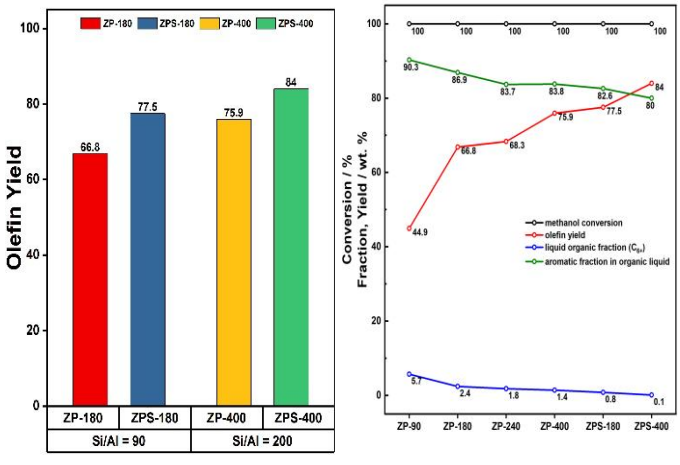

Figure 2 Conversion and olefin yield using steamed and unsteamed catalyst

Steaming tailored the acidity and framework of H-ZSM-5 via controlled dealumination, leading to enhanced olefin selectivity and improved catalyst stability in MTO. Further solid-state ^{27}Al NMR studies will clarify aluminum coordination changes and their correlation with acidity and catalytic performance.

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On the anchoring mechanism of metal nanoparticles on carbon supports

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Introduction

Carbon supported metal catalysts are key components of many emerging energy conversion and circular economy related processes. One of the most important tasks of a catalyst support is to anchor metal nanoparticles and thus stabilize the catalyst against sintering. However, up to date the anchoring mechanism of metal nanoparticles on carbon supports remains unclear; meaning that it is unknown which carbon nanostructures are suitable to synthesize carbon-supported catalysts of high sintering resistance.[1]

Results and Discussion

We employed two carbon model supports - platelet-type carbon nanofibers (CNF) and high-surface-area graphite (HSAG) - whose surfaces expose distinct graphite crystal facets: edge sites (CNF) and basal planes (HSAG). Cobalt nanoparticles were deposited via colloidal synthesis, yielding catalysts with identical initial Co particle-size distributions and supports with comparable specific surface areas and surface chemistry. Despite these similarities, the catalysts exhibited strikingly different Fischer-Tropsch Synthesis (FTS) activities (Figure 1a). This activity divergence originated from differences in the supports' ability to stabilize Co nanoparticles against sintering during catalyst activation. On the basal-plane-terminated HSAG, Co mobility was found to be substantially higher than on the edge-site-terminated CNF (Figure 1b). Combined in situ XAS/XRD coupled with online mass spectrometry revealed that cobalt anchoring on the carbon supports is likely driven by low-temperature carbothermal reduction of cobalt oxides, which competes with H_2-driven reduction. Because carbothermal reduction requires oxygen transfer from the metal oxide to the carbon surface, it proceeds more readily on the defect-rich, edge-terminated CNF. We propose that subsequent carbon gasification induces beneficial modifications at the Co/C interface, promoting strong Co anchoring. As a result, Co nanoparticles are effectively stabilized on CNF, leading to significantly higher FTS activity compared to HSAG-supported catalysts. In contrast, the greater oxidation stability of the basal-plane facet of HSAG suppresses carbothermal reduction, limits Co/C interface evolution, and ultimately reduces Co stabilization.

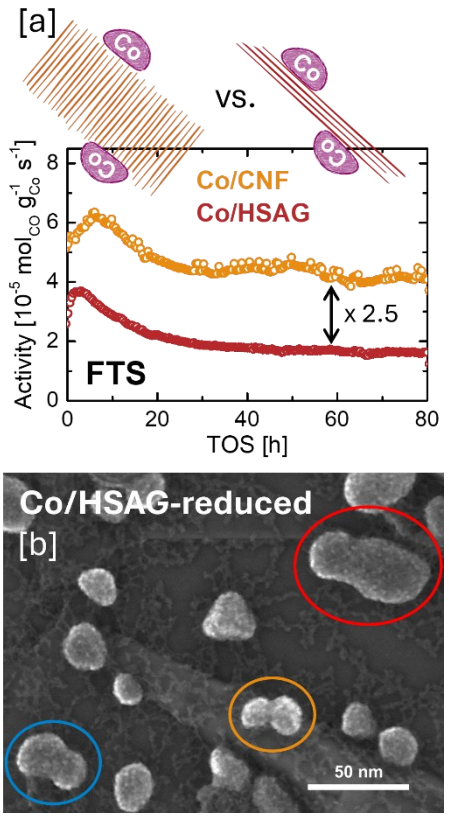

Figure 1. [a] FTS activity of Co supported on edge-site terminated CNF vs. basal-plane terminated HSAG support. [b] High resolution SEM micrograph of Co/HSAG after reduction, indicating severe Co sintering via migration/coalescence.

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Solventless hydrodeoxygenation of dihydroeugenol in a continuous reactor over Ni catalysts modified with Fe and Ce

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Introduction

There is an urgent demand of sustainable bioderived aviation fuels (SAF). Hydrodeoxygenation of lignin derived dihydroeugenol (DHE) was investigated for production of aviation fuels under solventless conditions in a trickle bed reactor at 300°C under 30 bar hydrogen using cheap transition metal catalysts, such as Ni-Fe/Al_2O_3 and Ni-Ce-Al. The aim was to study the effect of catalyst composition, reaction temperature and catalyst stability.

Results and Discussion

Among the five studied catalysts the best results were obtained with 3 wt% Fe - 3 wt% Ni/Al_2O_3 catalyst prepared by impregnation giving 84% yield of oxygen free products suitable for aviation fuel (Fig. 1). On the other hand, 8 wt% Fe - 2 wt% Ni/Al_2O_3 was not active, while microporous 5 wt% Fe-5 w t% Ni/H-ZSM-5 was active, but not selective due to its high acidity. In the final work, detailed information about catalyst properties and their correlation with activity and selectivity will be provided.

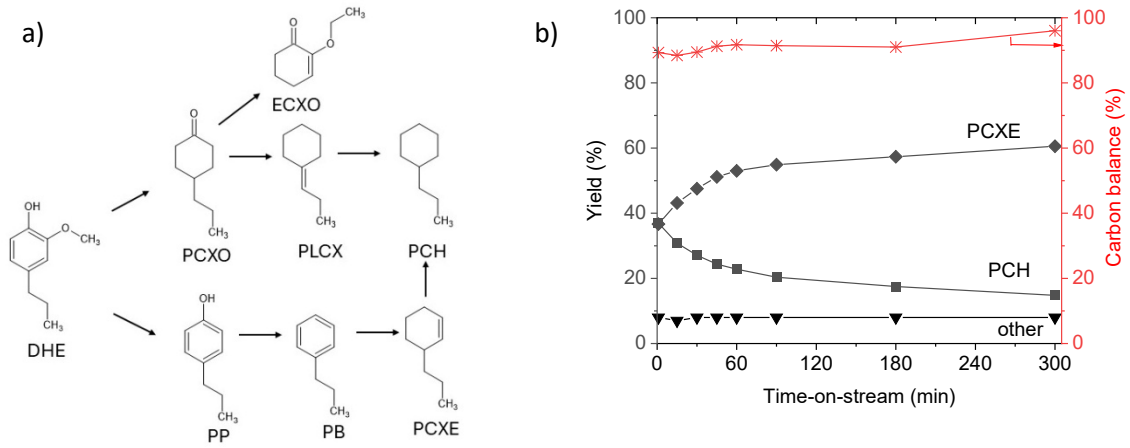

Fig. 1. a) Reaction scheme for hydrodeoxygenation of dihydroeugenol, b) Carbon balance (CB) and product yields in hydrodeoxygenation of dihydroeugenol for 3 wt.%Fe -3 wt.% Ni/Al_2O_3 at 300 °C under 30 bar H_2 using 0.04 ml/min feedstock flow and 0.1 g of catalyst.

Coupling low-temperature lignocellulose pyrolysis with vegetable oil catalytic co-processing over ZSM-5 zeolite: enhanced aromatic hydrocarbon production and extended catalyst lifetime

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Introduction

Catalytic pyrolysis of lignocellulosic biomass is a promising route for producing renewable fuels and valuable chemicals, particularly monoaromatic hydrocarbons (MAHs), which are key petrochemical intermediates and fuel components. ZSM-5 zeolites are widely used catalysts in this process due to their strong Brønsted acidity and shape selectivity, promoting deoxygenation and aromatization reactions.[1] However, its scale-up is limited by low MAH yields and rapid catalyst deactivation due to coke formation. Catalytic co-processing with hydrogen-rich feedstocks, such as plastics and alcohols, has been proposed to mitigate these limitations.[2] The present work investigates the catalytic co-processing of lignocellulosic biomass and vegetable oils over nanocrystalline ZSM-5 (n-ZSM-5) zeolite and discloses the strong effect of the thermal pyrolysis temperature on the castalyst deactivation.

Results and Discussion

Low-temperature operation in the thermal zone combined with the co-processing of camelina oil markedly improves the performance of lignocellulose (oak) catalytic pyrolysis, as shown in Figure 1. Although monoaromatic hydrocarbon yields decrease and oxygen content increases with time on stream due to progressive catalyst deactivation, this effect is sharply mitigated under co-processing conditions, particularly when the thermal zone operates at 350 °C. At higher thermal pyrolysis temperatures, the vapour stream becomes enriched in deactivating species, especially aromatic oxygenates derived from lignin decomposition, which accelerate catalyst deactivation. In contrast, low-temperature pyrolysis combined with oil co-feeding modifies the vapour composition and favours aromatization pathways over ZSM-5 through synergistic interactions between biomass-derived furans and olefins from vegetable oil cracking, while limiting the formation of coke precursors.

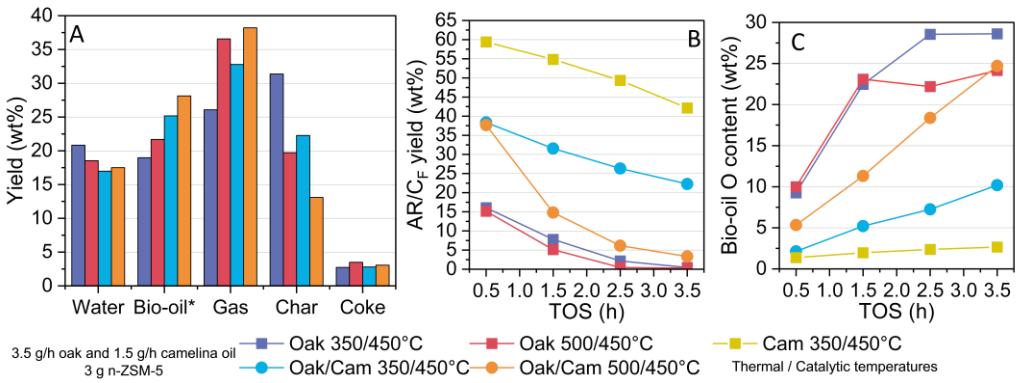

Figure 1. (A) Global and (B) carbon-to-aromatic hydrocarbons yields and (C) bio-oil* O content.

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Influence of hexagonal MoO_3 tunnel structure on HDO performance

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Introduction

To achieve a sustainable and resilient energy transition, a promising way is to upgrade biomass into biofuel via hydrodeoxygenation (HDO), which can be done by using catalysts that depolymerize feedstock by selectively cleaving CO bonds. Among various candidates, MoO_3-based catalysts have been of interest due to their cost-effectiveness, water-resistance, and structure diversity such as α, β, and h architectures. While the stable layered (α-MoO_3) is well-studied, the metastable hexagonal (h-MoO_3) polymorph remains poorly understood for its catalytic properties.[1] Its particularity is the unique hexagonal tunnels along the c-direction in the crystal (see inset Figure 1) which may facilitate feedstock diffusion and enhance HDO reactivity. However, h-MoO_3 application is challenged by an exothermic phase transition back to α-structure at temperatures around 350 - 400 C.[2] Here, we are studying the HDO of anisole catalyzed by h-MoO_3 under H_2 atmosphere and temperature ramping from 100 to 400 C to highlight changes in performance due to structural properties.

Results and Discussions

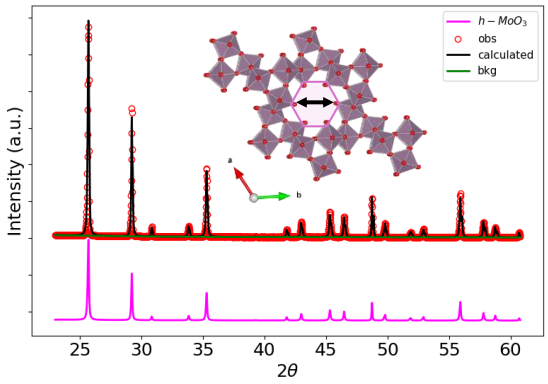

Figure 1. XRD of h-MoO_3.

The material h-MoO_3 has been synthesized through the hydrothermal method. Before reaction, the XRD shown in Figure 1 presents MoO_3 under its hexagonal structure (h-MoO_3), with a crystallite size of 100 nm, and the central tunnel expected to be of 7 Å.

Under reaction, Figure 2 shows a temperature inflective rise at 350 C, marking the onset of an exothermic event. This phenomenon coincides with h-MoO_3 activation for HDO of anisole, evidenced by the concurrent decrease of anisole signal with the raise of toluene and benzene in the MS. The reaction onset appears at a temperature 20 C lower than for layered α-MoO_3 (370 C from lab experiments) suggesting an enhanced catalytic performance with the hexagonal phase. We hypothesize that this thermal rise is linked to the transition from h-to-α: the collapse of the tunnel structure increases the number of oxygens vacancies, widely considered to be the active sites for HDO.

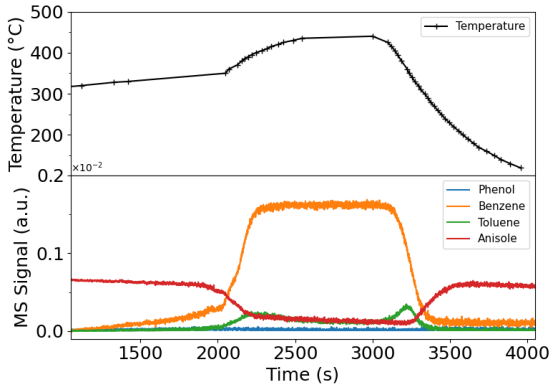

Figure 2. Mass spectrum during reaction of anisole with h-MoO_3 under H_2.

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Catalytic Valorization of Sugarcane Bagasse: Effect of Cu Loading to Ni in Y-Zeolite

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Introduction

The depletion of fossil fuels and climate concerns drive the search for renewable energy [1]. Agricultural residues like sugarcane bagasse offer potential as feedstocks for biofuel production. This study explores the catalytic conversion of sugarcane bagasse using nickel and copper supported on ultra-stable Y zeolite (NiY, CuY, 1Cu1NiY, 0.3Cu1NiY, 0.1Cu1NiY) within an autoclave reactor. The activity was initially screened using m-cresol (310 °C, 20 bar H_2, 600 rpm, 4h). The most active catalyst was then tested with fine bagasse fraction (330 °C, 30 bar H_2). Products were analyzed via GC-MS, and catalysts were characterized to elucidate structure-activity relationships.

Results and Discussion

Among the catalysts, 0.3Cu1NiY showed (Figure-1) the highest m-cresol conversion (~98%) at 310 °C and 20 bar H_2, yielding ~80% alkylbenzenes. Investigated with bagasse at 330 °C and 30 bar H_2, it achieved 75% biomass conversion. GC-MS analysis of the liquefied products revealed over 50% alkylbenzenes, with the remainder comprising alcohols, alkylphenols, naphthalene, cycloalkanes, and others.

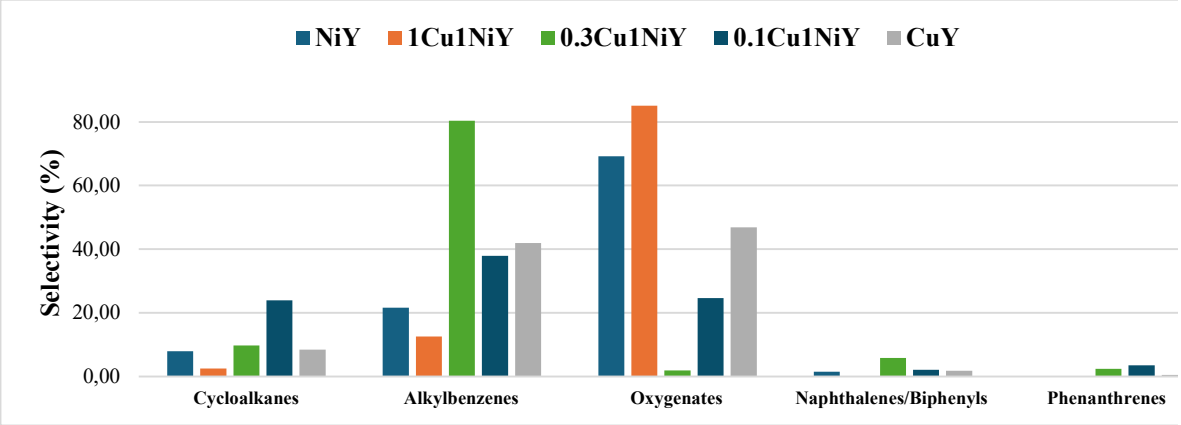

Figure-1: Comparative product selectivity of Cu-Ni/Y-zeolite catalysts for m-cresol deoxygenation

The high activity of 0.3Cu1NiY is attributed to synergistic Cu-Ni interactions on the Y zeolite surface, which promote bagasse depolymerization, fragment stabilization, and deoxygenation. SEM-EDX and XRD confirm that 0.3Cu1NiY retains structural integrity similar to the parent zeolite, with well-dispersed Cu and Ni phases. XPS analysis shows that Cu enhances the reducibility of Ni species, facilitating metallic nickel formation under reaction conditions. Furthermore, the catalyst's textural properties and acidity likely play a significant role in biomass liquefaction.

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AI-driven automated synthesis for zeolite-based catalyst discovery

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Introduction

Efficient catalysts are essential for the chemical industry, yet their development is inherently complex. Small variations in catalyst composition, structure, or synthesis conditions can profoundly affect performance, making the discovery of active materials both time-consuming and resource-intensive. Conventional workflows, which rely on iterative synthesis, characterization, and testing, are limited in their ability to rapidly explore the vast parameter space. Advances in automation, optimisation algorithms and artificial intelligence (AI) provide powerful opportunities to accelerate catalyst discovery by enabling systematic experimentation, integration of feedback loops, and data-driven optimization. [1;2]. High-entropy alloys (HEAs) are promising catalyst materials due to their compositional flexibility and tunable activity. HEA nanoparticles enhance catalytic performance while reducing metal loading.

Here we present our progress on a synthesis for zeolite-based HEA nanoparticle catalysts, using metal-ethylenediamine complexes directly introduced into zeolite synthesis mixtures [3]. Upon crystallization and reduction, these complexes form metal nanoparticles encapsulated within the zeolite framework.

Results and Discussion

This one-step synthesis is applied for Ru, Rh, Pt, Pd, and Cu alloy nanoparticles in Silicalite-1. This approach enables simultaneous zeolite and nanoparticle formation with diverse compositions [4]. These catalysts are subsequently evaluated for their activity in CO_2 hydrogenation and related gas-phase reactions, as well as in liquid-phase hydrogenation reactions such as furfural hydrogenation. Bayesian optimization is then integrated into the experimental workflow to establish closed feedback loops that guide the search toward highly active catalytic materials. The ultimate objective is to integrate this workflow into an automated synthesis platform to accelerate the synthesis–activity feedback loop.

Throughout this catalyst development process, comprehensive characterization using XRD, SEM, TEM, TPR, XPS, XRF and BET is carried out to validate the synthesis method and correlate structural features with catalytic activity.

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Computational Robustness of the Spin Effects in Chemisorption and Catalysis

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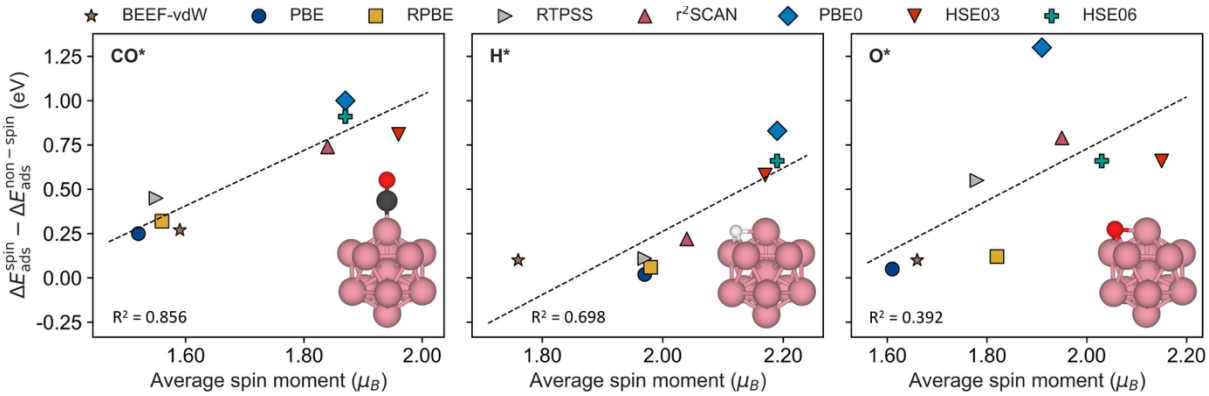
Introduction

A recently identified spin-mediated promotion effect has provided new insight into heterogeneous catalysis. Density functional theory (DFT) studies suggest that introducing certain promoter atoms onto the surfaces of magnetic metals can enhance reaction rates for ammonia synthesis [1,2], ammonia decomposition [3], and CO methanation [4]. The spin-mediated promotion effect relies on three key factors. First, and most importantly, non-spin-polarized surfaces bind adsorbates and transition states considerably more strongly than the spin-polarized solutions of the same material [5]. Although this difference is difficult to verify experimentally, it can be readily demonstrated computationally, where the spin state of the catalyst can be easily controlled. Second, certain adsorbates tend to partially quench the spin of nearby surface atoms [1]. Third, because this spin quenching is highly localized, transition states and intermediates, which are often stabilized at different surface sites can be strongly influenced by the presence of promoters.

Results and Discussion

In the present work, we extend the spin effect analysis beyond GGA functionals to confirm that the trends observed with semi-local functionals are not artifacts but persist in higher levels of theory. DFT calculations were used to evaluate the adsorption energies of carbon monoxide, hydrogen, and oxygen on a cobalt cluster and a cobalt surface. Eight exchange-correlation functionals at different level of theory were tested: three generalized gradient approximation (GGA) functionals (BEEF-vdW, PBE, RPBE), two meta-GGAs (RTPSS, r²SCAN), and three hybrids (PBE0, HSE03, HSE06). All functionals were applied to the cluster model, while six were used for the surface. In all cases, non-spin-polarized states exhibit stronger adsorption than spin-polarized solutions. The adsorption energy difference scales with the local average spin moment, with smaller energy differences corresponding to lower spin moments, providing direct evidence that adsorption energies decrease as the spin moment decreases (see Figure). The consistency of this trend across all tested functionals highlights the generality and robustness of the spin effect in chemisorption and its relevance for catalysis [6].



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Adsorption energy calculation on inverse catalysts with machine learning interatomic potentials

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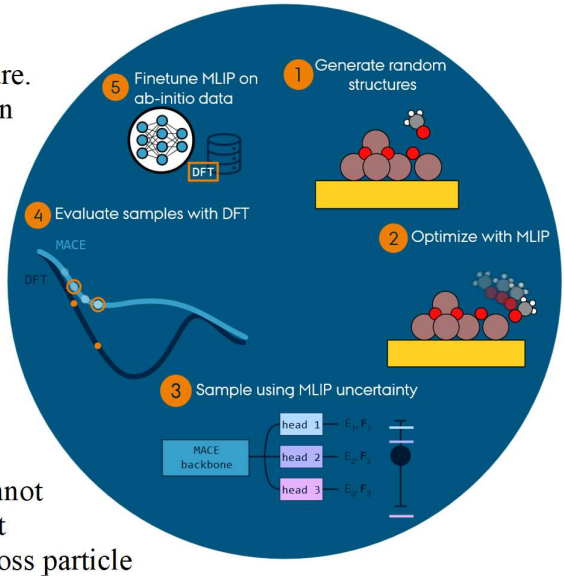
Introduction

Inverse catalysts, in which metal oxide nanoparticles are supported on a metal surface, have emerged as a promising class of materials for methanol synthesis via CO_2 hydrogenation[1,2]. One such candidate is InO_x/Au(111), which has been shown to be highly selective towards methanol production[3]. The experimental results have identified formate as a key intermediate in the reaction[4]. However, it remains unclear which active sites—arising from different oxide particle sizes and stoichiometries—govern activity and selectivity. This motivates the development of data-efficient computational approaches to screening sites.

Computational screening of inverse catalysts is challenging due to the amorphous structure of the oxide clusters, which gives rise to a large configurational space where density-functional theory (DFT) approaches are prohibitively expensive. Machine-learning interatomic potentials (MLIPs) pre-trained on foundational datasets are not applicable out of the box either, since inverse catalysts are out of domain for the most commonly used foundational datasets. Therefore, we develop here a machine-learning accelerated approach for obtaining adsorption energies at amorphous catalysts.

Results and Discussion

We present an iterative active learning strategy, see figure. A pre-trained MLIP is used to relax candidate adsorption configurations and estimate model uncertainty via a committee of readout heads within the MACE architecture[5]. Sampling of structures for DFT evaluation is guided by this uncertainty. The potential is then fine-tuned on the sampled data, before the next iteration. While the generation of candidate adsorption geometries involves simple heuristics, the overall workflow is otherwise system-agnostic. It thereby offers a general approach to screening adsorption sites on inverse catalysts and other low-symmetry surfaces, where the configurational space cannot be reduced to a handful of sites. This provides key input towards microkinetic modelling of inverse catalysts across particle sizes and stoichiometries.



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Reaction kinetics of liquid organic hydrogen carriers from first-principles: Conversion of Methylcyclohexane/Toluene on Pt(111)

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Introduction

The catalytic conversion between methylcyclohexane (MCH) and toluene on Platinum (Pt)-based catalysts is central for hydrogen storage as liquid organic hydrogen carriers (LOHC). However, a unified understanding of the reaction kinetics for the dehydrogenation of MCH (C_7H_{14}) and the hydrogenation of toluene (C_7H_8) is missing. Here, we use Density Functional Theory (DFT) calculations in combination with mean-field microkinetic modeling to investigate the reaction kinetics of both the hydrogenation of toluene and the dehydrogenation of MCH, including the parasitic toluene hydrodemethylation, on Pt(111) [1].

Results and Discussion

The DFT-based simulated temperature dependence of turnover frequencies, reaction orders, and apparent activation energies are in agreement with experimental trends. The rate controlling steps are identified and a sensitivity analysis is performed to propose improvements to the reaction rates. The analysis revals that thermodynamic control of adsorption/desorption steps can significantly improve the reaction rates. Stabilization of MCH adsorption (by 0.1 eV) is predicted to result in a filve-fold improvement of the MCH dehydrogenation rate. Similar improvements in the toluene hydrogenation rate are predicted by stabilization of toluene adsorption. The hydrodemethylation of toluene is found to be low on Pt(111), but is predicted to be detrimental to MCH dehydrogenation on undercoordinated sites. Additionally, the simulations show that moderate destabilization of toluene adsorption siginificanlty hinder MCH hydrodemethylation. The work suggests that surface modifications that change the adsorption energies are an under exploited thermodynamic handle to improve the rates of the reactions.

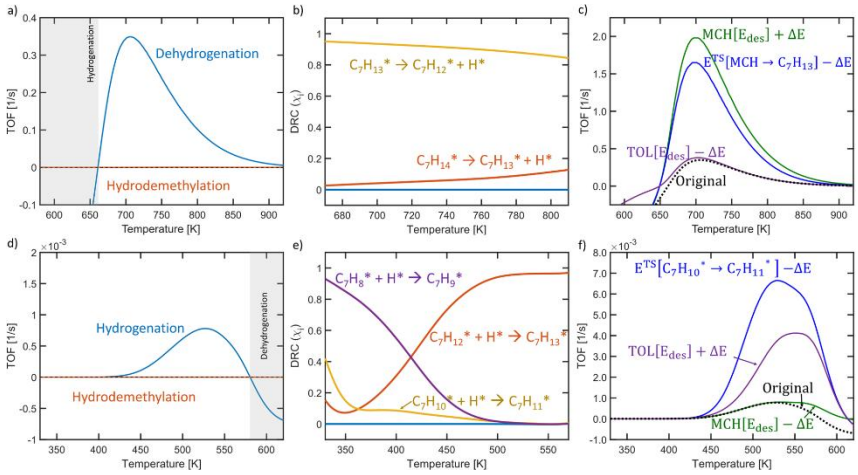

Figure 1. Temperature dependent kinetic analysis of MCH/toluene onversion. (**top**) MCH dehydrogenation. a) Turnover frequency. b) Degree of rate control. c) Sensitivity analysis of TOF to reaction steps. (**bottom**) Toluene hydrogenation. d) Turnover frequency. e) Degree of rate control. f) Sensitivity analysis of TOF to reaction step stabilization. Figures adapted from Ref. [1].

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Impact of Fe-Fe_3C-C phase evolution on methane pyrolysis kinetics: from catalyst structure to reactor scale

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Introduction.

Catalytic CH_4 pyrolysis is a promising route for low-C hydrogen production. Iron catalysts are attractive due to their low cost and high activity. Pyrolysis is inherently dynamic as growth of carbon and evolution Fe-Fe_3C-C strongly affect catalyst activity and stability [1]. These structural changes challenge kinetic analysis, hindering reactor design and scale-up. Here, we combine *operando* synchrotron measurements with packed-bed experiments and modeling to derive mechanistic kinetic expressions. Fe-Al_2O_3 catalyst was obtained by fusion-decomposition of nitrate salts (equimolar Fe-Al ratio [2]). *Operando* XAS and powder XRD with online MS tests were carried out at ESRF synchrotron (BM23), with focus on reduction, carburization, and CH_4-pyrolysis. Complementary kinetic tests were performed in a PBR. Dynamic PBR modelling supports multiscale quantitative data analysis.

Results and discussion.

Operando experiments in highly diluted streams and ultra-high space velocity showed that after CH_4 injection, the fraction of α-Fe declined, while crystalline Fe_3C grew, simultaneously with the onset and dynamics of H_2 formation (Fig.1a). At the PBR scale the same diluted feed experiments (Fig.1b) similarly revealed multiple kinetic stages: (1) rapid deactivation of metallic Fe due to C-blockage; (2) Fe_3C formation; (3) mitigated deactivation on Fe_3C and C-accumulation. Thermodynamics and integral regime due to lower space velocity stretched the global dynamic response. At high CH_4 concentrations and progressively increasing space velocity where quasi-differential regime established, the fingerprint of the particle dynamics turned into complex initial evolutions of the reactor performance, with a minimum-maximum trend in the conversion (circle in Fig.1c). This quantitative analysis enables the development of structure-dependent kinetic models linking catalyst dynamics to reactor performance for methane pyrolysis design and scale-up.

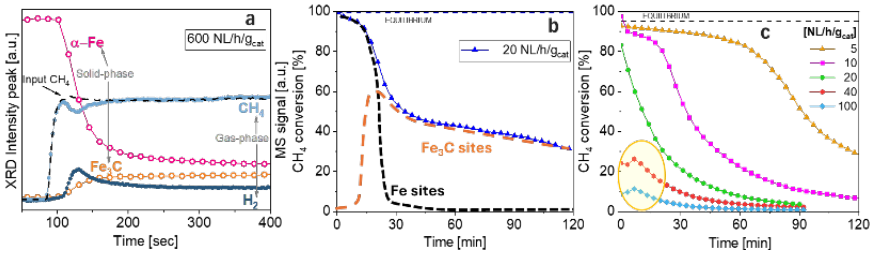

Fig.1: Pyrolysis tests: gas-phase with operando PXRD (a); PBR tests with 5% (b) and 40% CH4 (c).

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Electro-oxidation of Au(111) studied by *operando* EC-qXRR

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Introduction

The electrochemical (EC) process of water electrolysis, using renewable energy, is currently the only main pathway for green H_2 production [1]. The EC process involves the production of O_2 via the oxygen evolution reaction (OER) at the anode, and production of H_2 via the hydrogen evolution reaction (HER) at the cathode. The bottleneck of OER due to its sluggish kinetics leads to high overpotential needed for H_2 production; these potentials often coincide with anode oxidation, causing anode instability. We have studied the kinetics of the EC oxide formation on a Au(111) model electrode, and determined the thicknesses of these amorphous thin films, using quick X-ray reflectivity (qXRR) [2] (Petra III, beamline P08).

Results and Discussion

The qXRR spectra are shown as a 2D-map in Fig. 1a, where an XRR spectrum is obtained every 0.5 s. The cyclic voltammogram (Fig. 1b), with Au(111) as the working electrode, is performed while acquiring XRR spectra. Reference XRR spectra of metallic and electro-oxidised Au(111), corresponding to the potentials marked in Fig. 1b, respectively, are presented in Fig. 1c. Combining EC and qXRR allows for time-resolved studies during the electro-oxidation of electrocatalysts, and the determination of oxide film thickness, density, and surface roughness *in operando*.

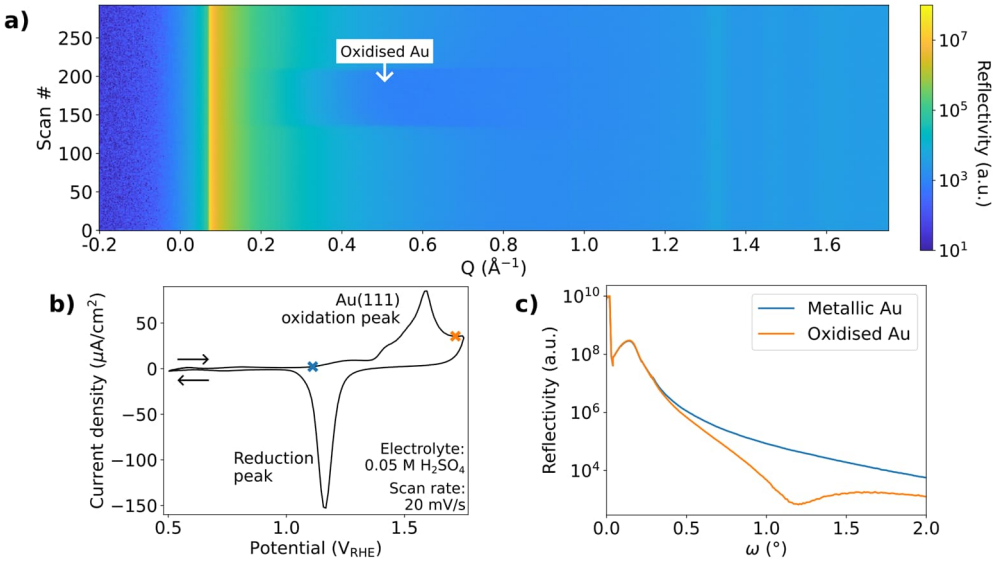

Figure 1: a) 2D-map of XRR spectra. b) CV from Au(111), the potentials (crosses) highlighted correspond to the XRR spectra in c). c) Reference XRR spectra of metallic and oxidised Au(111).

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Insights into Methane Reforming from Oscillations in the Reaction

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Introduction

Understanding how the detailed atomic arrangement of a catalyst creates the active sites is essential for practical advances in the utilization of chemical processes. An example is methane reforming reactions, which are essential for the global production of hydrogen [1]. For new emerging reactor concepts using electricity to drive the reforming reaction with more facile heat/mass transfer, it is important to identify the type of sites whose concentration needs to be maximized in the catalyst [2]. Here we show how the occurrence of oscillations in reforming reactions provide new insights into the most active sites on the catalyst [3].

Results and Discussion

While studying sulfur poisoning of reforming reactions with a Rh-based catalyst we discovered that dosage of SO_2 caused the reaction to settle into sustained oscillations correlated to S ad-/desorption (Fig. 1A). Transmission electron microscopy shows that the particle edges change during S ad-/desorption (Fig. 1B). From DFT calculations we have discovered that S adsorption causes the atoms at the stepped edges of the Rh particles to shift by one atomic spacing and even this minute structural change causes an order of magnitude drop in reaction rate (Fig. 1C). Oscillations between edge structures thus cause the oscillations in reaction rate and this identifies the most active sites for catalytic reforming.

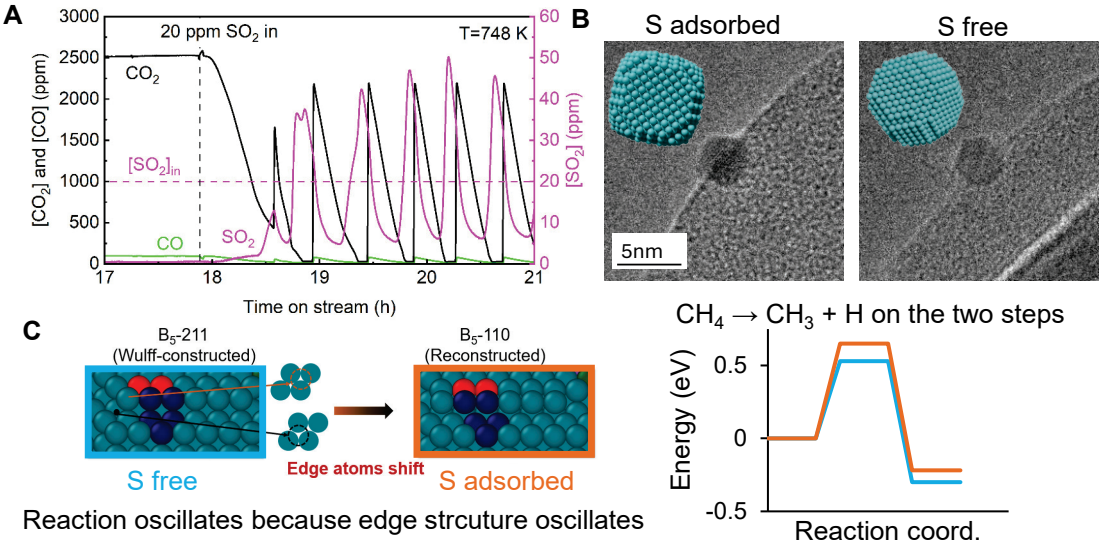

Fig. 1 A SO_2-induced Oscillations in the reforming reaction. **B** In situ microscopy showing particles changing from truncated cubes to polygonal shapes during S-desorption. **C** DFT calculations showing how stepped particle edges change with S ad-/desorption causing major changes in the catalytic activity of the stepped edges. See ref. [3] for details.

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Improvement of the performance of Fe-based catalysts by Ni in CO_2-free H_2 production by thermocatalytic decomposition of CH_4

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Introduction

The effects of climate change driven by greenhouse gas emissions are significant due to the enormous use of fossil fuels. Consequently, an effective alternative to these fossil fuels is essential. Hydrogen (H_2) presents a promising alternative; however, it does not exist in a free state and must be produced from various sources. Several techniques exist for H_2 production, yet they often pose challenges e.g. carbon oxides emission, energy consumption etc. [1] Nonetheless, thermocatalytic decomposition (TCD) of hydrocarbons provides more advantages compared to other techniques, such as low operating temperature, relatively insignificant CO_2, and the generation of valuable carbon materials. [2]

In this study, Ni is wet impregnated onto $FeAl_2O_3$ and onto the Fe-side stream (FeSS). The materials are employed in the TCD of CH_4 (CH_4-TCD) process. Physicochemical techniques were used to characterise the prepared catalysts. The CH_4 conversion and products (H_2 & carbon) results are used to improve the performance of the industrial iron side stream.

Results and Discussion

The characterisation techniques demonstrated that the desired active metals composition, structure and texture of the materials are achieved under our preparation conditions. The CH_4-TCD test results indicated that the maximum is about 50 mol-% of H_2 over high loading of Fe and at high temperature 750°C. While a decrease in temperature leads to a significant decrease in H_2 production. However, the addition of Ni remarkably improves the production of H_2 (Fig.1). After the CH_4-TCD, the materials were analysed to determine the quality and quantity of carbon. The TGA, TEM and SEM analyses demonstrates that the carbon materials are in the form of graphite structure and Fe_3C. Graphite is a high-quality carbon which can be used as a precursor in many applications, e.g. in energy storage devices etc. Several treatments of FeSS were not successfully improving their performance. However. the addition of Ni enhanced the H_2 production of FeSS materials by more than 20 times (Fig.2).

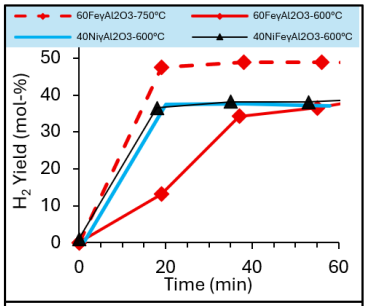

Fig. 1 Effect of Ni on Fe catalysts in CH_4-TCD

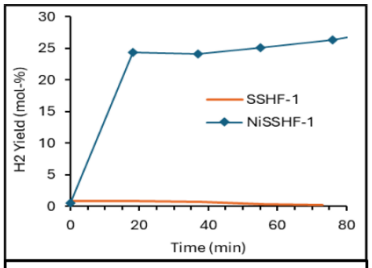

Fig. 2 Effect of Ni on FeSS material in CH_4-TCD

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Selective reduction of α-pinene by transfer hydrogenation with noble metals on carbon

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Introduction

Turpentine oil, a by-product of the wood and paper industry, is a raw material that can be used to obtain high-value products. The main constituent of turpentine is α-pinene which belongs to the group of monoterpenes. *Cis*-pinane is a valuable intermediate widely used in chemical and pharmaceutical synthesis and can be obtained through hydrogenation of α-pinene.[1] Two strategies exist for double bond saturation: catalytic transfer hydrogenation (CTH) with hydrogen donors or direct hydrogenation with pressurized H_2 gas.[2] From a mechanistic perspective, employing hydrogen donors instead of H_2 gas introduces alternative reaction pathways. Here, we propose a systematic study on the selective conversion of a-pinene to *cis*-pinane in the presence of Pt/C and Ru/C catalysts with both H_2 gas and various alcohols as hydrogen donors.

Results and Discussion

The hydrogen donors tested were primary and secondary alcohols (Figure 1A).

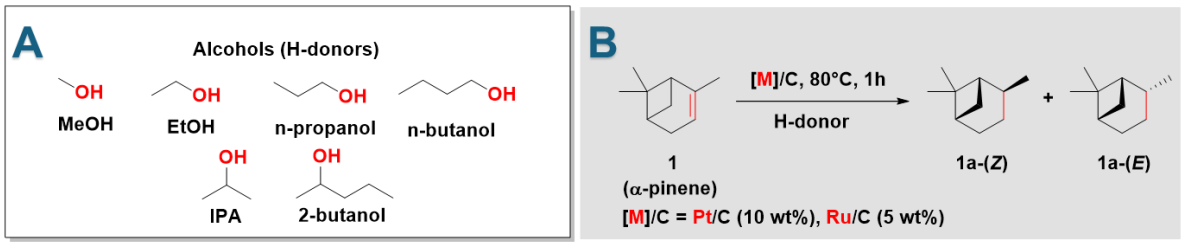

Figure 1. **(A)** Hydrogen donors and **(B)** CTH reactions of α-pinene.

Regardless of chain length and metal used, primary alcohols were entirely inactive in CTH. On the other hand, secondary alcohols exhibited complete conversion in the case of Ru/C even with longer chain. The reactivity of Pt/C towards CTH was lower, in accordance with its oxophilicity. Overall, CTH and direct hydrogenation with Ru/C showed higher selectivity towards the *cis* isomer compared to Pt/C. The activation parameters of the reaction were determined for both systems. Regarding Pt/C, the calculated TOF and initial rates in direct hydrogenation conditions are three orders of magnitude higher than the CTH one while for Ru/C the values are the same. Based on the activation parameters of Ru/C the use of H_2 gas does not exclude the possibility of the CTH to take place during the reaction. For that reason, isotope labeling experiments were carried out to get deeper mechanistic insights. Employing D_2 as a hydrogen source we observed a low amount of deuterated product in the case of Ru/C confirming that, as hinted by the activation parameters, CTH proceeds faster than direct hydrogenation, likely due to the higher oxophilicity of Ru.

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Catalytic Hydrodeoxygenation of Biomass Pyrolysis Oil Model Compounds in a Continuous Slurry Reactor

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Introduction

Biomass derived fast pyrolysis oil requires hydrotreating before it can be used as a fuel. This process has been performed in fixed bed reactors through hydrodeoxygenation at elevated temperatures and hydrogen pressures using various catalysts [1]. However, fixed bed reactors are known to clog when the catalyst is exposed to the very reactive bio-oil [2]. Slurry reactors are a promising alternative, since the catalyst and reaction liquid are vigorously stirred and well mixed, and the fresh, reactive bio-oil is instantaneously diluted into already upgraded oil [3].

In this work, a continuous slurry reactor was employed to hydrotreat a bio-oil model mixture, consisting of 2-ethylhexanol (68 wt%), acetophenone (10 wt%), guaiacol (8 wt%), furfural (6 wt%), diacetone alcohol (6 wt%) and octanoic acid (2 wt%). The 500 ml reactor (Parr) was equipped with continuous liquid/H_2 feed and product removal. The liquid level was 100 ml, kept constant by a dip tube. The pressure was 100 bar of H_2 and the temperatures varied from 200 to 350 °C. The H_2 flow rate was 300 ml_N/min, and the liquid flow rate was 0.5 ml/min. 2 to 6 g of a sulfided NiMo/Al_2O_3 catalyst provided by Topsoe A/S was used, as extrudates, inside catalyst containers. These consisted of 8 perforated cylinders secured between two perforated circular frames. The stirring speeds varied from 300 to 750 rpm. Run times were 50 to 100 h.

Results and Discussion

Experiments at 200 and 250 °C, with 750 rpm and 6 g of catalyst, had very low reactant conversions, which, over time, resulted in catalyst deactivation. At 300 °C, and even more at 350 °C, the reactant conversion and oxygen removal increased substantially, at the cost of slightly lower liquid carbon yield. For experiments with less catalyst, 4 and 2 g, at 300 °C, lower reactant conversion and oxygen removal were achieved, but the liquid carbon yield was slightly higher. Despite the lower conversion, no catalyst deactivation was observed, even after 100 h on stream.

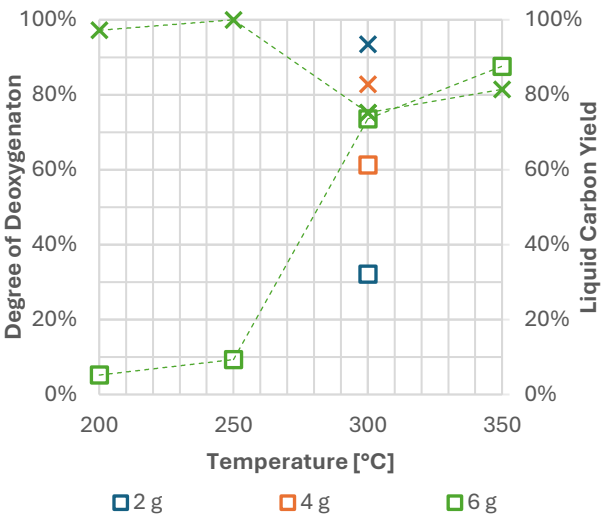

Figure 1 – Degree of Deoxygenation (□) and Liquid Carbon Yield (x) with temperature and catalyst mass

The continuous slurry reactor design appears very promising and bio-oil upgrading will soon be performed.

The authors acknowledge Innovation Fund Denmark for funding this research through the project "HyProFuel" (case # 0224-00029A) and Topsoe A/S for the close cooperation.

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Active phase of a Cu-Mo catalyst supported on alumina for HDO of biomass

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Introduction

One of the process steps necessary to produce hydrocarbon fuels from biomass is catalytic hydrodeoxygenation (HDO). In this process, oxygen-containing functional groups are removed as water *via* reaction with hydrogen.

Among different HDO catalysts, Mo-oxide based catalysts have recently drawn attention, owing to advantages compared to traditional MoS_2 hydrotreatment catalysts such as not requiring sulfur in the feedstock to maintain activity, as well as activity at near-atmospheric H_2 pressure. In particular, Cu-promoted Mo oxides have received attention as a particularly promising bimetallic system [1,2]. However, the active phase of this catalyst type has yet to be studied on an industrially relevant mineral support. To remedy this knowledge gap, we here present an *operando* X-ray absorption spectroscopy/X-ray diffraction (XAS/XRD) study of the active phase in an Al_2O_3-supported CuMo catalyst, using HDO of anisol as a model reaction.

Results and Discussion

The catalytic activity of a $CuMo/Al_2O_3$ catalyst (Cu:Mo 1:10 by weight) for HDO of anisol was monitored using MS (Fig. 1a) while continuously performing XAS and XRD (Fig 1bcd). The onset of catalytic activity between 300-350 °C can be correlated to an immediately preceeding shift in the Mo XANES indicative of the previously suggested oxycarbide phase [2]. Simultaneously, the Cu K edge XANES shows the presence of metallic Cu, while a small peak appears in the diffraction pattern at 3.0 $Å^{-1}$, corresponding to the Cu 111 reflection. Taken together, these results corroborate previous hypotheses that Cu acts as a promotor by providing a metallic surface for the dissociation of H_2 [1,2], and confirm the oxycarbide as the active phase for alumina-supported Mo catalysts.

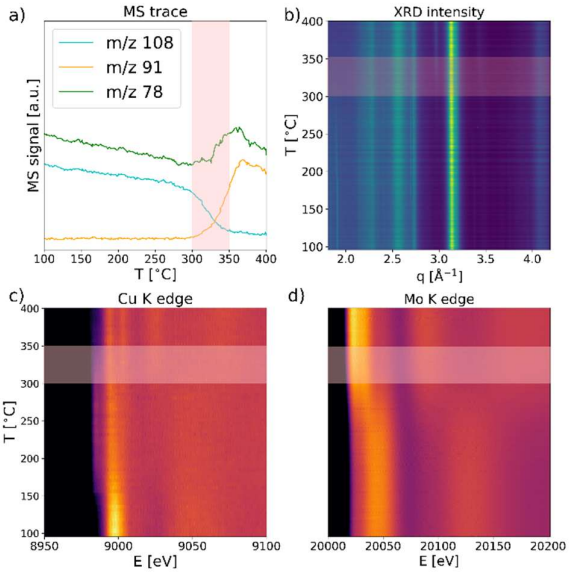

Figure 1: a) MS trace vs. temperature for m/z 108 (anisole fragment), m/z 91 (toluene fragment), and m/z 78 (benzene/general monoaromatic fragment) b) XRD intensity vs. temperature. b) XRD pattern. c) Cu K edge XANES. d) Mo K edge XANES.

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Activity of NiMo/Al_2O_3 catalyst in waste tire pyrolysis oil upgrading: the effect of sulfidation degree

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Introduction

The accumulation of end-of-life (EOL) tires, driven by the rapid growth of the automobile industry, has led to serious environmental and public health concerns. Pyrolysis enables the valorization of waste tires by producing waste tire pyrolysis oil (WTPO). This oil contains high concentrations of hydrocarbons and possesses a high calorific value, making it a promising alternative to fossil oils for fuel production [1]. However, WTPO also contains high levels of impurities, particularly sulfur compounds, olefins and polycyclic aromatic hydrocarbons. These contaminants lead to pollutant emissions, engine damage, and instability during storage [2]. Catalytic hydrotreatment offers an effective route for upgrading WTPO, enabling its use in fuel production while also enhancing its storage stability. In this study, the effects of catalyst sulfidation degree on catalyst structure and WTPO upgrading performance were investigated.

Results and Discussion

Varying the amount of sulfidating agent (DMDS) produces catalysts with different sulfidation degrees. Catalysts with lower sulfidation degrees exhibited similar GC-detectable liquid product yields, whereas higher GC yields were achieved with highly-sulfided catalysts (**Figure 1**). The increasing trend in GC-detectable yield corresponded to a progressive rise in saturated species and a reduction in olefins. Compared with reduced mixed oxides, the sulfided catalysts exhibited superior hydrodesulfurization (HDS) performance (**Table 1**). This observation suggests that sulfidation generated metal sulfides (MoS_2 and NiMoS) on the catalyst surface, which enhances hydrogenation, cracking activities, and HDS. For high sulfidation degree, the HDS efficiency remained similar.

Figure1. GCxGC-MS composition of oil products.

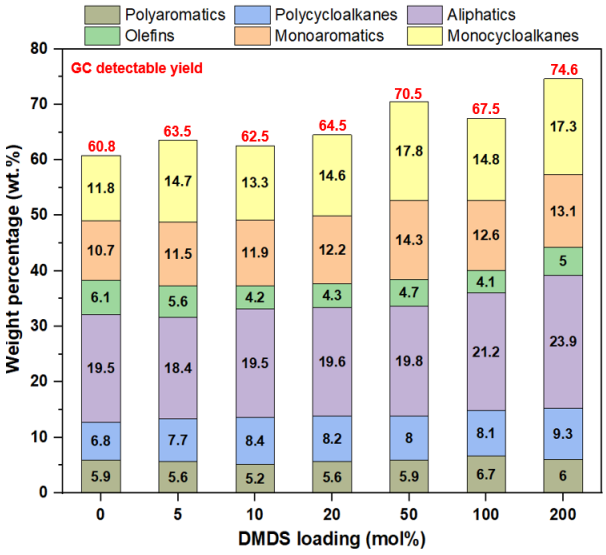

Table 1. HDS performance of catalyst with varying sulfidation degrees.

DMDS amount (mol%)	HDS efficiency (%)	DMDS amount (mol%)	HDS efficiency (%)
0	72.1	50	82.9
5	76.9	100	86.4
10	76.9	200	87.2
20	78.6		

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Electro-Catalytic Ammonia Synthesis in Proton-conducting Ceramic Cells

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Introduction

Recent advances in electrocatalytic ammonia synthesis in proton-conducting ceramic cells (PCCs) are discussed with a focus on iron-based electrodes [1, 2]. The effects of temperature, gas flow, voltage, and electrolyte thickness on electrochemical ammonia synthesis are investigated. To differentiate the various effects and mechanisms contributing to the electrocatalytic formation of NH_3, three gas flow configurations are studied (Fig. 1).

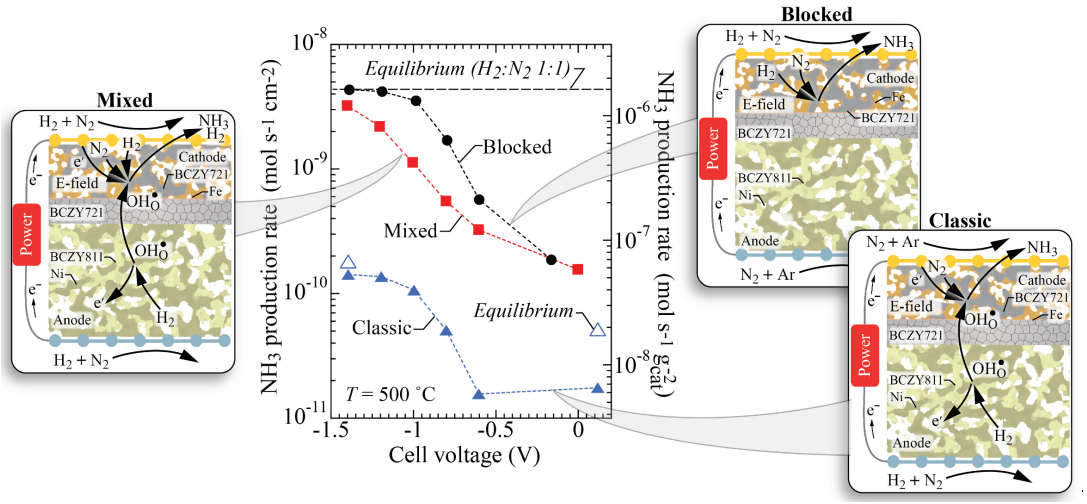

Figure 1: Schematic representation of reactions in the three configurations, adapted from [2].

Results and Discussion

The experimental results demonstrate that NH_3 formation is primarily governed by the applied cell voltage. Co-feeding H_2 at the cathode (Mixed, Blocked) proved very advantageous for optimizing reaction conditions and increasing NH_3 synthesis rates to values of 3×10^{-8} mol s^{-1} cm^{-2}, the highest reported in open literature. Furthermore, the results highlight the strong influence of thermodynamic equilibrium on the achievable NH_3 yield. Lower operating temperatures and higher volumetric gas flow rates per electrode area proved beneficial. Notably, at reduced temperatures, the rate enhancement factor (with vs. without applied cell voltage) increased up to 24, exceeding values typically reported in the literature. The experiments were conducted using a PCC with an iron-based electrode of an active area of 12.6 cm^2, representing the largest electrode area reported to date for electrochemical NH_3 synthesis. This combination of thermo-catalytic and electrochemically supported ammonia synthesis opens a new pathway for the electrification of NH_3 production using the rather inexpensive material iron.

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Highly dispersed Pt for Low-temperature Ammonia Oxidation: Insight into Ligand Environment with HERFD XAS

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Introduction

A growing role of ammonia in energy storage can cause its undesired release into the atmosphere. This release can occur during extraction of energy stored in ammonia, for example NH_3 combustion or cracking to H_2. Therefore, the use of ammonia slip catalysts (ASCs) is required to selectively oxidise NH_3 to N_2. Key challenges for ASCs are reducing the costly noble-metal content while retaining high activity and selectivity. In order to achieve this, the NH_3 oxidation mechanism needs to be understood. Previously, we reported on a change of the reaction mechanism depending on Pt dispersion and described the surface species involved in the reaction on Pt nanoparticles larger than about 2 nm.[1,2] Here we describe a less-explored NH_3 oxidation pathway on close-to-atomically disperse Pt that is characterised with low activity during a light off which significantly increases during a light out (cooling ramp).[1]

Results and Discussion

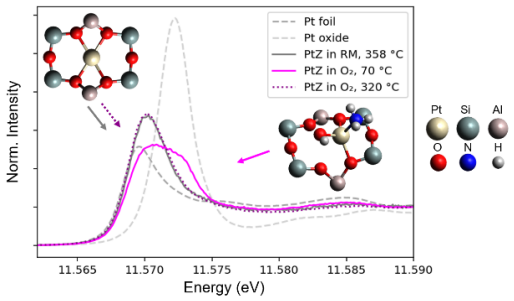

Figure 1. HERFD XAS spectra of a Pt-ZSM-5 catalyst in ammonia oxidation RM and in O_2 immediately after the reaction detected at Pt L_α emission line.

Fingerprinting properties of high-energy resolution fluorescence detected (HERFD) X-ray absorption spectroscopy (XAS), which is highly sensitive to electronic configuration and nature of ligands of the absorber atom,[3] were used to monitor *in situ* the change of the coordination sphere of nearly atomically disperse Pt in a Pt-ZSM-5 catalyst. This approach allowed to distinguish highly informative features that were not evident in conventional XAS. In particular, we detected a double-maximum Pt L_3 spectrum in oxygen environment at low temperatures but only after heating and cooling in NH_3-containing atmospheres (fig. 1). The state of the catalyst at the origin of this feature can be related to the formation of the active species during the pronounced hysteresis typical for this system.[1] Therefore, its identification is required to understand the reaction mechanism. In this regard, a comparison of the experimental spectra with theoretically calculated reference spectra showed that the double maximum may be explained by the change of Pt coordination environment from square planar to distorted tetrahedral with NH_3 and OH^- as ligands. This finding advances towards overcoming the activity limitation of near-atomically dispersed Pt, while leveraging its high atomic availability to enable more efficient catalysts.

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Water Tolerance as a Key Challenge for Ammonia Decomposition Catalysts

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Introduction

Ammonia is emerging as a vital vector for green hydrogen transport and heavy-duty fuel applications.[1] To mitigate stress corrosion cracking in steel infrastructure, industry standards advocate for "fuel-grade" ammonia containing 0.2–0.5% water.[2,3] Despite this established industrial practice, the water tolerance of decomposition catalysts remains largely unexplored in academic research, representing a critical knowledge gap.

Results and Discussion

Here[4], we investigate catalyst water tolerance, revealing substantial performance losses under typical industrial purities (Figure 1). While unpromoted catalysts show moderate deactivation (10–30% at 0.2% water), a barium-promoted iron catalyst (BaFe) loses ~80% of its activity, indicating a complete loss of the promotional effect. Conversely, the BaCo catalyst retains high activity (>80% conversion at 450 °C), losing only ~20% of its rate.[5] DFT calculations reveal that while barium forms inert bulk $Ba(OH)_2$ on iron, it forms a resilient Co–Ba–O species on cobalt that preserves the promotional effect.

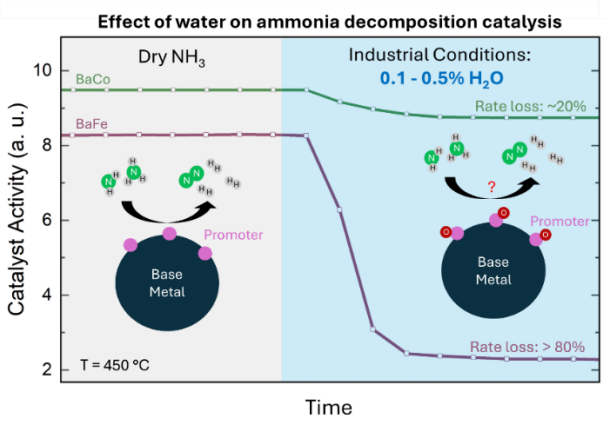

Figure 1: Schematic representation of the effect of water on catalyst activity for two promoted catalysts BaFe and BaCo. The catalysts consist of transition metal nanoparticles supported on carbon and promoted by barium.[4]

In summary, we show that water tolerance is an overlooked but critical descriptor for ammonia decomposition catalysts: while some promoters deactivate completely, water-tolerant ones remain active by forming stable, promoting oxygen-containing species.

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Inductively Heatable Catalysts for Ammonia Synthesis

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Introduction

Green electricity cannot be stored and transported over long distances. One option to solve the problem is to synthesize green ammonia using electricity for both the production of the reactant hydrogen and the ammonia synthesis. This way, ammonia serves as energy carrier for long-term storage and long-distance transportation.[1]
Electrification of the heterogeneously catalyzed NH_3 synthesis requires new materials that stay magnetic under reaction conditions to facilitate induction heating while not deactivating the catalytic species.

Results and Discussion

Magnetic nanoparticles were synthesized by impregnation of 15 wt% of inductively heatable metals on Al_2O_3, followed by impregnation of Ru as active species for ammonia synthesis.[2] The size-dependency of the Curie temperature (T_C) made Ni nanoparticles unsuited to reach the aimed reaction temperature by induction heating, while Co and Fe exhibit low heating efficiency.[3] Thus, alloyed Co-Ni particles were synthesized, which resulted in higher heating efficiency than the single elements. Reducing the crystallite size increased the magnetic coercivity (h_c), optimizing the heating efficiency.

The catalysts reached the reaction temperature of up to 650 °C (30 bar to 50 bar) in less than 60 s, where the NH_3 productivity was limited by the thermodynamic equilibrium. Multiple heating-cooling cycles proved the stability of the catalyst under discontinuous process conditions, which is required for the application due to the fluctuating nature of green electricity. Doping with Cs and Ba increased the activity of the catalyst, which allowed reducing the reaction temperature, which was no longer limited by the thermodynamic equilibrium, hence, leading to higher NH_3 productivity.[4] In addition, the catalysts show no activity loss after 48 h on stream, proving the feasibility of replacing conventionally heated NH_3 synthesis with induction heated.

This work shows the potential to inductively heat NH_3 synthesis catalysts, by which the reaction temperature is reached in very short time. This allows for the design of a discontinuous process, enabling NH_3 as a potential long-term energy carrier for excess electricity.
During this study, it turned out that the synthesized materials without Ru catalyze the cracking of NH_3 at 600 °C back to H_2, which closes the cycle for NH_3 as a versatile energy carrier.

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Acknowledgments

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Synthesis of hydrogen peroxide and epoxides: catalysts, kinetics, mechanism and reactor modelling

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Introduction

Hydrogen peroxide and alkene epoxides are among the key intermediates for chemical industry. Hydrogen peroxide (H_2O_2) is a green oxidant in chemical industry since only water and oxygen are obtained as side products. The traditional anthraquinone route for hydrogen peroxide production is safe, but it does not enable on line production in smaller scale, which would be desirable for many future applications. Therefore, intensive research is going on on the direct synthesis of H_2O_2 from molecular hydrogen and oxygen. H_2O_2 is an excellent reagent to convert alkenes and fatty acids to corresponding epoxides, such as ethylene, propylene and butulene oxides as well as fatty acid epoxides. Epoxides are valuable chemical intermediates for the production of polyols, carbonates, and bio-based lubricants. Bimetallic gold-palladium catalysts were used in this work for direct synthesis of H_2O_2 and titanium silicate (TS-1) for the epoxidation of alkenes. These two catalysts were also integrated to a single matrix to explore the possibility of one-pot epoxide synthesis. The catalysts were characterized with XRD, SEM-EDS, TEM-SAED, STEM-EDS, ICP-OES, XPS, UV-vis DRS, N_2-physisorption and ammonia-TPD. Stationary and transient experiments were performed in a continuous laboratory-scale trickle bed reactor to reveal the reaction mechanism and to collect kinetic data. The organic components in gas and liquid phases were analyzed by gas chromatography.

Results and Discussion

The step response epoxidation experiments revealed the dynamics of the chemical system: in the first stage of the experiment, the epoxides appeared and the ring-opening products were observed after a time delay. The experimental results were described with a dynamic model, where the key steps were the activation of the TS-1 catalyst by H_2O_2; the surface complex reacted further with the alkene in the bulk liquid forming the epoxide. The mathematical model described the data very well. At the last stage of the research, the one pot process was studied, on an integrated catalytic system: Direct synthesis & Epoxidation: $H_2+O_2 \rightarrow H_2O_2$; $H_2O_2+CH_3\text{-}CH{=}CH_2 \rightarrow PO+H_2O$. The TEM studies of the catalyst structures revealed the diversification of the active sites on the PdAu-TS-1. Commercial TS-1 included anatase as impurity and the metals (Pd and Au) where concentrated on the anatase phase, where the direct synthesis took place, after which H_2O_2 shifted to TS-1, to the epoxidation sites. The propene hydrogenation proceeded as a side reaction mainly on the metal nanoparticles on anatase. This separation of active sites on anatase and TS1 was the key issue for successful one-pot operation.

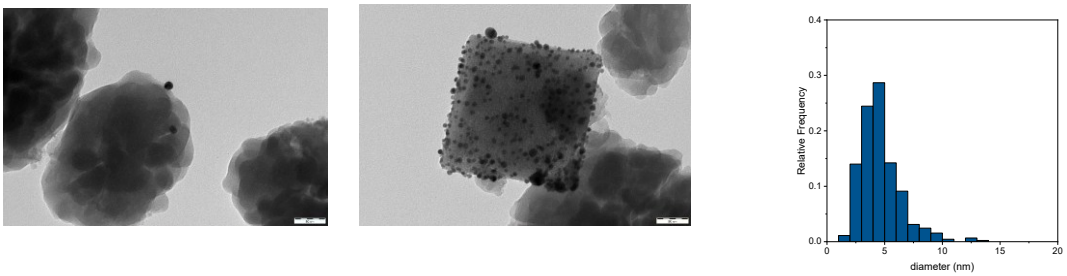

Figure: TS-1 (left), PdAu on anatase (middle), nano particle size distribution (right).

Size-dependent bulk hydride diffusion in Pd nanoparticles and its impact on H_2O_2 synthesis

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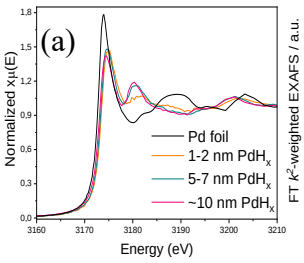
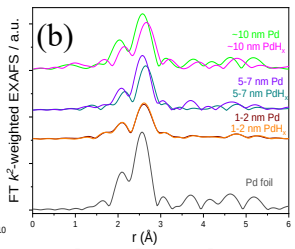
Introduction

The direct synthesis of H_2O_2 using Pd-based catalysts is a sustainable alternative to the anthraquinone autooxidation (AO) process. Palladium hydrides (PdH_x) have been known to play a crucial role in the direct synthesis of H_2O_2. Surface H and α-PdH_x are thought to enhance H_2O_2 selectivity, while β-PdH_x (or bulk PdH_x) promotes over-hydrogenation to H_2O. The formation and decomposition of these PdH_x phases may also affect the overall selectivity and activity of H_2O_2 formation. [1] In this study, we have tracked PdH_x formation and decomposition across different Pd/TiO_2 nanoparticle (NP) sizes (1-2nm, 5-7nm, & ~10nm) using QEXAFS and synchrotron XRD, and investigated its effect on the direct catalytic H_2O_2 synthesis.

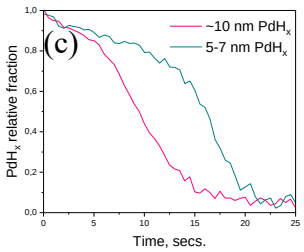
Results and Discussion



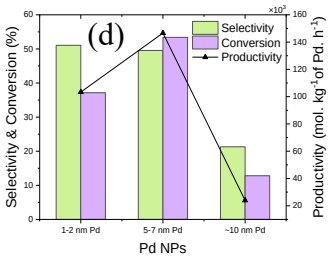
(a) Pd L_3-edge XANES of PdH_x NPs



(b) Pd-K edge EXAFS of Pd & PdH_x NPs



(c) PdH_x decomposition profiles



(d) Catalytic tests for H_2O_2 synthesis

PdH_x is evidenced by the appearance of ~3180 eV peak on H_2 exposure (Fig. a), as probed by Pd L_3-XANES. Pd K-edge shows an increase in the Pd-Pd bond distance in the R-space, suggesting lattice expansion (Fig. b), due to bulk PdH_x formation. Notably, the features associated with bulk PdH_x formation were suppressed for 1-2 nm Pd NPs, which is an indication of the presence of predominantly surface H. Hence, the amount of surface-to-bulk H ratio increases with a decrease in particle size. [2] The PdH_x decomposition profiles (Fig. c) reveal that 5-7 nm PdH_x exhibit slow bulk H diffusion as compared to the ~10 nm PdH_x NPs. This is attributed to the lower lattice strain in ~10 nm Pd NPs, which allows H to diffuse freely from the interstitial sites in the bulk to the surface. As seen from the catalytic tests (Fig. d), ~10 nm Pd NPs showed the least selective H_2O_2 formation, which is tentatively attributed to the presence of more bulk hydride and faster bulk H diffusion that can overpopulate the surface H concentration and form the side product H_2O. In contrast, 1-2 nm Pd and 5-7 nm Pd NPs showed good selectivity towards H_2O_2 synthesis. In conclusion, the presence of more surface H and slower bulk H diffusion resulted in high selectivity for H_2O_2 formation. [3] Hence, the selective synthesis of H_2O_2 exhibits a strong dependence on Pd NP size. [4]

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Methanol-to-jet fuel (MTJ) pathway and catalysts

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Introduction

Converting methanol to jet fuel offers a promising route for producing sustainable aviation fuel (SAF). A viable concept involves converting methanol to C_3–C_6 olefins (MTO) — while suppressing ethylene, aromatics, and light paraffins — followed by olefin oligomerization (OLI) to produce jet-range C_8–C_{16} *iso*-olefins, which can then be hydrogenated to *iso*-paraffins. One-dimensional 10-membered-ring zeolites such as H-ZSM-48 have shown the required MTO selectivity [1], while both micro- and mesoporous silica-alumina solid-acid catalysts can catalyze the OLI step [2]. This presentation summarizes the targeted process, catalyst performance, and integration between the MTO and OLI steps.

Results and Discussion

To demonstrate targeted MTO performance, H-ZSM-48 (RFE framework) was synthesized and tested at 400 °C with a feed of 10% MeOH and 1% propene (Figure 1a). The catalyst maintained high methanol conversion with sustained olefin selectivity of approximately 80–85% in the C_{4+} fraction. Compared with H-ZSM-5 — a three-dimensional zeolite of similar pore size — the formation of paraffins and aromatics was significantly reduced [1].

Propene oligomerization was studied in the gas phase using nanocrystalline H-ZSM-5 with varying acid-site densities, amorphous and hierarchical silica–alumina (ASA and HSA), and mesoporous Al-MCM-41 at 200–300 °C and 35 bar (Figure 1b). At <10% conversion, hexenes were the primary products for all catalysts. At higher conversions, cracking reactions became dominant, producing olefins that were not multiples of propene, especially over H-ZSM-5. Trimers and higher oligomers formed with total selectivity around 20 %.

Ongoing work includes advanced zeolite characterization, liquid-phase OLI studies, and process-integration.

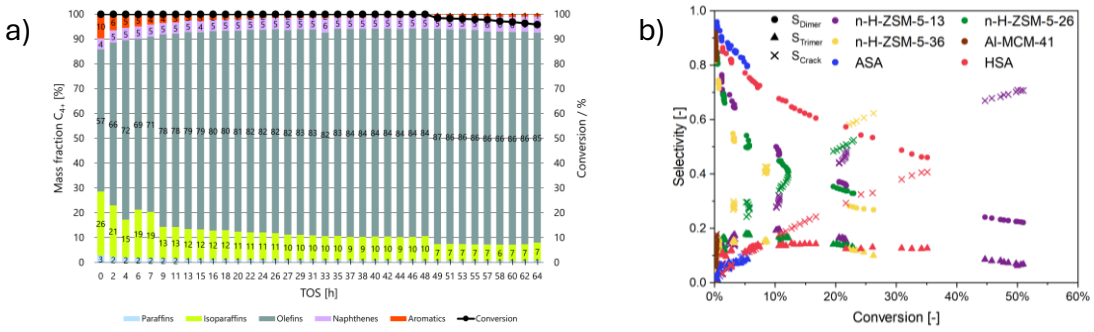

Fig. 1: a) Conversion of methanol and PIONA selectivity using a H-ZSM-48 catalyst at 400 °C, 15 bar, 2 h^{-1}. b) Selectivity vs. conversion for propene OLI using H-ZSM-5 and mesoporous silica-alumina catalysts at 200-300 °C and 35 bar.

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Size and shape effect of silver nanoparticles on ethylene epoxidation: a multiscale simulation

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Introduction

Ethylene epoxidation is a significant industrial selective oxidation process that enables the large-scale production of ethylene oxide, amounting to several million tonnes per year. [1] Silver remains the benchmark catalyst for this reaction and, despite decades of efforts to find improved alternatives, has not been surpassed. [2] First-principles modelling has played a key role in elucidating the reaction mechanism and linking catalytic efficiency to surface structure. In this study, we used density functional theory (DFT) and kinetic Monte Carlo (kMC) to investigate how different nanoparticles perform in silver epoxidation. We compared silver nanoparticles of different sizes and shapes, such as icosahedra, octahedra and cubes, examining their performance.

Results and Discussion

We used DFT to map the complete reaction mechanism of ethylene epoxidation on silver and several other noble metals. By comparing the activation barriers and reaction energies of individual elementary steps with various descriptors, we identified BEP correlations. These enabled us to model the entire surface of different nanoparticles and postulate the reaction kinetics at different sites on the nanoparticles. We then used these results as input for kMC simulations.

The simulations were run under different reaction conditions (pressure, temperature, inlet composition), and the surface coverages of the nanoparticles were compared. Ultimately, turnover frequencies (TOFs) for the production of ethylene epoxide were compared across nanoparticles.

Generally, smaller nanoparticles perform better but are less stable. Interestingly, undercoordinated sites are not universally more suitable for the production of ethylene epoxide. Their high activity often leads to overoxidation, producing CO_2 instead. Thus, a balance between the activity and selectivity of the catalyst is achieved on nanoparticles of 300–400 atoms, where facets perform better than edges and vertices.

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Pulse-mediated electrodeposition of shaped structures for HMF electrocatalysis

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Introduction

Pulse-mediated electrodeposition is a versatile technique to tailor the shape of deposited structures by adjusting applied potential and electrolyte composition. Shape structures are well-defined surfaces that preferentially expose certain crystallographic orientations. Different crystallographic orientations have different performance towards the same electrocatalytic process. Therefore, the use of cyclic voltammetry to distinguish sites of distinct geometry is crucial to advancing understanding of structural effects in electrocatalysis.(1)

Results

In this talk, I will present our recent work on pulse-mediated refactoring of copper in which we alternate anodic and cathodic pulses to tune the terrace-to-step or defect ratio on copper. Here, we also introduce blank cyclic voltammograms in 0.1 M NaCl to characterise surface geometries on copper (Figure 1 i). We demonstrate that this electrochemical probe can unambiguously distinguish terrace from step sites on refaceted copper. Finally, the influence of refaceted copper with different terrace-to-step ratios on HMF electrocatalysis will be discussed.(2)(3)

Afterwards, I will present our recent results on pulse-electrodeposition of shaped gold particles in a deep eutectic solvent. I will illustrate how both pulses and electrolyte structure influence the formation of different structures (Figure 1 ii), affecting HMF oxidation.(4)

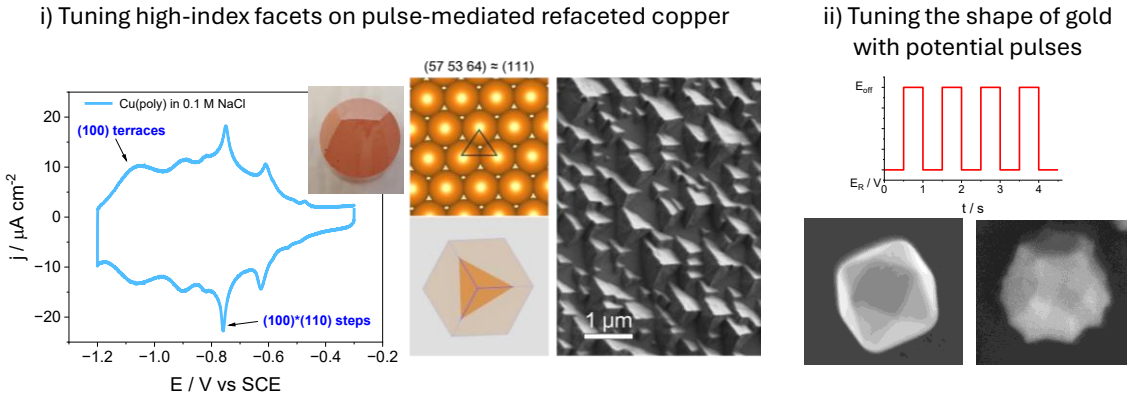

Figure 1. i) Voltammetric and SEM analysis of a Cu(poly) modified with potential pulses to induce shaped structures with (100) sites. Blank CVs were recorded in 0.1 M NaCl. ii) Electrodeposited gold-shaped nanostructures in deep eutectic solvent using potential pulses.

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In Operando Studies of the Synthesis and Structural Evolution of Supported Electrocatalysts

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Introduction

Electrocatalysis underpins a range of critical technologies needed for the Green Transition from fossil fuel–based energy systems to a sustainable future. The precision synthesis of electrocatalysts with well-defined structures, together with an understanding of their dynamic structural transformations under operating conditions, is essential for developing electrocatalysts that are active, selective, and, especially, durable for industrial applications.

Results and Discussion

Here, I will present the latest results from our group on in operando studies of the synthesis of supported Pt- and Ir-based nanoparticles, as well as their structural evolution under industrially relevant operating conditions of polymer electrolyte membrane fuel cells and electrolyzers. A range of in operando techniques, including high-temperature X-ray diffraction, TG-MS, TPR-MS, environmental TEM, electrochemical XRD, and online ICP-MS, have been employed to provide complementary insights into the physical and chemical processes involved during catalyst synthesis and electrochemical testing, as illustrated in Figure 1.[1, 2] We believe the presented results represent a small but solid step toward the atomically precise synthesis of electrocatalysts with predictable catalytic properties tailored to their intended working conditions.

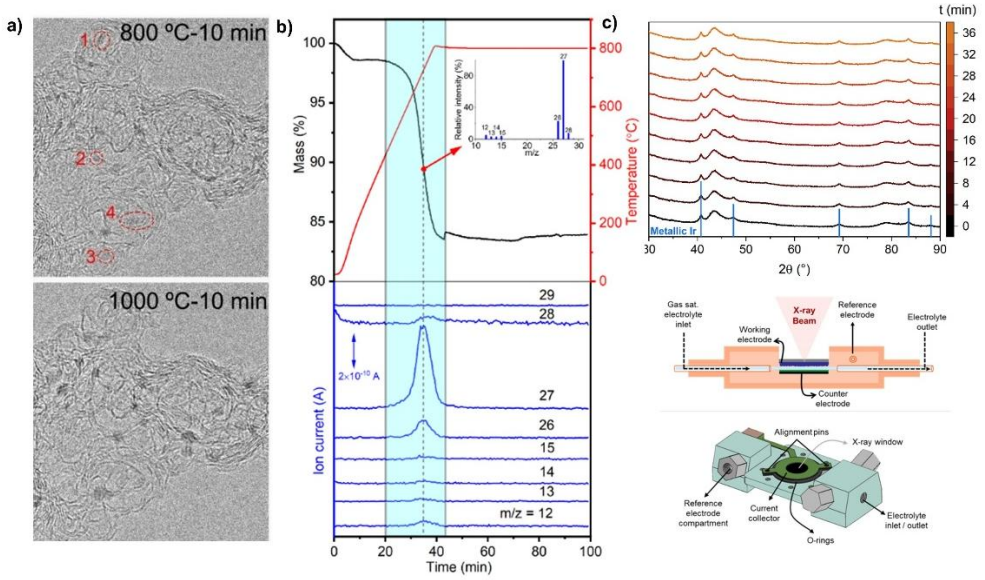

Figure 1. a) in-situ TEM studies on the synthesis process, b) TG-MS studies on the synthesis, and 3) electrochemical XRD on the structural transformation under industrial conditions.

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Ni–Cu Alloy–Decorated TiO_2 Nanotubes for Photocatalytic Degradation of Pharmaceuticals

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Introduction

Catalysis research increasingly focuses on sustainable, energy- and cost-efficient strategies. Photocatalysis is a versatile approach for addressing environmental challenges, particularly water contamination by recalcitrant pharmaceuticals, which are often insufficiently studied and poorly removed by conventional treatments [1]. Here, we propose a Ni–Cu bimetallic alloy–decorated TiO_2 nanotube system as an advanced, earth-abundant, and low-cost photocatalyst for degrading widely used over-the-counter pharmaceuticals, including acetaminophen, naproxen, and acetylsalicylic acid.

Results and Discussion

In our previous work, we developed and optimized a photocatalyst based on anodic TiO_2 nanotube arrays decorated with Ni, Cu, and NiCu alloys for the photo-oxidation of acetaminophen [2]. The catalytic performance of the different materials was evaluated under UV irradiation (365 nm) monitoring the degradation of the parent compound via HPLC-UV. Among the tested catalysts, TiO_2 nanotubes decorated with a NiCu alloy with a 50:50 composition exhibited the highest photocatalytic activity attributed to the synergistic interaction between Ni and Cu, enhancing charge separation and photocatalytic activity [3]. Based on these results, NiCu–TiO_2 was selected for the degradation of additional pharmaceuticals, specifically acetylsalicylic acid and naproxen. After 3 h of irradiation, paracetamol showed ~50% degradation, acetylsalicylic acid ~80%, while naproxen was completely degraded, indicating faster degradation kinetics. Further studies were conducted to investigate the degradation mechanism of the three pharmaceutical compounds. Photocatalytic tests were performed in the presence of scavengers: formic acid (hole scavenger) and benzoic acid (•OH scavenger). The addition of formic acid completely suppressed the catalytic activity, confirming that the degradation of all three pharmaceutical active ingredients proceeds predominantly via a hole-mediated mechanism. HR-MS (Orbitrap) analysis was then used to identify intermediates and propose plausible degradation pathways consistent with this mechanism. We then studied pharmaceutical mixtures, revealing competitive processes due to the limited availability of catalyst surface active sites, consistent with a surface-hole-mediated mechanism. The degradation was influenced by the relative concentrations of the compounds and their intrinsic kinetics, with faster-reacting molecules dominating. Current work focuses on binary and ternary mixtures to develop quantitative mechanistic models that account for the effects of co-existing pollutants.

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Automated 3D characterization of small nanoparticles for high-throughput screening with transmission electron microscopy

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Introduction

Experimentally determining the properties of specific sites and nanostructures in a heterogeneous catalyst is a grand challenge. It could possibly be done by operando transmission electron microscopy (TEM) in one of two ways, 1) extremely precise measurements of individual sites under working conditions by low dose imaging and spectroscopy, or 2) in a data-driven way from large datasets of 3D-structure ensembles paired with simultaneously measured catalytic performance. Benefits of the latter is that it is less demanding from an experimental point of view and catches all types of sites in the sample. However, to enable such workflows, both instrument automation and accurate and automatable data analysis techniques have to be further developed. Specifically, extracting 3D information directly from single atomically resolved TEM images arises as a crucial challenge. In this presentation we introduce machine learning workflows to extract size and morphology of small nanoparticles from single scanning TEM (STEM) images. We benchmark the workflows and explore the accuracy of the techniques. Finally we apply the technique to real high-angle annular dark-field (HAADF) STEM images of a Pt/CeO_2 catalyst, demonstrating good generalization of the machine learning models to experimental data.

Results and Discussion

A large dataset of 256.000 physical HAADF-STEM image simulations of Pt nanoparticles on CeO_2 supports were generated with the multislice algorithm and by a learned surrogate model[1]. These image – atomic model pairs were used to train neural networks to predict size and morphology of the imaged nanoparticles given only the image as input. Size was predicted with a ResNet18, yielding a size prediction mean absolute percentage error (MAPE) of 21.0%, 5.1%, and 2.8% for Pt particles in the 1-10, 10-100, and 100-1000 atom size range, respectively. For morphology, a diffusion model was trained to iteratively denoise random point clouds into reasonable atomic structures that fit to the HAADF-STEM image used to guide the process.

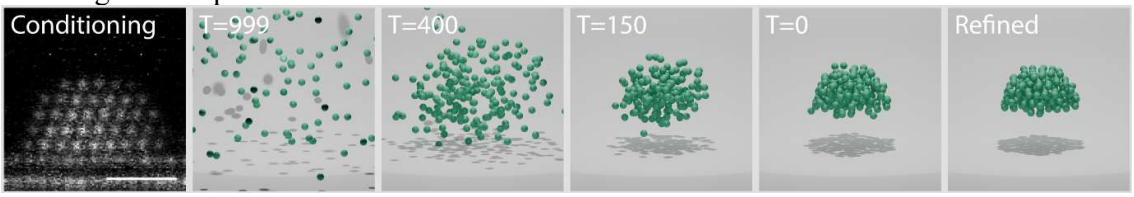

Figure 1: A diffusion model predicts the morphology of an imaged nanoparticle over 1000 denoising steps.

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Electrified Hydrogen Storage and On-Demand Release via Ammonia Using Magnetically Heatable Ru–CoNi Nanocomposite Catalysts

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Introduction

Ammonia is an attractive carbon-free hydrogen carrier due to its high hydrogen density (17.8 wt%), established storage infrastructure, and moderate liquefaction conditions [1]. Efficient ammonia synthesis enables hydrogen storage, while catalytic ammonia decomposition provides hydrogen release. Both processes are thermally demanding and traditionally constrained by reactor-scale heat transfer and thermal inertia. Conventional externally heated reactors exhibit slow start-up and limited dynamic controllability, restricting integration with intermittent renewable electricity [1]. Magnetic heating offers an alternative electrification strategy in which heat is generated volumetrically inside magnetically active catalyst components exposed to an alternating magnetic field (AMF). This approach enables localized heat generation, rapid temperature modulation, and potentially reduced heat-transfer limitations.

Results and Discussion

The eveloepd catalyst consists of ferromagnetic $Co_{0.67}Ni_{0.33}$ alloy nanoparticles embedded in γ-Al_2O_3 nanosheets (CN-A), decorated with Ru nanoparticles and optionally promoted with Ba. The CoNi alloy converts AMF energy into heat via hysteresis losses and retains magnetic stability under reducing conditions. Calorimetric and kinetic analyses indicate that local temperatures at catalytically active sites exceed the thermocouple-measured bed temperature by >100 °C under magnetic heating [2]. This localized overheating explains the high reaction rates observed compared to conventional external heating. For ammonia synthesis at 5.5 MPa (H_2:N_2 = 2:1), Ba–Ru/CN-A achieves rates above 1,500 mmol NH_3 gRu^{-1} h^{-1} at thermocouple-measured bed temperatures of 350–400 °C [2]. Ba promotion lowers the apparent activation barrier for N_2 dissociation at Ru–BaO interfacial sites, as confirmed by density functional theory and microkinetic modelling. For ammonia decomposition at atmospheric pressure, complete conversion of diluted ammonia is achieved near 400 °C, while pure ammonia conversion exceeds 99% at ~525 °C. Reaction rates up to ~2,000 μmol NH_3 gRu^{-1} s^{-1} are obtained under pure NH_3 [3]. Dynamic experiments demonstrate full activation within 2–3 minutes after AMF switching, and rapid shutdown upon field removal, indicating minimal thermal inertia. Stable performance is maintained for 90–120 h under both synthesis and decomposition conditions without significant nanoparticle growth or loss of magnetic properties. These results demonstrate that magnetically heated Ru–CoNi nanocomposites enable electrified, dynamically responsive ammonia-based hydrogen storage and release, offering a promising route toward modular, load-following hydrogen systems.

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Structural and chemical stability of $LaSrCoFeO_3$ perovskite thin films for ammonia oxidation

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Introduction

NH_3-fueled solid oxide fuel cells can efficiently convert chemical energy into electricity with zero or low carbon emissions [1]. $LaSrCoFeO_3$ perovskites are promising electrode materials due to their wide range of tunable electrical and catalytic properties. Although these perovskites have been widely studied, little is known about their performance in NH_3 oxidation. Co on the B-site enhances catalytic activity, but Co species are prone to reduce at relevant conditions, which may compromise stability [2,3]. This study investigates the chemical and structural stability of $LaSrCoFeO_3$ perovskite thin films to optimize their performance in NH_3 oxidation.

Results and Discussion

Perovskite thin films $La_{0.6}Sr_{0.4}Co_yFe_{1-y}O_3$ (y = 0.1, 0.3, 1) were prepared on single crystal (100) YSZ substrates via pulsed laser deposition. Operando APXPS+NEXAFS on a $La_{0.6}Sr_{0.4}Co_{0.1}Fe_{0.9}O_3$ thin film was collected at the HIPPIE beamline at MAX IV, Sweden, in NH_3+O_2, (up to 750ºC, ~1 mbar). La, Co and Fe remain stable during heating, whereas pronounced SrO surface segregation is observed. Switching from reactive to inert atmosphere at 750 °C induces partial reduction of Co and Fe, likely due to residual NH_3 in the chamber. This reduction is immediately reversible when switching back to NH_3+O_2. This switch between reactive and inert atmospheres leads to dynamic surface restructuring and changes in catalytic activity. A second reaction cycle reproduces the overall trends but reveals significant differences in the O1s, N1s and Sr3d regions (Figure 1a) together with higher catalytic activity (Figure 1b), suggesting surface reconfiguration under dynamic conditions. Increasing Co content enhances the selectivity towards NO and accelerates Co reduction. This shows the key role of the B-site in the surface dynamics and catalytic activity on these materials.

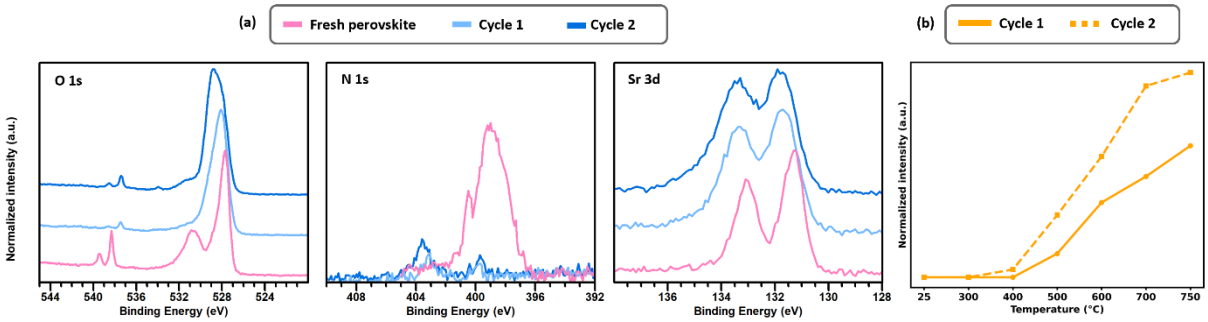

Figure 1. $La_{0.6}Sr_{0.4}Co_{0.1}Fe_{0.9}O_3$ thin film (a) Sr3d, N1s and O1s spectra measured in NH_3 + O_2, 750 ºC, ~1 mbar during the 1st and 2nd cycle and (b) NO production comparing the first and second heating cycles. Collected at MAX IV, Sweden

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Magnetically-heated Ru/C hydrotreatment of levulinic acid in cold fluid by electrified slurry reactor

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Introduction. Electrification of the chemical and energy sector is a crucial step in the transition to a carbon neutral society. The heating of magnetic nanoparticles embedded within the catalyst can selectively heat the catalyst at the reaction site, overcoming the troublesome temperature gradients in the reactor, eventually favoring bulk-phase reactions or degradation of thermally unstable compounds (Figure 1c). Hereby, the concept has been successfully applied in biomass valorisation by our research team. Namely levulinic acid (LA) or furfural (F) were hydro(deoxy)genated by molecular H_2 in a stirred slurry reactor, where magnetic nanoparticles (MN) coated by carbon and finely dispersed Ru clusters were heated directly by AC field.

Materials and methods. The synthetized MN-C-Ru catalyst contained three layers. Maghemite nanoparticles of 15 nm size (MN) exhibiting ferrimagnetic characteristic are confined within a carbon matrix (C) formed by hydrothermal carbonization of glucose, and finally Ru nanoparticles are deposited by solvothermal reduction of Ru3+ in iso-propanol (i-PR). For catalytic hydrotreatment experiment, MN-C-Ru, levulinic acid and i-PR were placed in a quartz reactor (to prevent inductive heating), pressurized with H2 to 1 MPa, and subjected to vigorous stirring and an AC field (frequency of 273 kHz and amplitude of 46 mT).

Results and discussion. The nanocatalyst showcased its capability as both a heating agent and catalytically active material. Detailed examination and modeling of the hydrogenation and deoxygenation processes revealed that the nanocatalyst's surface attains a higher temperature (137 °C) compared to the bulk liquid phase (85 °C). This temperature differential led to enhanced conversion rates of isopropyl levulinate to γ-valerolactone, consequently boosting yields under mild conditions. Remarkably, MN-C-Ru maintained stability and retained its activity, achieving a consistent 100% yield of GVL even after four cycles.

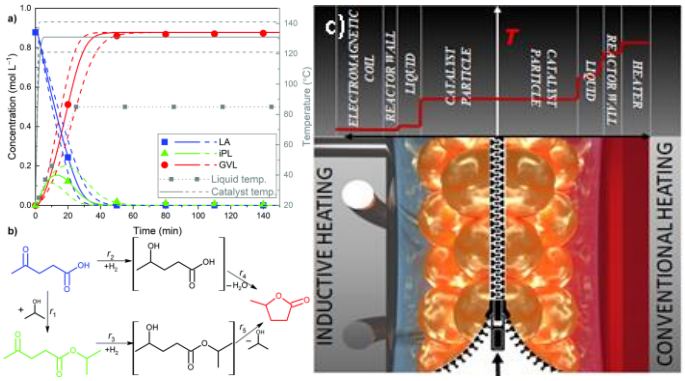

Figure 1. Reaction kinetics[a] (measured points, modelled lines) and mechanism[b] for HDO of LA to GVL in a slurry reactor with targeted magnetic heating of catalyst grains, resulting in beneficial temperature profiles[c] over conventional heating.

The elevated surface temperature resulting from magnetic heating of the catalyst boosts the production of γ-valerolactone through direct hydrogenation (with an activation energy of 22 kJ mol^{-1}) and hydro(deoxy)genation of isopropyl levulinate (with an activation energy of 93 kJ mol^{-1}). The latter is inherently formed due to the low activation energy of esterification (32 kJ mol^{-1}).

Acknowledgments *The authors acknowledge the financial support from ARIS (P2-0089, P2-0152, N2-0242, J2-70093).*

Ammonia oxidation on perovskites for ammonia SOFCs

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Introduction

The activity of perovskites in ammonia oxidation to nitric oxide has been investigated extensively[1], [2], [3], but corresponding kinetic data is scarcely reported. In addition, doping strategies of those mixed oxide catalysts have mostly focused on a narrow range of compositions with only one component varying in concentration. In this work, a Design of Experiment approach has been implemented to screen a wide range of perovskite materials with the general formula $LaFe_xCo_yNi_zO_3$, followed by a detailed kinetic study over the candidate showing highest selectivity to the desired product.

Results and Discussion

Selectivity screening led to results shown in Fig 1. Based on those, an optimal catalyst candidate – $LaFe_{0.25}Ni_{0.75}O_3$ – has been suggested and synthesized. The NO selectivity for the optimized catalyst was confirmed to be highest of all tested catalysts. A kinetic study of ammonia oxidation to nitric oxide over the optimized candidate led to following conclusions: First order in ammonia, between 0th and 1st order in oxygen, oscillatory behavior at lower oxygen partial pressures (indicates MvK mechanism), linear Arrhenius behavior for the desired product, and inverted "V" Arrhenius behavior for undesired products, making the selected perovskite a promising candidate for ammonia SOFC anode material.

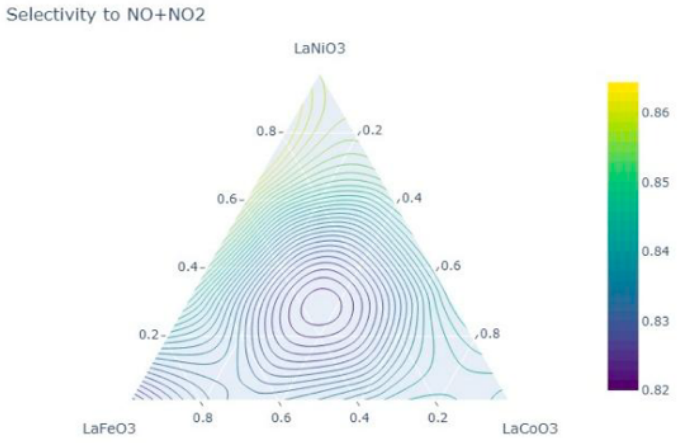

Figure 1 Selectivity screening results

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Entropy-Enthalpy Compensation in Electrocatalytic Rates

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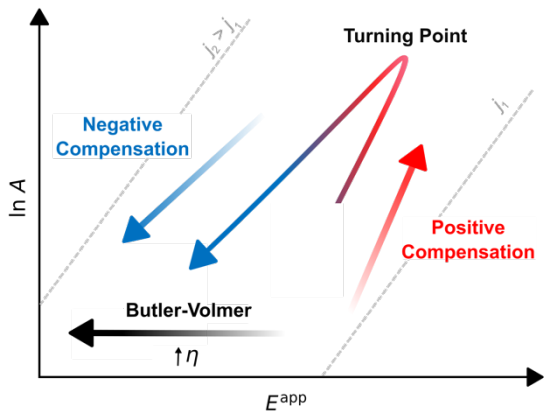
Introduction

Measuring the temperature dependence of electrocatalytic reaction rates is a powerful, yet underexplored, way of investigating the underlying kinetics. Although temperature is a key parameter in industrial electrolyzers, the vast majority of mechanistic lab-scale studies ignore temperature variations by operating at room temperature. This is somewhat surprising since existing experimental evidence has shown that even modest heating can significantly affect the rate and selectivity of electrocatalytic reactions. Arrhenius analysis of electrocatalytic rates has shown a surprisingly large variation in both the activation enthalpy and the entropy-dependent prefactor [1]. Understanding the origin of such effects could be crucial for advancing fundamental electrocatalysis and exploiting temperature as a control parameter.

Results and Discussion

We explore temperature effects on the hydrogen evolution reaction (HER) by developing a mean-field microkinetic model based on first-principles energetics [2]. Despite the simplicity of the model, the trends in our extracted Arrhenius parameters are in remarkable qualitative agreement with experiments. We explore how the Arrhenius parameters depend on potential and rationalize a series of entropy-enthalpy correlations in experimental HER rates. We find that the entropy-dependent prefactor changes drastically alongside the apparent activation energy, thus signaling deviations from established Butler-Volmer kinetics. Different groups of metal catalysts show distinct kinetic fingerprints which we rationalize in terms of shifting kinetic regimes, drawing parallels to the compensation effect in thermal catalysis [3]. We further generalize our findings to other electrocatalytic reactions and setups, leading to a comprehensive description of the compensation effect as a ubiquituous phenomenon in electrocatalysis, caused by surface kinetics.



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Lab-scale Operando X-ray Diffraction Reveals Temperature-Accelerated Coalescence-Dominated Growth of Pt Nanoparticles

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Introduction

The continuous increase in global energy demand, combined with the urgent need to reduce greenhouse gas emissions associated with fossil fuel consumption, has accelerated the development of sustainable energy technologies. Despite the critical role of the electrocatalysts in these technologies, much of the research is still performed under experimental conditions that differ significantly from those encountered in real industrial operation.[1,2] In this work, we showed the development of a lab-based operando X-ray diffraction (XRD) technique that enables simultaneous acquisition of high-quality electrochemical data and XRD patterns under industrially relevant electrochemical conditions. We investigated the growth of Pt particles in a high-metal-loading Pt/C under room temperature (28°C) and elevated temperature (70°C). Post-mortem transmission electron microscopy (TEM) was performed to further elucidate the structural changes.

Results and Discussion

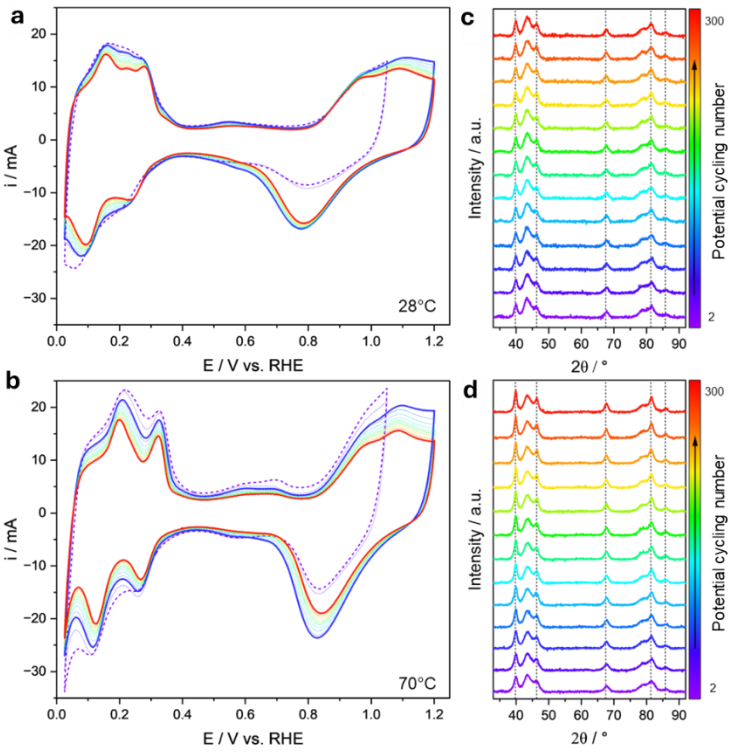

Figure 1. CV profiles of Pt/C recorded at a)28 °C and b) 70 °C at a scan rate of 50 mV s^{-1} in 0.5 M H_2SO_4. c, d) Corresponding XRD patterns of the samples collected at c) 28 °C and d) 70 °C during electrochemical cycling. The rainbow palette indicates the electrochemical cycling numbers, with purple for cycle 2 and red for cycle 300.

The developed operando XRD technique was employed to study the degradation of a high-loading Pt/C catalyst (60wt% Pt on carbon black) at two operating temperatures: 28 and 70°C (Figure 1). At 28°C, the pristine Pt particles with a volume-weighted mean size of 4.9 ± 0.2 nm grew nearly linearly to 5.5 ± 0.1 nm after a series of potential cycling tests in acidic media. In comparison, at 70 °C, the particle growth was significantly accelerated, reaching a final size of 7.9 ± 0.1 nm. To ensure sufficient mass transport for the high-metal-loading catalyst, a high electrolyte flow (70 mL/min) was used. The results suggested that particle growth in the present study was primarily driven by migration and coalescence, as evidenced by post-mortem TEM, which reveals coalesced and elongated particles.

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Exploiting the tunability of dilute alloys for sustainable electrocatalytic reactions

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Introduction

The production of chemicals and energy must be reimagined to become more efficient and diverge from fossil fuel dependence. Electrocatalytic reactions, like the oxygen reduction reaction (ORR) and the hydrogen oxidation reaction (HOR), will have increasing key roles to a more sustainable future in processes such as hydrogen peroxide production or fuel cells. Thus, a need to produce more efficient electrocatalysts and mitigate their cost has emerged.

Dilute alloys are a class of catalysts that increases atom efficiency of rare and expensive metals. Typically, dilute alloys consist of a reactive metal in dilute amounts initiating the catalytic cycle by activating key bonds and a host metal propagating selectivity [1]. More importantly, the surface of dilute alloys is key to catalytic enhancement. It is crucial that the dilute reactive metal is present *at the surface* to initiate the reaction. Yet the surface of dilute alloys is highly dynamic, and methods to tune the surface for sustainable electrocatalytic reactions are lacking.

Results and Discussion

In this work, AuPd dilute alloy thin films were synthesized using physical vapor deposition and annealed at 400°C in vacuum, creating an inactive Au surface [2]. The surface composition of the thin films was studied with a combination of cyclic voltammetry in a three-electrode cell in both alkaline and acidic electrolytes and with X-ray photoelectron spectroscopy (XPS).

Cyclic voltammetry confirmed the formation of a Au surface after annealing (Fig. 1). Strikingly, our work shows that Pd can revisit the surface after performing appropriate potential holds in an O_2 atmosphere. XPS measurements were employed to confirm that the Pd sites migrate from bulk to the surface and reverse. Electrocatalytic reactions such as ORR were performed showing that the Pd distribution influences the electrocatalytic performance.

This work demonstrates that the surface of AuPd dilute alloys can be tuned for sustainable electrocatalytic reactions.

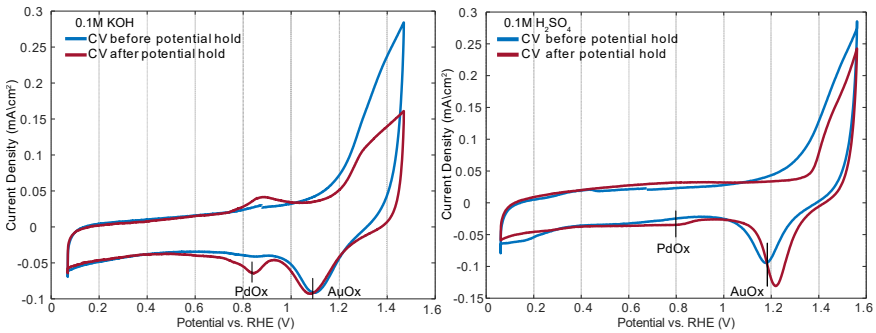

Figure 1: Left, CVs of AuPd before and after potential hold in oxidative potential with O_2 flow in alkaline solution. Right, CVs of AuPd before and after potential hold in oxidative potential with O_2 flow in acidic solution

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Scale-Bridging characterization of Pd/Al_2O_3 Methane Oxidation Catalysts during Sulfur Poisoning

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Introduction

Industry is transitioning from a system dominated by fossil-based fuels to a diversified energy landscape which relies on transition technologies. In this context, methane (CH_4) from natural gas, biogas, and power-to-X processes, offers high potential as an energy carrier.[1] However, CH_4 slip poses a major threat to the environment due to the high global warming potential of CH_4. Although Pd-based catalysts exhibit the highest catalytic activity for CH_4 oxidation, Pd suffers from deactivation under reaction conditions, with S-poisoning being a major challenge leading to the formation of stable and catalytically inactive $PdSO_4$.[2,3] Sulfur may originate from biogas, odorants, or the fuel itself. This study aims to elucidate the multidimensional nature of S-poisoning in technical catalysts. The combination of the spatially resolved characterization methods X-ray absorption spectroscopy (XAS) at the Pd L_3- and K-edges and the S K-edge, X-ray fluorescence (XRF), and spatially resolved gas-phase profiling enables tracking sulfur-induced deactivation in technical catalysts.

Results and Discussion

A series of 1.8 wt.% Pd/Al_2O_3 washcoated honeycomb catalysts were tested under lean conditions (0.3 vol.% CH_4, 10 vol.% O_2, and 12 vol.% H_2O in N_2). The honeycomb catalysts were poisoned in a S-containing atmosphere (2.5 ppm SO_2) at 450 °C for 5 min, 60 min and 20 h, respectively. After S exposure, a second set of samples was regenerated in 2 vol.% H_2 for 5 min. S-poisoning caused a pronounced catalytic activity loss, resulting in a minimum reaction rate after 20 h (Fig. 1), which could be recovered by regeneration. However, XRF revealed S gradients along the catalyst bed, that became more pronounced with increasing poisoning time and persisted, even after regeneration. The highest amount of S was found towards the start of the catalyst bed and correlates inversely to the catalytic activity as revealed by spatial profiling. Furhtermore, complementary XAS revealed the formation of PdS as function of poisoning time following the regeneration, increasing up to 35 %. More interestingly, S remained in the +6 oxidation state across all treatments, highlighting that conventional regeneration is unlikely to provide full recovery. By demonstrating the persistence of S-poisoning in technical catalysts, these results highlight the need to redesign regeneration strategies for robust and effective treatments.

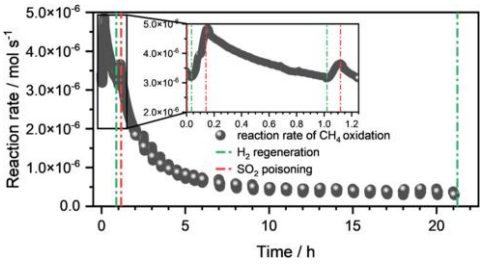

Fig. 1 Reaction rate of CH_4 oxidation as a function S exposure (2.5 ppm SO_2) at 450 °C for 5 min, 60 min, and 20 h (red lines). After each step H_2 treatment was applied (green lines).

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Influence of Support on Alloying and Segregation Behavior in Palladium-Silver Alloy Catalysts During Methane Oxidation

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Introduction

As methane is a potent greenhouse gas, its abatement by catalytic oxidation is of wide importance. Pd-based catalysts have been extensively studied due to their high oxidation activity, for example in the removal of hydrocarbons, CO, and NO_x from vehicle exhaust [1]. However it is of interest to reduce the consumption of this costly metal, for example by alloying with a less expensive and more abundant metal, such as Ag. Pd-Ag alloys have been investigated during CO oxidation, and strong alloying and segregation effects were observed; $Pd_{75}Ag_{25}$ alloy single crystals exhibited drastically lower activity and reversed hysteresis behavior (extinction temperatures above ignition temperatures) compared to their pure Pd counterparts, potentially explained by segregation of Ag to the surface upon heating [2].

Results and Discussion

Methane oxidation activity testing on monometallic Pd (2 wt%) and Pd-Ag alloy (1.5 wt% Pd, 0.5 wt% Ag) catalysts supported on γ-Al_2O_3 showed that replacing 25% of the Pd with Ag yields virtually no effect in catalyst activity or hysteresis behavior, with extinction temperatures above ignition temperatures (Figure 1). However, on an equivalent SiO_2-supported catalyst, opposite hysteresis was observed in the monometallic catalyst, and replacing 25% of the Pd with Ag led to a drastic reduction in activity.

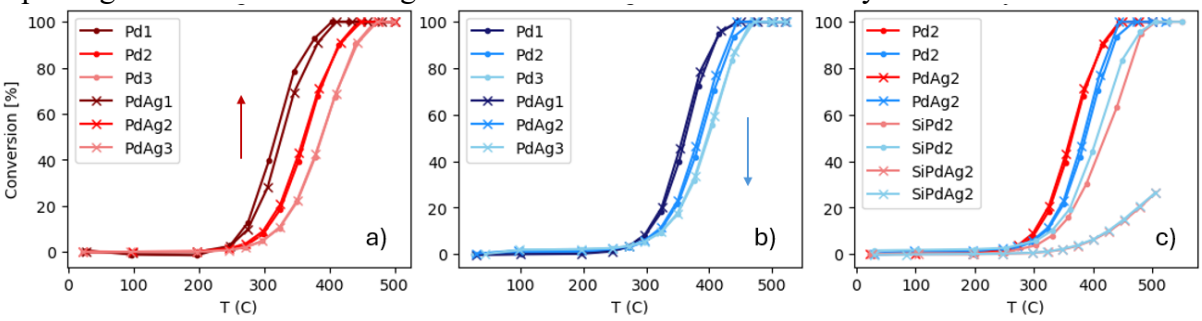

Figure 1. Methane oxidation heating (a) and cooling (b) cycles on γ-Al_2O_3-supported Pd (2wt%) and Pd-Ag(1.5wt% Pd, 0.5wt% Ag) catalysts; (c) comparison with equivalent SiO_2 -supported Pd and Pd-Ag catalysts.

The metal-support interactions, therefore, play a significant role in modulating the effect of alloying Pd with Ag. Characterization of the catalyst surfaces was undertaken in order to correlate structural differences to the observed disparities in activities. XRD in both catalysts showed predominantly a PdO phase with no Ag species visible; upon reduction of the catalyst in hydrogen, XRD suggested the existence of a Pd-Ag alloy phase, with no evidence of separate Pd or Ag particles. This is supported by STEM-EDS of the alumina-supported catalyst, which showed Pd and Ag phases collocated within particles. CO chemisorption on the alumina-supported catalysts showed a significantly higher fraction of Pd available on the surface of the alloy catalyst than the monometallic catalyst, which could partially explain the high activity of the alumina-supported bimetallic catalyst despite the lower Pd loading.

Acknowledgments

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Carbon subsurface traffic jam as driver for methane oxidation activity and selectivity on palladium surfaces

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Introduction

Disentangling the roles of surface and subsurface species is essential for understanding heterogeneous catalysis. While surface adsorbates directly participate in elementary reaction steps, subsurface species can influence activity and selectivity by modifying electronic structure or acting as dynamic reservoirs. Probing these contributions independently is challenging under reaction conditions where deposition and segregation occur simultaneously and are strongly coupled. Here, we introduce an operando approach that directly correlates surface and subsurface composition with catalytic function [1].

Results and Discussion

Our methodology applies controlled temperature modulations to periodically drive carbon deposition and segregation on Pd catalysts during methane oxidation. This perturbation oscillates the distribution of carbon between surface and subsurface sites while catalytic activity is monitored using Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS).

Analysis of the time evolution of XPS components shows that surface carbon coverage governs selectivity toward partial oxidation, where surface carbon accumulation promotes CO formation. In contrast, subsurface carbon controls the overall methane turnover frequency by acting as a dynamic reservoir that regulates carbon removal from the surface and the availability of adsorption sites. We further identify a subsurface “carbon traffic jam”: once carbon exceeds a critical threshold, selectivity shifts from H_2 to H_2O formation. This transition reflects a reorganization of the catalytic pathway and highlights the strong influence of subsurface carbon reservoirs on surface reaction networks.

These findings provide a new perspective on the catalyst subsurface, often considered inert or neglected in kinetic models. Instead, our results show that the subsurface actively participates in oxidation catalysis and can decisively control both reaction rates and product selectivity.

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Operando AP-XPS on Plasma Catalysis for Ammonia Production: A Temperature study

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Introduction

The conventional Haber-Bosch process requires high operating pressures and temperatures to overcome the rate-limiting step of dissociative adsorption of N_2. Plasma catalysis breaks this limitation by supplying vibrationally excited N_2 and atomic nitrogen directly to the surface, allowing for yhhe formation of ammonia at ambient temperatures and pressures. However, optimising plasma catalysis is difficult due to a fundamental lack of understanding of the plasma-surface reaction mechanisms [1].This study utilizes Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS) at Max IV's HIPPIE beamline to investigate surface species on nickel (Ni) and gold (Au) foils during ammonia synthesis from room temperature to 300°C. By exploring how these materials interact with the plasma and subsequent gas phases, this research provides critical mechanistic insight into the intermediate species and limiting reaction steps.

Results and Discussion

AP-XPS measurements across plasma and gas environments successfully identified atomic N, NH, NH_2, and NH_3 species (see fig 1). At lower temperatures (room temperature and 100°C), abundant NH_2 and NH_3 on both Ni and Au catalyst surfaces suggest the rate-limiting steps are NH_2 hydrogenation and subsequent NH_3 desorption. As the temperature increased, both catalysts exhibited an increase in adsorbed NH with temperature, indicating that NH hydrogenation is the rate-limiting step at higher as compared to N_2 dissociation in traditional ammonia synthsis. Additionally, the consistent shift in the gold N1s spectra between the plasma and gas environment, absent in nickel, highlights a fundamentally different interaction with the nitrogen species depending on the catalyst surface. These highly promising insights provide a foundation for understanding the plasma-surface interaction to help optimise catalyst design in the broader plasma catalysis field.

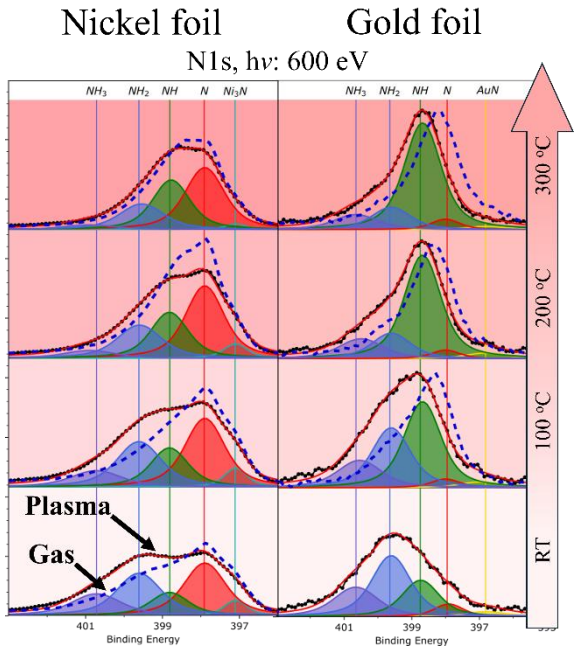

Figure 1. AP-XPS on a Ni and Au foil in plasma (solid) followed by a gas (dashed) environment at increasing temperatures.

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Effect of potassium promotion of the Haber-Bosch process, investigated by *in-situ* X-ray photoelectron Spectroscopy

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Introduction

The Haber-Bosch (HB) process, in which H_2 reacts with N_2 to form ammonia (NH_3) over Fe- and Ru-based heterogeneous catalysts, is essential to produce, e.g. artificial fertilizers. Yet, the use of fossil feedstocks and harsh reaction conditions results in a disasterous climate impact. Adapting the process to sustainable and reneawable feedstocks requires a substantial lowering of the operable temperature and pressure, and the first steps towards benign conditions is a detailed understanding of the reaction mechanism.[1] We previously used X-ray photoelectron spectroscopy at operating conditions between 0.2-1 bar to conclude that both Fe and Ru surfaces were metallic during active conditions, with a very low coverage of N-based adsorbates, due to limitation in the chemisorption and dissociation steps of the N_2 molecules.[2] In this contribution, we provide a comparison between the previously reported unpromoted surfaces to K-promoted crystals.

Results and Discussion

On both Fe and Ru, we observe evidence of increased coverage of N adsorbates for K-promoted surfaces, along with slower rates of hydrogenation of the adsorbates. On Fe (example spectra given in the **Figure**), K is present both on the surface and in the bulk, with a distinct temperature dependence: the surface coverage of K increase at colder temperatures and this coverage is correlated with the growth of a thick Fe nitride – contrary to the metallic resting state of the unpromoted catalyst. This observation indicates that the of rate ammonia production is limited by hydrogenation of nitride species, once again contrary to what was observed on unpromoted surfaces. On Ru, we similarly note an increase of the surface coverage of N-adsorbates, yet the rate-limitaion clearly remains with the dissociative chemisorption of N_2.

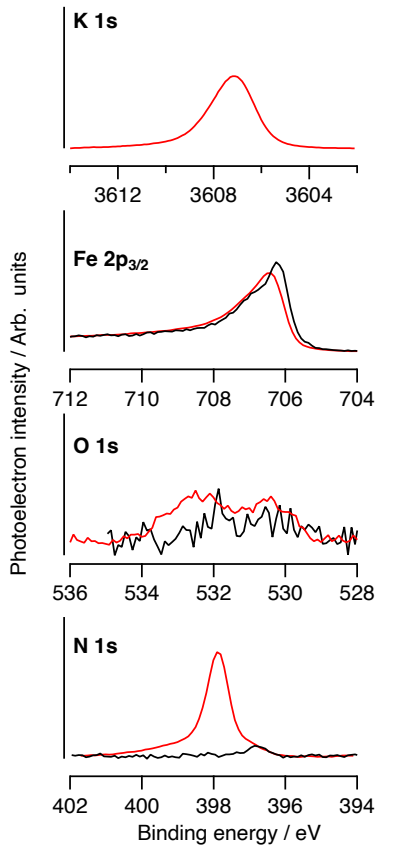

***Figure**: Comparison of X-ray photoelectron spectra acquired during the Haber-Bosch process over an unpromoted, and K-promoted Fe catalyst.*

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Photodriven reduction of N_2-to-NH_3 and mechanistic lessons learned along the way

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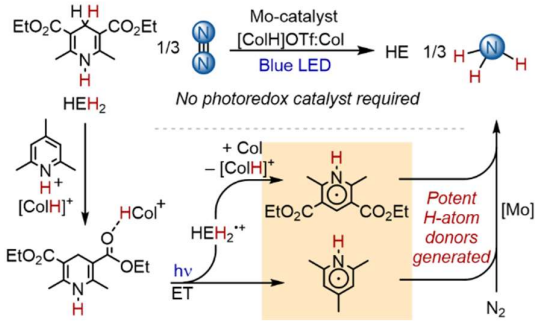
Introduction

The reduction of N_2 to NH_3 (N_2R) is critical due to the importance of NH_3 as a synthetic fertilizer and its potential as a solar fuel.[1] While N_2 hydrogenation is mildly exothermic, the kinetic barriers associate with N≡N triple bond activation requires a substantial energy input, either in the form of temperature and pressure in the industrial Haber-Bosch reaction, ATP hydrolysis in biological N_2R or through a large chemical overpotential in (electro)chemical N_2R catalyzed by homogenous or heterogenous catalysts. Well-defined molecular catalysts enable detailed mechanistic studies which can help develop strategies for lowering the overpotential of chemical N_2R.[1]

Results and Discussion

In this talk I will discuss the development of photodriven N_2R conditions, in which the dihydropyridine Hantzsch ester (HEH_2), when paired with a molybdenum catalyst and organic collidine/collidinium buffer (Col-buffer) under blue light irradiation, acts as a $2e^-/2H^+$ photoreductant enabling hydrogen delivery to N_2 for the $6e^-/6H^+$ conversion to NH_3.[2] While the inclusion of an Ir catalyst improved yields it is not required, raising interesting mechanistic questions.

Next, I will then describe mechanistic studies elucidating how excitation of HEH_2 in the presence of Col-buffer, reduces the acid via an H-bonding interaction, forming a potent H-atom donor (ColH•-radical). This species can readily hydrogenate diverse substrates, given a sufficient match with the reduced acid N–H bond strength.[3] Finally, this mechanism of photodriven acid reduction is extended to the reduction of Lewis acids, specifically the reduction of Sm^{III}-to-Sm^{II} with applications in organic C–C coupling.[4]



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Poster presentations

Oxide phases on Rh(001) during the partial oxidation of methane

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Introduction

Methane is an abundant energy resource and an important feedstock for the production of synthesis gas (CO and H_2), which is a key intermediate for fuels and chemicals. Among the various methane conversion routes, the partial oxidation of methane (POM) is particularly attractive because it is mildly exothermic and produces a syngas composition suitable for downstream processes such as Fischer–Tropsch synthesis and methanol production.[1-3] However, POM remains challenging due to the strong C–H bond and the complexity of the reaction network. Noble metal catalysts, especially Rh-based systems, exhibit high activity and resistance to carbon deposition in POM and therefore serve as valuable model systems for studying methane activation and reaction mechanisms.[2,4] Understanding how the surface structure and oxidation state of the catalyst evolve under reaction conditions is essential for establishing structure–reactivity relationships and guiding catalyst design.

Results and Discussion

Fig. 1 presents high-energy surface X-ray diffraction measurements of the Rh(001) surface under different oxidation conditions. The reduced metallic surface (Fig. 1a) shows diffraction features characteristic of pristine Rh(001). Upon exposure to O_2 at 375 °C (Fig. 1b), additional Bragg reflections appear, indicating the onset of oxide formation. Increasing the oxidation temperature to 500 °C (Fig. 1c) and 600 °C (Fig. 1d) leads to a progressive increase in oxide-related diffraction intensity.

The diffraction features are consistent with the formation of corundum-type Rh_2O_3 surface oxides. With increasing temperature, the oxide Bragg reflections become progressively narrower, suggesting improved ordering and larger oxide domains. At the same time, some Bragg reflections disappear, indicating structural changes in the oxide phase.

Preliminary catalytic measurements indicate that oxides formed at higher oxidation temperatures exhibit higher activity and selectivity toward the partial oxidation of methane, suggesting a strong link between oxide structure and catalytic performance.

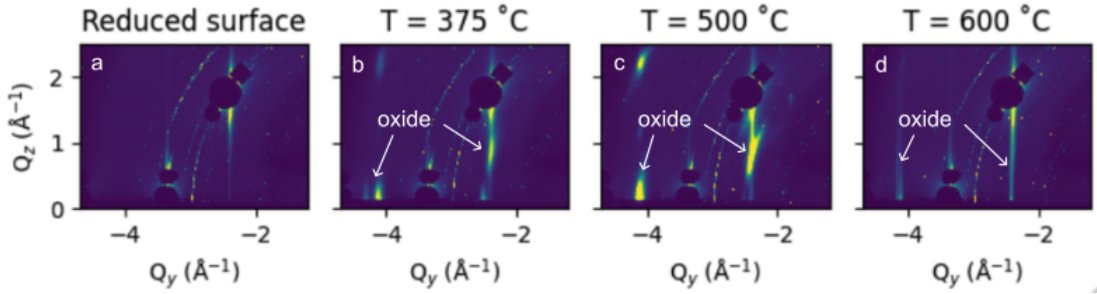

Figure 1. HESXRD patterns of Rh(001) showing progressive formation of corundum Rh_2O_3 surface oxides with increasing oxidation temperature.

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Effect of pillaring loading and calcination temperature on product distribution for waste plastic pyrolysis along with characterization.

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Introduction

Recent reports have shown presence of waste plastics found almost everywhere. From oceans to landfills, plastic waste is piling up. In 2025 global plastic waste reached 460 million tons and in 2024 only 10% recycled and 22% have been mismanaged. Plastic waste management can be a way out of this challenge, to sustain the environment by improving the circularity of already present plastics in the environment. This study underlines in-house prepared novel clay-based catalyst. The experiments were performed both in small lab scale batch reactor setup and the results are validated on small pilot scale continuous feeding reactors. The pyrolyzing reactor was at 550ºC, and fixed bed reactor was at 550ºC at 1 bar pressure.

Results and Discussion

Two different sets of catalyst prepared with different pillaring oxide (mmol to gm of clay) ratio and different calcination temperatures of novel clay-based catalyst. The oil obtained from LDPE and waste plastics are comparable in carbon distribution having around 70% or more in C_1-C_{15}. Gases obtained from LDPE experiments have negligible CO and CO_2 as compared to waste plastics which contains environmental contaminants. Solids are considerably high with waste plastics as well in comparison to LDPE. The pyrolysis oil contains more olefins than paraffins and aromatics showing more unsaturated products identified. XRD spectra showed change in basal spacing from untreated clay to pillared clay catalyst. XRF analysis showed change in composition of the catalysts. NH3-TPD were performed to check the number of acid sites on the catalyst. Pyridine FTIR will give number of Brønsted or Lewis acid sites. TGA give thermal stability of catalyst at high temperature and to observe the mass changer at process temperature. BET also performed to check the specific surface area, pore volume and pore size distribution.

Acknowledgments

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Towards Understanding Carbon Corrosion for Intermediate Temperature PEM Fuel Cells Using Mass Spectrometry

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Introduction

Proton Exchange Membrane Fuel Cells (PEMFCs) is a technology that has been implemented in a wide range of fields such as energy storage, off grid power, and transportation. PEMFC vehicles have been successfully implemented from personal vehicles to heavy transport vehicles such as trucks and ships. In some of these applications such as fuel cell trucks, conventional low temperature PEMs are not operating optimally mainly due to their narrow temperature window. Intermediate Temperature PEMFCs (IT-PEMFC) where the operating temperature is raised from 80 °C towards 120 °C with the intention of improving on FC stack design and efficiency. (Kakinuma, o.a., 2022)The raised temperature will change how the system operates but also how the materials fair and degrade over time. (Jianlu Zhang, 2006)

With a focus on the carbon corrosion reaction in a Pt/C cathode catalyst, an online mass spectrometer is applied to study the temperature effects on the reaction. By cycling a single cell 5cm^2 MEA between 0.95 and 0.4V in a controlled environment and analysing the cathode gas exhaust for carbon corrosion products such as CO_2. Cycling at temperatures ranging from 40 to 120 °C, the goal is to investigate the temperature dependence of the carbon corrosion reaction. When switching between low and high potential the carbon support in the cathode catalyst layer will oxidise into CO_2 and measured by the mass spectrometer. As the potential is held constant, carbon corrosion rate will decrease, and a mass spectrometer peak is formed. Initially, the peaks have a high intensity and will diminish over the cycling to a steady state scenario. Analysing the data for the different temperatures indicates how the carbon corrosion reaction develops and changes over the cycling.

Results and Discussion

Results indicate that there is a correlation between temperature and the reaction rate of carbon corrosion, increasing at higher temperatures. The degradation at 40 °C is almost negligible while at 100 and 120 °C it becomes increasingly prevalent. Measurements at intermediate temperatures (up to 120 °C) show that the effect increases further and indicate that the degradation is intensified significantly at higher temperatures. From the measurements, an apparent activation energy can also be expressed and compared with literature values. During the square wave cycling, the shape carbon corrosion peaks going from high to low potential and low to high potential differ for the increasing temperature. This indicates that the corrosion is dependent on cycling behaviour as well as temperature.

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Influence of iron doping in hydrotalcite-derived Ni-MgO@Al_2O_3 DFMs for integrated CO_2 capture and methanation

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Introduction

Dual-functional materials (DFMs) offer a promising strategy for integrated carbon capture and methanation (ICCM) by using renewable hydrogen, particularly for flue gas emitting industries. Nickel-based (Ni) DFMs supported on MgO@Al_2O_3 have demonstrated high CO_2 uptake and stable cyclic performance with moderate methane yield. Herein, we propose iron (Fe) doped Ni-MgO DFMs synthesized via hydrotalcite (HT) precursors with varying Fe loadings (5, 10 and 15 wt.%) to enhance methane yield. Fe was selected for its promotional activity towards methane, low cost and non-toxic nature. The DFMs were studied under simulated flue gas conditions (15 vol.% CO_2) at 300 and 350 °C. Overall, the DFM containing 5 wt.% Fe (Ni_3Fe_1) exhibited significantly improved methane yield and superior stability over ten consecutive cycles as compared to pure nickel DFM (Ni_1Fe_0).

Results and Discussion

The methane yield over 10 cycles at 300 °C for all DFMs are presented in **Figure (a)**, while the capture–conversion performance of the best performing Ni_3Fe_1 is shown in **Figure (b)**. At 300 °C, The Ni_3Fe_1 DFM demonstrated an average methane yield of 0.9208 mmol/(gDFM) and 94% conversion with no CO formation over 10 consecutive cycles, higher than the pure Ni_1Fe_0, 10 wt.% (Ni_1Fe_1) and 15 wt.% (Ni_1Fe_3) Fe doped DFMs. At 350 °C, Ni_3Fe_1 demonstrated slightly higher methane yield and more stable CO_2 conversion than 300 °C. The methane selectivity is always 100% at both temperatures for all DFMs. The methane yields for the HT-derived Ni/Fe-MgO@Al_2O_3 DFMs in this study are much higher than that reported in literature. Fe doping in Ni-MgO DFMs increases the number of surface basic sites and induces oxygen vacancies, thereby improving CO_2 adsorption [1]. Additionally, Fe enhances the reducibility of NiO, providing more active metallic Ni sites for methanation [2]. The results highlight the effectiveness of cheap and abundant Fe in improving DFM performance and provide insights for advancing integrated carbon capture and utilization (ICCU) technologies.

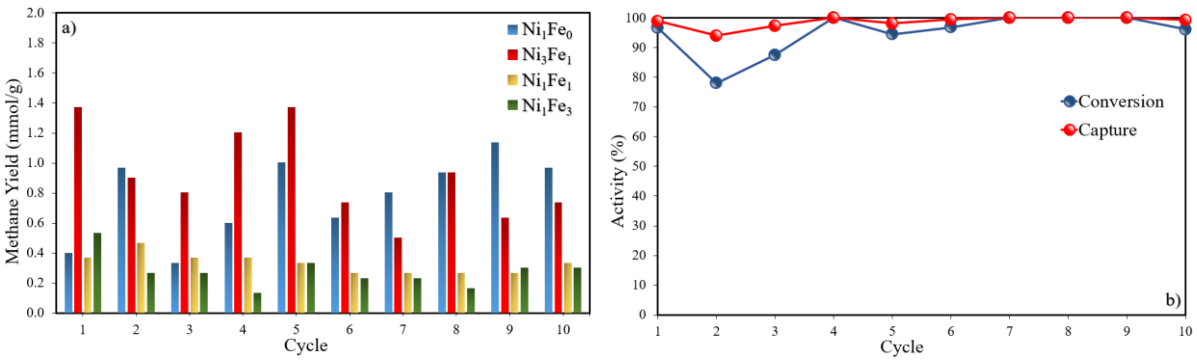

Figure (a) Methanation at 300 °C of four DFMs with increasing Fe content over ten cycles. (b) Conversion and capture activity performance of Ni_3Fe_1 at 300 °C over ten cycles.

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Freeze-Casted NiCu-Based Cryogel Catalysts for the RWGS Reaction

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Introduction

Atmospheric CO_2 concentrations have increased rapidly since the beginning of the industrial era, contributing significantly to global warming and environmental degradation. To address the issues, technologies such as carbon capture and utilization (CCU) and Power-to-X (P2X) are emerging, aming to close the carbon loop and minimize atmospheric CO_2 emissions. The reverse water gas shift (RWGS) reaction is an alternative route to convert CO_2 into the valuable intermediate product. Instead of considering CO_2 as an emission, CO_2 can be seen as a raw material to produce chemicals for needs of industries. To achieve cost-effectiveness, research around both catalysts and reactors is required. [1]

Results and Discussion

The novel NiCu-based cryogel catalysts with 10 wt-% active metal loading were fabricated for CCU -processes. The catalysts were synthesized from $Al(OC_4H_9)_3$, $Ni(CH_3COO)_2{\cdot}4H_2O$, and $Cu(CH_3COO)_2$ precursors via a sol-gel method, followed by freeze-casting and freeze-drying steps. During the freeze-casting, the formed gel were placed into the casting mold and frozen with liquid nitrogen. The frozen liquid media of the gel was sublimated during the freeze-drying to avoid the collapsing of the solid gel network by the evaporation of liquid. As a result, the catalysts achieved cryogel structure. [2,3] The catalysts were calcined at 500 °C, and reduced with 10% H_2/N_2 (100 ml/min) before the activity tests conducted with 3 vol% CO_2 and 12 vol% H_2, balanced with inert gases. The total gas flow was 420 ml/min in the activity tests. The catalysts were characterized with BET, XRD, FE-SEM/EDS, and DRIFTS.

The $NiAl_2O_3$ catalyst showed the most promising CO_2 conversion (~35%), while the $CuAl_2O_3$ reached around 12% and the $NiCuAl_2O_3$ around 7% conversion. All the catalysts showed activity in the RWGS reaction, providing significant amounts of CO; for example, with the $NiAl_2O_3$ catalyst, 0.77 vol% of CO and 0.89 vol% of H_2O were produced at 600 °C. The selectivity towards CO exceeded above 99% with all the catalysts. The $NiAl_2O_3$ catalyst showed also slight activity towards the methanation reaction producing 863 ppm of CH_4 at 440 °C.

Acknowledgments

This work was funded by ERDF/JTF project (2021/900356/09).

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Overcoming thermodynamic limitations in dimethyl carbonate synthesis from CO_2 and methanol using ionic liquids

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Introduction. Dimethyl carbonate (DMC) is an outstanding chemical with several industrial applications such as polycarbonate synthesis, production of electrolytes, solvent for paints and coatings, chemical intermediate (e.g. in methyl isocyanate synthesis) or fuel additive [1]. The conventional methanol phosgenation route with $COCl_2$ for DMC synthesis is now giving way to greener methods, such as methanol carboxylation with CO_2: $2CH_3OH + CO_2 \leftrightarrow OC(OCH_3)_2 + H_2O$ [2]. This reaction is thermodynamically limited with equilibrium conversions < 1%. Therefore, shifting the equilibrium to the product side by e.g., in-situ removal of water, is essential for obtaining significant conversion and DMC yields. The most reported method for shifting the equilibrium involves 2-cyanopyridine [3]; however, its regeneration requires an additional chemical, making the approach less sustainable for industrial applications. One approach involves the use of novel ionic materials that can have a high attraction towards polar and protic components, such as water [4]. Functionalized ionic liquids (ILs) can in-situ interact with water and shift the equilibrium towards the formation of DMC. In this work, we address the challenge of surpassing equilibrium constraints in dimethyl carbonate (DMC) synthesis by employing an ionic liquid combined with a Lanthanum-Ceria catalyst (spindle-like).

Results and Discussion. The spindle-like Lanthanum-Ceria catalyst was synthesized via hydrothermal synthesis method with urea and Ce, La nitrate as precursors. The physicochemical properties of the catalyst were studied by physisorption, X-ray diffraction and scanning-electron microscopy (SEM). The DMC synthesis was carried out in a batch reactor. In a typical experiment, the reactor was charged with 100 mg of catalyst, 15 mL of methanol, and the required amount of ionic liquid to achieve a MeOH/IL molar ratio of 10 or 30. The reactor was sealed and flushed several times, pressurized with 30 bars of CO_2 and heated to the target temperature (120-140 °C). The DMC yields were calculated from the H NMR analysis. Reactions were conducted for either 4 h or 24 h. The DMC yields are shown in Figure 1. The combination of the catalyst and the ionic liquid enabled DMC yields that overcomes the equilibrium limit (~0.20%). Under conditions of 130 ºC, a MeOH/IL molar ratio of 10, and a 24 h residence time, the DMC yield approached 2%, representing an order-of-magnitude increase relative to the equilibrium value. For reasons of confidentiality and pending invention disclosure, the ionic liquid's identity is not revealed in this abstract.

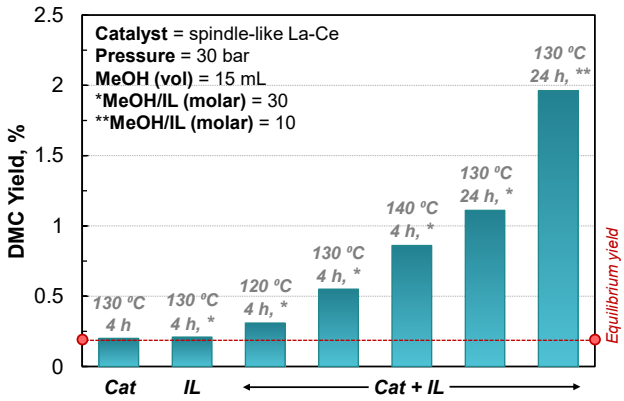

Figure 1. DMC yields obtained with spindle-like La-Ce catalyst combined with ionic liquid for different reaction conditions.

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Optimization of the Photocatalytic Production of Acetonitrile with Hydrous Ruthenium Oxide Supported on TiO_2

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Introduction

Acetonitrile is used widely as a solvent in the refinery, battery, and pharmaceutical industry. The global market size of acetonitrile was estimated to 390.3 million USD in 2023, and its demand is expected to grow with 5.4% anually from 2024 to 2032 [1,2]. Acetonitrile is, despite its applicabilty, currently mainly being produced as a by-product in the production of acrylonitrile by ammoxidation of fossil-based propylene. The industry is, therefore, interested in an alternative production route, in which acetonitrile is produced as the main product, ideally derived from a renewable starting material. We have previously showcased that aqueous ethylamine can be converted into acetonitrile through photocatalytic oxidation using blue light and a $RuO_2{\cdot}xH_2O/TiO_2$ catalyst [3]. The aim of this study is to optimize the system through an initial 2^3 multifactorial Design of Experiments (DoE) approach with Ru catalyst loading, ethylamine concentration, and ethylamine-to-Ru ratio as experimental factors.

Results and Discussion

The response variables, i.e. ethylamine conversion, acetonitrile selectivity, and yield are plotted as a function of factors or combination of factors that are found to be statistically significant ($p< 0.05$) in Figure 1.

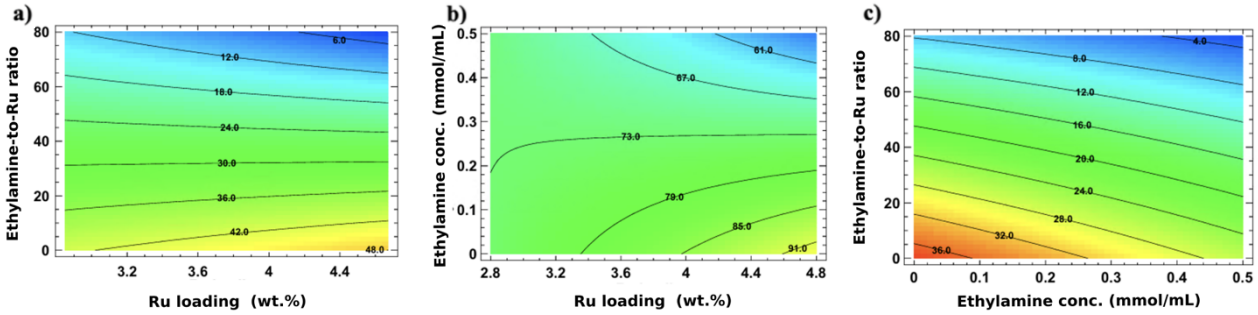

Figure 1: Contour plots for the response variables a) ethylamine conversion, b) acetonitrile selectivity, and c) yield.

The DoE study revealed paramount importance of the ethylamine-to-Ru ratio with preferential acetonitrile production obtained at low ethylamine-to-Ru ratio, high Ru catalyst loading, and low ethylamine concentration. Under sub-optimal conditions an ethylamine conversion of 53% and an acetonitrile selectivity of 65% were found, suggesting that the application of the photocatalytic approach for industrial acetonitrile production might be limited. Nevertheless, the photocatalytic approach could be useful in other diluted systems.

The authors thank Merck KGaA, Darmstadt, Germany for supporting the work.

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High-Throughput Method for Site-Specific Investigations of Lithium-Mediated Nitrogen Reduction Catalysts

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Introduction

Ammonia is a key component of nitrogen-based fertilizers and an attractive fuel candidate[1]. The non-aqueous Li-mediated electrochemical nitrogen reduction reaction (Li-NRR) is a promising sustainable alternative for NH_3 production where Li deposited on the electrocatalysts surface promotes N_2 activation and subsequent NH_3 formation[1,3]. In Li-NRR, Cu can be used as the working electrode where addition of Ag is favorable as it lowers the Li nucleation energy and promotes uniform Li plating[1,3]. The Li-transfer at the $Cu_{(1-x)}Ag_x$ electrode is governed by the chemical potential of lithium, μ_{Li}, acting as its primary driving force for the charger-transfer reaction. However, the theoretical determination of μ_{Li} using high-fidelity models is computationally demanding due to the many possible atomic-scale surface morphologies. This study presents a high-throughput model based on the coordination-environment-based alpha parameter scheme[2] to qualitatively determine μ_{Li} in different surface nanoenvironments (Fig. 1a).

Results and Discussion

Two different sets of alpha parameters for Li were calculated using DFT-computed binding energies (BEs ≈ μ_{Li}) of Li onto different surface models. Alpha parameters were trained for both BCC and FCC structures with mean average errors (MAE) of < 0.06 eV (Fig. 1b). This is the first successful application of the alpha parameter scheme to a non-transition metal and to a BCC crystal structure. In addition, scaling relations between the BE of Li with the BE of the Cu or Ag surface site were established (Fig 1.c). This method can now qualitatively determine the BE of Li on Li, Cu and Ag based only on the local coordination of the site, which can be used to determine distribution of Li-NRR activity on complex catalyst surfaces.

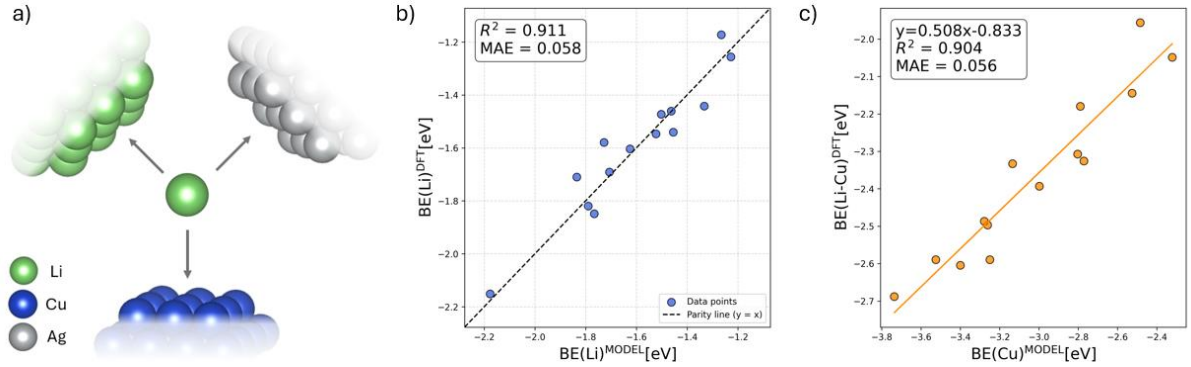

Figure 1: a) Li adsorbs on Li/Cu/Ag surface; b) parity plot between the Li BE from the model and DFT calculations; c) scaling relationships between Li BE and BE of Cu on Cu slab from the model compared to DFT calculations.

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Dipentaerythritol production: the importance of catalyst preparation

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Introduction

Currently dipentaerythritol (DPE) is produced as a byproduct from the condensation reaction of formaldehyde and acetaldehyde to form pentaerythritol (PE).[1] In this process, $NaOH_{(aq)}$ is used as homogenous catalyst which yields between 1-10 % DPE. The demand for highly functional polyols, including DPE is growing due to applications in lubricants and coatings.[2–4] With this rising demand, a dedicated process is needed. Our approach is the direct transformation of PE to DPE using a heterogeneous catalyst. To our knowledge, there is only one other report within the literature successfully achieving this transformation.[5] We have successfully manufactured a heterogenous catalyst.[6] Upon catalyst synthesis, the precise synthesis of the catalyst is of high importance, therefore we investigated the pH of the starting sol-gel and its effects on the final material.

Results and Discussion

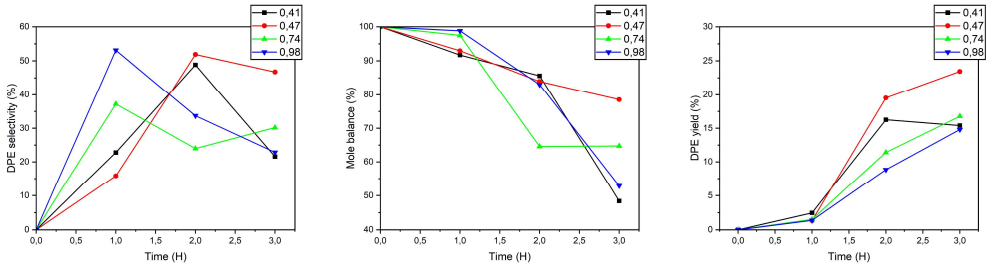

Figure 1. DPE selectivity, mole balance and DPE yield for the production of DPE showing the differences between the starting pH of the sol gel. Black line- pH=0,41 red line -pH=0,47 green line- pH=0,78 and blue line- pH=0,98.

Small variations within the support material synthesis led larg changes in the activity and selectivity. The pH ranges from 0,41 to pH 0,98. At the highest pH, the highest DPE is achieved at the start of the reaction however this is rapidly lost over time. At the medium pH (0,47) the highest DPE yield is achieved after 3 hr. The most acidic sample shows the fastest loss in the mole balance and a decrease in DPE yield. The small changes in the synthesis have resulted in different structures which have different catalytic performances. The activity data is systematically compared with various characterization techniques.

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Continuous Pilot-Scale Hydroprocessing of Fast Pyrolysis Bio-oil Using Unsupported Slurry Catalysts

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Introduction

Using fast pyrolysis, lignocellulosic biomass can be converted into a bio-oil that could potentially replace fossil oils for various applications. However, the produced bio-oil contains high levels of oxygen, which needs to be removed before any advanced applications are possible. Deoxygenation can typically be achieved by processing with hydrogen, but the very reactive nature and the tendency of the oil to form coke at elevated temperatures makes hydroprocessing in conventional fixed bed reactors very challenging. An alternative process where catalyst suspended in the feedstock as a slurry, rather than closely packed in the reactor, can work as a more robust alternative. This process, referred to as slurry hydroprocessing, has in this work been studied in a pilot plant where feed is continuously fed to the reactor and product is continuously withdrawn from it. The resulting oil is an intermediate product with reduced oxygen content and improved properties that can undergo further hydrotreatment in a conventional fixed bed setup to produce renewable hydrocarbons.

Results and Discussion

A recent publication has reported results from slurry hydroprocessing of fast pyrolysis bio-oil (FPBO) and clearly showed that the hydrogen consumption can be well correlated to the properties of the resulting oil product [1]. A screening of the process conditions also revealed that the reaction temperature and concentration of catalyst in the feed are the primary factors influencing the consumption of hydrogen. The catalyst in the process was supplied as oil-soluble molybdenum octoate that formed active MoS_x catalyst particles in-situ. Repeated recovery and reuse of the in-situ activated catalyst was also demonstrated, which showed an initial minor decrease in activity, followed by stable performance. However, in-depth characterisation of in-situ activated catalyst has revealed strong effects of the surrounding matrix on its structure when compared to the catalyst formed in a pure hydrocarbon matrix [2], resulting in reproducibility issues.

Based on these results, the catalyst activation procedure was changed to an ex-situ method under optimal conditions, which could produce a highly active catalyst with high reproducibility. This refined method, in addition to the knowledge about the effect of the process variables, was utilized in a scale up of the process under optimal conditions. Using slurry hydroprocessing, followed by fixed bed hydroprocessing, 17 kg of liquid hydrocarbon product was produced from FPBO. This product was distilled into a naphtha fraction (22 wt%), a diesel fraction (67 wt%) and a distillation residue (11 wt%).

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Evolution and Electrocatalytic Performance of Au–Cu Bimetallic Microstructures on Carbon Screen-Printed Electrodes for Sugar Oxidation

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Introduction

The development of high-performance, cost-effective and easily fabricated electrocatalysts is critical for sustainable electrochemical energy conversion and sensing applications, Screen-printed carbon electrodes (SPCEs) are attractive catalyst substrates due to their low cost, disposability, and scalability to mass production, yet they remain largely underexplored in catalyst development compared to their widespread use in sensing [1]. In this work catalysts were prepared by galvanostatic electrodeposition of Cu particles on SPCEs, followed by galvanic displacement to deposit Au over Cu. The incorporation of Au into the Cu matrix to form Au-Cu bimetallic microstructures creates a synergistic effect that enhances the electrooxidation of sugars and sugar alcohols such as xylose, xylitol, sorbitol and glucose [2].

Results and Discussion

The electrodeposition process was analysed using Sand's time to elucidate the nucleation and growth mechanism, while morphological evolution was characterized using scanning electron microscopy (Fig 1). Correlating catalyst surface evolution following Sand's time behaviour with catalytic performance towards small molecules provides insight into how deposition kinetics and resulting particle morphology influence electrocatalytic activity.

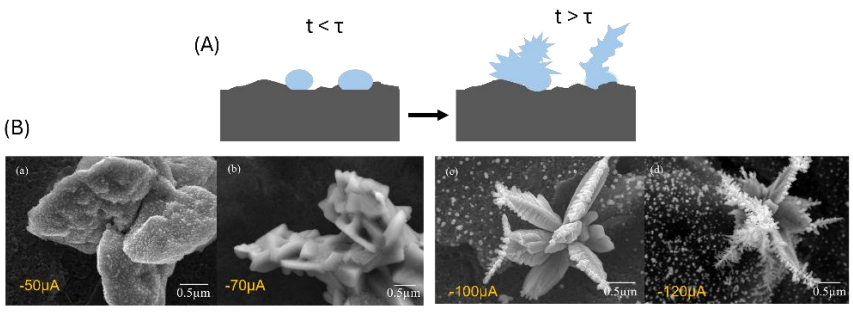

Figure 1. (A) Schematic of morphology evolution with the Sand's time. (B) SEM images of electrodeposited Cu particles at different deposition currents.

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Hydrogen production from a biomass tar model compound over active nickel–iron surfaces

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Introduction

Organic tar is an undesired byproduct of biomass gasification. Its complex chemical composition, rich in condensed aromatic compounds, leads to fouling and reactor pipe clogging, reverberating in process limitations and expensive industrial maintenance costs **[1]**. Additionally, tar has limited applications; hence, it is generally treated as waste **[2]**. Exploring the possibility of converting tar into valuable products, such as hydrogen, represents a significant step towards advancing biomass gasification, enabling improved process performance and the valorisation of its unwanted byproducts.

Results and Discussion

Naphthalene is a model compound of light tar **[3]**. We investigated its decomposition on different surfaces: Ni(111) **[4]**, Fe(100) **[5]**, NiFe(100) **[6]**, and stepped NiFe (i.e., (332), (755)). In all the studies, we opted for preliminary investigations using Temperature-Programmed Desorption (TPD) and Sum Frequency Generation (SFG) in Ultra-High Vacuum (UHV) conditions. Here, we observed that each surface saturates at a naphthalene dose of 10 L (Langmuir). In addition, we employed X-ray photoelectron spectroscopy and X-ray absorption spectroscopy to obtain key insights into surface chemistry. Overall, on all surfaces, naphthalene decomposes to produce hydrogen, making this process promising, especially for the valorisation of low-value feedstocks. Beyond the decomposition of naphthalene alone, we evaluated the influence of oxygen on the reaction at both low (1 L) and high (3 L) O_2-doses. Interestingly, we noticed that oxygen – especially on NiFe(100) – keeps the surface active even after cycling the surface up to 5 times. We assume this phenomenon is related to the co-participation of oxygen in keeping the surface clean, by decomposing both graphitic and carbide species, reaction by-products. On stepped surfaces, naphthalene's decomposition shows overall similar trends, and we plan to gather additional insights into the influence of the surface steps on the conversion. On each surface, naphthalene reacts to produce hydrogen and other by-products. We noticed that oxygen plays a crucial role in promoting the durability of the active surface, thereby laying a strong basis for investigating this reaction under more realistic conditions.

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Hydrogenation, *N*-debenzylation; so many catalysts? So many differences

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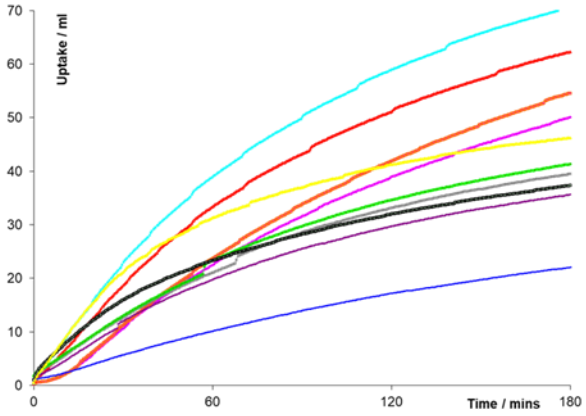
Introduction

Johnson Matthey's PGM Services business offers a wide range of Pd/C and Pd/alumina catalysts; these are extensively used for hydrogenation reactions and hydrogenolysis to remove protecting groups as last stage in pharmaceuticals synthesis. Fast reaction, selective reaction, no metal leaching are vital in these applications. The reaction solvent but especially the type of catalyst used strogly affect activity and selectivity. We are experts in matching the catalyst to the reaction that makes the synthesis work.

Results and Discussion

PGM catalysis is a mature science but each substrate presents different challenges; pharmaceutical molecules become more complex in functional group variety, molecular architecture, and contain less-familiar moieties that confer drug activity such as the cyclopropyl group. Searching for the correct catalyst for the required hydrogenation step can lead to fruitless hours without expert knowledge. The figure below is a graph of the hydrogen uptake over 3 h for a debenzylation reaction for ten Pd/C catalysts; they are definitely not the same!



An extended discussion of the results shown above as well as some examples from aromatic hydrogenation and nitro hydrogenation will be presented to show why a catalysis expert is the synthetic chemist's friend. Examples of tailored catalysts that increase conversion and selectivity will be presented with model and real substrates.

Tunable Halometallate Ionic Liquids for Low-Temperature Polypropylene Conversion

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Introduction

Plastic use generates large quantities of waste with significant environmental impact. Around 300 million tons of plastic are produced annually worldwide, yet less than 9% is recycled, while the remainder is incinerated or accumulates in landfills and natural ecosystems.[1] A large fraction of plastic production consists of polyolefins such as polyethylene (PE) and polypropylene (PP), whose chemically inert C─C backbone makes their catalytic upgrading particularly challenging and generally requires harsh reaction conditions. Recent advances, including work by Zhang and co-workers, highlight the potential of halometallates for polyolefin conversion under mild conditions.[2] In this context, this work investigates the performance of halometallate ionic liquids (ILs)as catalysts and reaction media for PP efficient cracking. The work is primarily focused on the influence of heating source (MW vs. conventional), IL Lewis acidity, cation-anion structure, and ratio.

Results and Discussion

Catalytic screening experiments were performed under mild conditions, with PP cracking conducted at 70 °C for 3 h under conventional heating. The results showed a strong dependence of catalytic activity on the IL structure. [Im]-based systems displayed the highest activity, reaching polymer mass losses of up to 15 wt%, whereas [C14]- and [Pyr]-based ionic liquids were less active. The metal (M) center also influenced performance, with M2-based halometallates slightly improving M1-based systems. Moreover, increasing the halometallate ratio significantly enhanced polymer conversion, leading to mass losses exceeding 30 wt% for [P][M2] systems, likely due to increased Lewis acidity. Ongoing work is exploring microwave-assisted heating and nanoparticle additives to further improve catalytic performance.

Cation	Anion	Ratio (Catio:Anion)	PP wt% loss
[Pyr]	[M1]	1:1	7.0
[C14]	[M1]	1:1	10.3
[Im]	[M1]	1:1	15.3
[Im]	[M2]	1:1	16.7
[C14]	[M2]	1:1	15.5
[C14]	[M2]	3:1	30.2

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Calculations of CO molecules at Steps and/or Impurities on Copper Surfaces and C2 Product Formation in Electrochemical CO2RR

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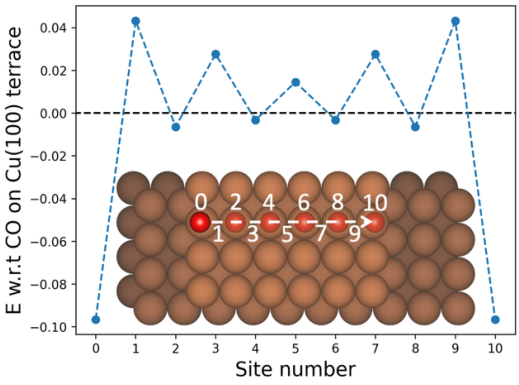
Introduction

The initial step in electrochemical reduction of CO2 molecules involves two competing mechanisms: (1) concerted H-atom and electron transfer to the C atom to generate formate which is then repelled from the negatively charged electrode, or (2) two concerted proton/ electron transfer processes to an O atom to form H2O and CO [1,2]. While formate is more stable thermodynamically, a roughly equal amount of CO is formed on Cu(111) at low overpotential due to kinetic effects but methane becomes the main product at larger bias. On the Cu(100) surface, CO admolecules can more easily dimerise, leading to production of C2 products such as ethylene, but recently it has been shown experimentally that this requires the presence of steps and/or other surface defects [3]. The reason for this remains unclear since theoretical calculations have indicated facile dimerisation on the flat Cu(100) surface. The addition of substitutional impurities of more reactive transition metal (TM) atoms in Cu surface have also been proposed as a way to increase the yield of C2 products.

Results and Discussion

DFT/BEEF-vdW calculations of surfaces with striped islands (see figure, traditional sawtooth models of steps suffer from strain build-up) and flat surfaces have been carried out of the adsorption and diffusion of CO admolecules on Cu surfaces with and without TM impurities. The TM atoms are found to bind up to 4 CO molecules and this can provide a mechanism for the leaching and subsequent vacancy/defect formation [4,5]. Also, step sites are found to provide higher adsorption energy for CO resulting in higher probability of filling adjacent step sites while this is unlikely to occur on the flat terraces unless the coverage is high. The calculated energy landscape for the binding of CO on a striped island on Cu(100) is shown in figure 1. The adsorption energy and activation energy barriers for OCCO and OCCOH formation are calculated as a function of applied voltage using a cluster of a few H2O molecules to represent the solvent supplemented by the VASPsol++ implementation of the implicit solvent and countercharge.



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Particulate matter emission properties - soot formation and oxidation – of various fuels

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Introduction

The development and research directions of internal combustion engines are increasingly driven by environmental regulations to support the transition toward a sustainable transport. A primary driver is the officially adopted Euro VII legislation, which introduces a new lower cut off limit of 10 nm for aerodynamic particle diameter [1]. This regulation not only requires the evolution of aftertreatment systems, but also a deeper understanding of particulate matter (PM) emission characteristics of fuels. This study examines and compares the PM emission properties of three fuels: Diesel (7% FAME), Biodiesel (100% FAME), RenFuel (hydrated Lignol® blend with ~10% bio-content, 15 wt% in gas oil). By defining the physical and chemical properties of the generated soot; size distribution; particle number, this research seeks to define how fuel composition affects emission profiles, how they perform compared to the minimum limit, and provides the soot-characterization data needed to develop and optimize the design of a suitable, catalyst.

Results and Discussion

Experiments were carried out using a Diesel Particulate Generator (DPG) across four soot loading modes (1, 2, 5, and 10 g/hr) to examine the fuels under different engine loads. Upstream online and offline measurements were conducted before the Diesel Particulate Filter (DPF). Real-time particle size distributions were performed using Engine Exhaust Particle Sizer (EEPS), while Aerodynamic Particle Counter (APC) was used to monitor PN10 and PN23 concentrations. TGA, SEM-EDS, TEM analysis were carried out to gain valuable information about the structure, morphology, and oxidizing behavior of the soot particles. Analysis of the EEPS data supports that the trends follow an expected behavior, as the soot load increases, a shift in the diameter, from nucleation-mode to accumulation-mode particles, is observed across all fuel types. APC measurements in each case reveal that PN10 were higher than PN23, reflecting on the presence of fine particles in the region of 10-23 nm. Meanwhile the highest amount of soot was produced by RenFuel, Diesel, and Biodiesel respectively, which can be supported by the structural and compositional differences in the fuels. Overall, determining the characteristics, morphological properties of the particles, it helps to provide a blueprint to tailor a oxidation catalyst for efficient soot and filter regeneration.

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Comprehensive understanding of the homogeneous thiamine-catalyzed 5-HMF self-condensation reaction mechanism

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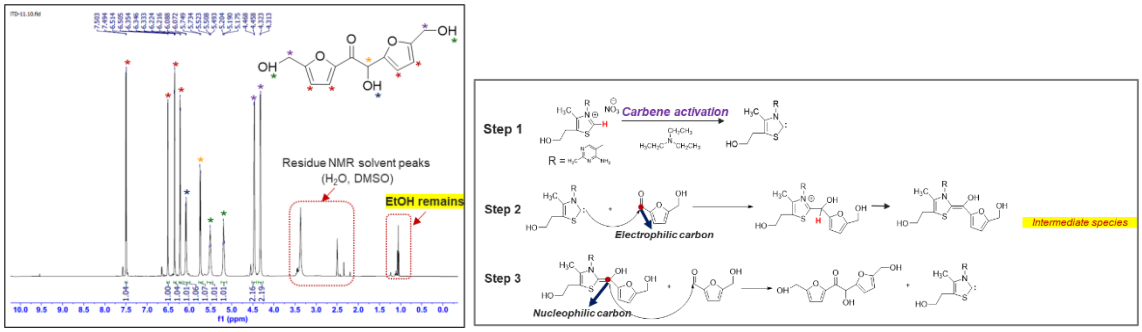
Introduction

As fossil resources continue to decline, biomass is increasingly regarded as a sustainable alternative feedstock for biofuel production and the synthesis of high-value biobased chemicals [1-3]. In this context, 5-hydroxymethylfurfural (5-HMF) stands out as a key platform molecule for renewable fuel and fine chemical applications. Beyond the conventional conversion routes for 5-HMF, recent years have witnessed substantial advances in carbon-chain elongation strategies for biomass-derived furanic oxygenates, particularly in the aldol self-condensation of 5-HMF [4, 5]. From a theoretical standpoint, the absence of an α-hydrogen in the molecular structure of 5-HMF prevents it from undergoing self-condensation to form 5,5'-bis(hydroxymethyl) furoin. However, recently, Liu *et al.* [6] demonstrated that well-defined N-heterocyclic carbenes (NHCs) can effectively catalyze the self-condensation of 5-HMF to produce DHMF. Building on this catalytic concept, thiamine nitrate was employed in this study as an affordable and efficient homogeneous catalyst for the self-condensation of 5-HMF. Our approach enabled the production of high-purity DHMF and provided a comprehensive understanding of the underlying catalytic reaction mechanism.

Results and Discussion

The desired product, DHMF, was successfully produced via self-condensation of 5-HMF catalyzed by $VB1.NO_3$, and its molecular structure was verified by ^{1}H-NMR analysis. Furthermore, based on GC-MS interpretation, a plausible reaction mechanism was proposed.



Scheme 1. ^{1}H NMR spectrum of the DHMF product and the proposed mechanism for VB1-catalyzed 5-HMF self-condensation.

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Revisiting pressure modulation as a method to increase reaction rates

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Introduction

Catalysts enable the production of fuels, chemicals, and materials indispensable to modern society. As global demands for resources increase, further improvements in catalytic performance are required. However, many conceptual and technical challenges in optimising catalytic processes remain. A significant number of industrial chemical processes operate under steady-state conditions, yet catalysts in industrial reactors restructure and deactivate indicating that they are not static entities and respond to their environment. Given the intimate relationship between catalyst structure and catalyst activity, we propose an alternative approach that exploits this dynamic nature by using oscillations in reactant feed compositions to enhance reaction rates.

Results and Discussion

Herein we revisit a more direct and industrially accessible form of dynamic operation: oscillation of reactant partial pressures. Using CO oxidation over a Pd/Al_2O_3 catalyst, we demonstrate that the periodic oscillation of CO and O_2 partial pressures in the reactant feed can enhance catalytic activity up to three-fold relative to the steady-state maximum under otherwise identical conditions (Fig. 1). Additionally, measurable activity can be induced under conditions where no steady-state conversion is observed. Numerical simulations of the experiments find a rate enhancement under oscillatory conditions, demonstrating that solely kinetic effects can enhance rates. However, the simulations consistently underpredict the degree of rate enhancement implying more complex phenomena is involved.

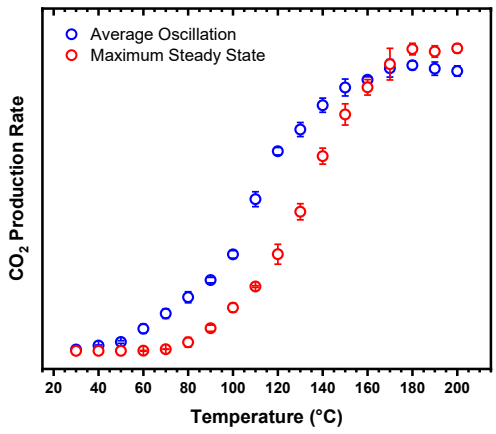

Fig. 1. Maximum steady-state (red) and average oscillatory (blue) rates measured for CO oxidation over Pd/Al_2O_3 as a function of temperature.

The numerical model and experimental in situ diffuse reflectance IR spectroscopy demonstrate that CO surface coverages oscillate with external modulation. We rationalise that the observed rate enhancement is partially caused by a decoupling between gas-phase composition and surface coverage. However, we also conclude that more complex phenomena such as surface reconstructions or metastable surface states that are inaccessible under steady-state conditions are at play. By demonstrating that the oscillation of a pre-existing process variable can bypass steady-state maxima without changing catalyst formulation or reactor design, this work reframes non-steady-state operation as a practical strategy for enhancing catalytic performance in mature industrial systems.

Support-Dependent Platinum Deposition on Low-Dimensional Materials by Atomic Layer Deposition

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Introduction

Low-dimensional (LD) materials are promising catalyst supports because of their high surface area, abundant edge sites, and tunable metal-support interactions. Beyond graphene-based systems, non-carbon LD materials such as transition metal dichalcogenides (TMDs) and transition metal phosphorus trichalcogenides (TMPTs) are particularly attractive due to their layered structures, which facilitate nanoparticle anchoring and can modify catalytic behavior. Platinum (Pt) is one of the most effective catalytic metals, but its high cost makes efficient utilization essential. In this study, atomic layer deposition (ALD) was employed to fabricate Pt clusters on TMD and TMPT supports and to examine the resulting Pt-support interactions for the rational design of highly efficient Pt-based supported catalysts.

Results and Discussion

Platinum clusters were deposited on TMD and TMPT supports by ALD, a method that offers precise control over metal loading, dispersion, and metal–support interactions. Morphological and chemical information was obtained from identical catalyst regions using a correlative spectro-microscopy approach. Scanning electron microscopy (SEM) showed that the LD surfaces were uniformly covered by Pt, while energy-dispersive X-ray spectroscopy (EDS) mapping verified the presence of Pt along with the principal elements of the LD materials. The same catalyst sites were subsequently analyzed using SEM and atomic force microscopy (AFM) in a correlative AFM–SEM configuration, allowing direct comparison of morphology and surface topography. Simultaneously, conductivity maps were recorded together with the topographic signal using a biased conductive AFM probe, yielding complementary understanding into the local electrical properties of the catalyst.

Taken together, the results indicate that Pt interacts more strongly with TMDs than with TMPTs, as evidenced by the higher Pt loading and the more homogeneous conductivity distribution observed for the former. This difference is likely associated with the oxidative environment of the Pt ALD process, which may induce at least partial surface oxidation of TMDs and thus facilitate Pt nucleation. By contrast, Pt on TMPTs did not form readily detectable clusters, indicating either the presence of highly dispersed Pt species or weaker anchoring on the thin flakes. Notably, conductivity mapping showed that Pt was localized mainly at the edges of the TMPT flakes, which could be beneficial for catalytic performance.

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Acknowledgements

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Scale-Up-Oriented Vanadium Catalysts for Efficient Furfural-to-Maleic Anhydride Conversion

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Introduction

Maleic anhydride is an important chemical intermediate used in the production of unsaturated polyester resins, alkenyl succinic anhydrides, and 1,4-butanediol for engineering plastics and specialty polymers.[1] Global output amounts to several million tonnes annually and continues to expand, driven primarily by demand from the construction and automotive sectors. As production volumes consequently increase, interest in more sustainable manufacturing routes is gaining momentum. To date, industrial production is dominated by the catalytic oxidation of butane and, to a lesser extent, benzene.[2] Although biobased routes from furanic feedstocks have been demonstrated at laboratory and pilot scales, they have not achieved commercial maturity due to economic and efficiency limitations.[3] At the same time, the growing emphasis on renewable carbon utilisation and chemical industry defossilization is stimulating renewed efforts to develop biobased pathways for the sustainable production of bulk and specialty chemicals, such as maleic anhydride.

Results and Discussion

The selective oxidation of furfural to maleic anhydride can be achieved using vanadium oxide catalysts, the same class employed for industrial butane oxidation. However, commercially deployed catalyst systems are optimized for butane rather than furanic substrates, which exhibit higher reactivity and introduce more complex side reactions, including cycloaddition pathways and resinification phenomena.[4] While the general principles governing catalyst performance are broadly understood, catalysts must be specifically reformulated and optimized to enable efficient and stable industrial processing of furfural and other furanic feedstocks.[5]

Our studies demonstrate that catalyst performance strongly correlates with key chemical and textural properties, including the presence of structural modifiers, support type and porosity, and the efficiency of catalyst carriers and fillers in heat propagation. Vanadium-based catalysts modified with phosphorus achieve near-quantitative selectivity at 60-70% conversion, compared to 85% selectivity at full conversion for unmodified systems. Product distribution is strongly influenced by the choice of carrier material, with titania-based catalysts yielding complete oxidation, whereas alumina supports exhibit little cooperative catalytic contribution. Furthermore, support porosity governs mass and heat transport, influencing the accessibility and distribution of active sites. As a result, resinification reactions intensify with increasing surface area, approximately doubling when moving from low/intermediate to high-surface-area supports. Fillers exert a similar influence: efficient heat dissipation around active components – achieved, for example, by incorporating thermally conductive ceramic fillers – moderates overoxidation and degradation pathways while extending catalyst lifetime. Understanding the delicate trade-off between these features has enabled the development of an improved catalytic system, with enhanced selectivity and stability, suitable for scale-up and evaluation.

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Electrochemical Conversion of Lignin on Metals and Metal Oxides

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Introduction

Lignin is an abundant biopolymer in plants and trees and is produced in the paper industry as a by-product. Many studies nowadays are trying to come up with a process that can transform this biomolecule into value-added chemicals (valorization). A technique that is receiving increasing attention is electrochemical conversion due to its potential to offer high selectivity, high atom efficiency and renewable energy [1]. In the present work, computational modeling based on density functional theory (DFT) and machine learning potentials is used to gain understanding about the mechanisms of electrocatalytic lignin conversion. This includes investigations of the adsorption of a model lignin molecule onto catalysts' surfaces and studies of the depolymerization mechanisms of these molecules.

Results and Discussion

We first investigated the adsorption energies of the lignin model (Hg-Ac) (Figure 1a) on copper oxide-based catalyst and compared to experimental data [2]. Favorable electron-sharing interactions are found between aromatic rings and oxygen atoms on surfaces (Figure 1b). We also find that dispersion forces are important drivers of surface adsorption and that adsorbate-adsorbate interactions play a crucial role in promoting a surface-parallel to perpendicular adsorption mode with increasing coverage.

In a parallel work, we systematically study ionization potentials, electron affinities and bond dissociation energies for a large set of model lignin dimers. The results reveal relevant trends in the effect of substituents and electronic properties in the cleavage of interunit C-C bonds under oxidative or reductive conditions. This lays the foundation for future studies on electrochemical depolymerization reactions on surfaces of metal and metal oxide catalysts.

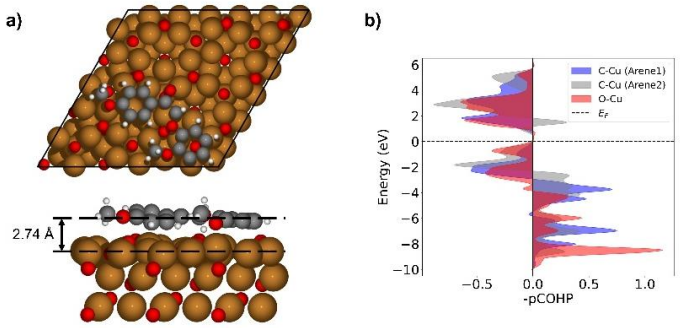

Figure 1.: Most stable configuration for the adsorption of Hg-Ac on $Cu_2O(111)$. A COHP plot describing interactions between the aromatic rings and lignin oxygen atoms is displayed.

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Photo-based analysis of technical catalysts for clean air applications

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Introduction

Structured coated catalysts play a key role in industry because they combine a high surface-to-volume ratio with low pressure drop and excellent mechanical and thermal stability.[1] One of their most important application is the clean air sector. For reducing methane and other hydrocarbon emissions from mobile and stationary sources, Pd-based catalysts are among the best-performing systems.[2] However, Pd is scarce and expensive, making an efficient and optimized catalyst design indispensable. Typically washcoating, in which a slurry containing the active species is deposited onto metallic or ceramic honeycomb structures, is applied. To ensure efficient catalyst utilization, a highly uniform coating is desirable. The resulting coating quality can be assessed using methods such as X-ray tomography. However, these techniques, often image only subsections of the samples, making lab-scale characterization desirable.[3]

Results and Discussion

This work introduces a newly developed characterization method for washcoated catalysts (here Pd/Al_2O_3) using an in-house-developed, photo-based analysis. Changes in coating thickness measured by this approach are validated by complementary and established characterization techniques, including X-ray microtomography (µ-CT). To systematically induce variations in the catalytic layer, preparation parameters, such as ball-milling, and binder concentration (wt.%) are varied. The washcoated catalysts were then tested for their CH_4 oxidation activity. The photo analysis identifies clear variations in coating thickness as a function of milling rate. This trend is consistent with the results obtained by µ-CT (Fig. 1). Also, the catalytic activity profiles are affected by changes in layer thickness: Spatially resolved actvitiy measurements show that by optimized milling intensity, particularly the activity at the inlet could be improved. This suggests the reduction of mass-transport limitations by tuning of the catalyst layer. Finally, the integral CH_4 oxidation activity was investigated as function of milling intensity and binder concentration using the photo analysis showing a correlation with the average open channel area. Such rapid feedback during the manufacturing of structured, industrially relevant catalysts is highly desirable. The work offers a practical, lab-based way to characterize washcoated catalysts. This approach enables streamlined washcoating processes and supports the development and production of multilayer coatings.

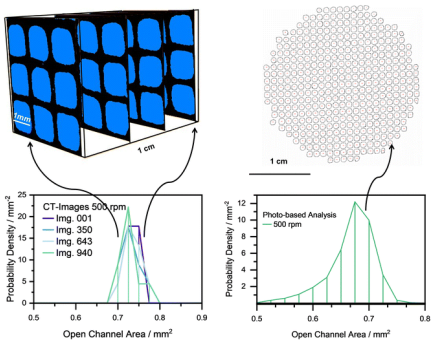

Fig. 1 Comparison of open channel area (OCA) derived from µ-CT and photo-based analysis.[3]

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Alkaline earth metal modified Ru/ZrO_2 for depolymerization of nylon

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Introduction

The lack of efficient recycling and upcycling technologies has made post-consumer plastic waste a major global environmental challenge. Nylon-based materials, such as carpet fibers, account for approximately 4% of total waste in the United States and pose a significant recycling problem due to their high chemical stability, which often leads to the production of lower-grade recycled materials [1]. Recently, catalytic hydrogenative depolymerization using noble metal catalysts has emerged as a promising strategy for the upcycling of polymers, including nylons [2]. Among various catalyst supports, zirconia (ZrO_2) is widely used, owing to its thermal stability, tunable surface properties, and cost-effectiveness. However, the systematic modification of ZrO_2 for nylon-6 depolymerization has not been investigated, leaving its potential to enhance catalytic performance largely unclarified.

Results and Discussion

Our studies reveal that the depolymerization of nylon-6 to caprolactam proceeds through hemiaminal intermediates, followed by C-N bond cleavage and intramolecular cyclization. The depolymerization activity strongly depends on the metal active sites and their electronic environment. In particular, the basicity introduced by alkaline-earth metal modifiers can alter the electron density of the supported metal, thereby influencing catalytic performance. To systematically tune these electronic and basic properties, SrO was deposited onto ZrO_2 at varying loadings, followed by the addition of 1 wt% Ru. A series of Ru/SrO–ZrO_2 catalysts were then evaluated for nylon-6 hydrogenative depolymerization. XRD analysis (Figure 1c) indicates that monolayer SrO coverage is achieved at 5-10 wt% loading, while higher loadings (>10 wt%) lead to the formation of a 3D $SrZrO_3$ phase. Monolayer SrO coverage enhances Ru dispersion and increases electron donation to the metal sites. CO_2-TPD measurements (Figure 1b) further confirm that surface basicity increases with SrO loading up to 10 wt%, indicating progressively stronger electron-donating characteristics of the support. As a result, the caprolactam yield nearly doubles compared to unmodified Ru/ZrO_2 (figure1a). Overall, this study highlights that tuning catalyst properties via SrO-modified ZrO_2 supports can substantially improve caprolactam recovery, providing a promising pathway toward sustainable closed-loop recycling of nylon-6.

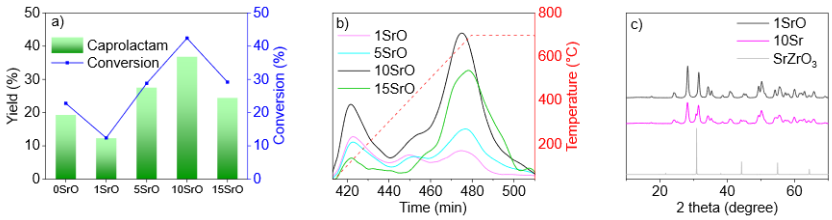

Figure 1.a) Yield and conversion for nylon-6 depolymerization, b) CO-TPD profiles of catalyst, and c) XRD patterns of catalyst

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Na decorated Mn-Zn-Fe spinel-derived catalysts for CO_2 hydrogenation to light olefins

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Introduction

Alkali-modified iron catalysts are widely used for CO_2 hydrogenation to light olefins with minimal methane byproducts, where CO_2 is first converted to CO over Fe_3O_4 via RWGS and then to hydrocarbons over Fe_5C_2 via FTS [1]. While dynamic Fe_3O_4–Fe_5C_2 cooperation ensures high olefin selectivity, alkali dopents (Na_2CO_3) can also accelerate irreversible oxidation of Fe_5C_2 to Fe_3O_4, causing deactivation and increased CO selectivity [2]. To address this issues, we synthesized a Fe–Zn–Mn spinel catalyst via solvothermal method and confirmed its stability and high olefin selectivity through accelerated deactivation tests and characterization.

Results and Discussion

Fe-based spinel catalysts (Na-$Zn_{0.5}Mn_{0.5}Fe_2O_4$) were synthesized via a one-step solvothermal method using ethylene glycol as solvent. Fresh catalyst were activated under H_2 (3% in Ar, 400 °C, 6 h) and syngas (3% H_2 + 1.5% CO in Ar, 350 °C, 6 h), then mixed with Na_2CO_3 (n_{Fe}:n_{Na} = 1:0.02) powder, pelletized, crushed, and sieved. Fresh and spent catalysts were evaluated in CO_2 hydrogenation under an accelerated deactivation protocol: 0.7 g catalyst, GHSV 6000 → 1000 → 6000 Nml·g^{-1}·h^{-1}, H_2: CO_2 = 3:1, 325 °C, 20 bar. Products were analyzed online by GC. Catalyst were characterized by XRD, TPR, Mössbauer spectroscopy, and HRTEM. The results indicated that the Na_2CO_3-modified spinel catalyst (Na-$Zn_{0.5}Mn_{0.5}Fe_2O_4$) was more stable than Na_2CO_3-modified pure iron oxide catalyst (Na-Fe-RS). Even after accelerated deactivation, Na-$Zn_{0.5}Mn_{0.5}Fe_2O_4$ showed minimal changes (CO selectivity increased by 27.9%), whereas Na-Fe-RS lost the olefins' selectivity seriously, with CO selectivity increased by 119% (**Figure 1**). Their structure characterization showed that a strong Fe–Zn or Fe–Mn interactions in spinel catalysts modify the reduction, carburization, and oxidation of iron species, forming FeO in fresh catalysts that convert to stable Fe_5C_2 during reaction rather than oxidizing to Fe_3O_4. This phase transition preserves high catalytic activity of Na-$Zn_{0.5}Mn_{0.5}Fe_2O_4$, and enhances its stability in CO_2 hydrogenation to light olefins.

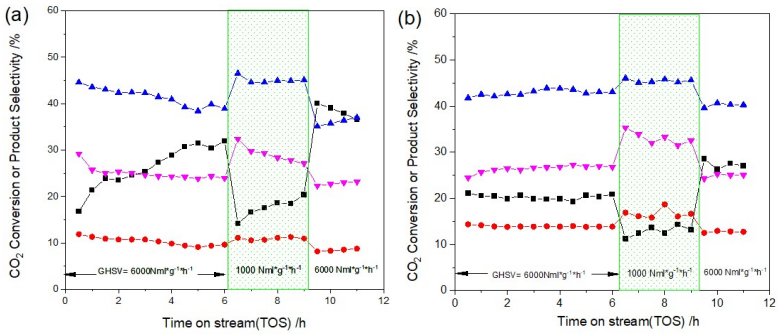

Figure 1. CO_2 hydrogenation over reference catalyst Na-Fe-RS (a), and spinel-derived catalyst Na-$Zn_{0.5}Mn_{0.5}Fe_2O_4$ (b). Accelerated deactivation protocol: 0.7 g catalyst, GHSV 6000 → 1000 → 6000 Nml·g^{-1}·h^{-1}, H_2: CO_2 = 3:1, 325 °C, 20 bar.

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Impact of La/Ce doping on the structure and CO_2 methanation performance of ilmenite-type $NiTiO_3$

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Introduction

Nickel titanate ($NiTiO_3$) having ilmenite-type structure is a thermally stable mixed oxide, the structural and electronic properties of which can be tuned through cation substitution [1]. Pure $NiTiO_3$ typically exhibits low surface area, motivating the exploration of compositional modifications to adjust its physicochemical behavior [1,2]. Rare earth cations such as lanthanum (III) (La^{3+}) and cerium (IV) (Ce^{4+}) are known to induce lattice distortion, modify vibrational modes, and influence defect chemistry of the crystalline structure. These effects can alter the catalytic response of $NiTiO_3$ [2]. In this study, La- and Ce-doped $NiTiO_3$ was synthesized via the Pechini sol–gel method, a route that enables homogeneous cation distribution and controlled phase formation [3]. The objective of this work is to investigate on how the incorporation of La and Ce affects the structural and bonding properties of $NiTiO_3$, and to relate these changes to materials catalytic performance in CO_2 methanation.

Results and Discussion

X-ray diffraction (XRD) confirmed the formation of the ilmenite-type structural $NiTiO_3$ phase for all compositions. Specifically, La and Ce doping produced a systematic reduction in crystallite size and changes in peak intensity indicative of lattice modification. Raman and FTIR analyses revealed shifts and variations in the intensity of characteristic vibrational modes. These observations are consistent with modifications in the local bonding environment and the structural stabilization induced by dopant incorporation into $NiTiO_3$.

Prior to catalytic testing, all samples were pretreated under 10% H_2 flow at 500 °C for 20 min. Under methanation conditions at 300 °C, the undoped $NiTiO_3$ sample exhibited the highest CO_2 conversion of approximately 60% and CH_4 selectivity about 99%, maintaining stable performance over the 40-minute test period. Increasing the La or Ce contents resulted in a systematic decrease in activity, with higher dopant loadings leading to progressively lower conversion values. Among the doped systems, Ce-containing samples consistently outperformed the La-modified samples, although both remained less active than the undoped material. $NiTiO_3$ reached the maximum conversion of 76% at 350 °C, while 1% Ce-doped $NiTiO_3$ achieved only 65% at a higher temperature of 444 °C. These results show that adding La and Ce significantly alters the catalytic behavior of $NiTiO_3$, reducing its activity and shifting the temperature of maximum conversion.

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Unraveling the surface structural dynamics of Ir(100) under realistic conditions for the partial oxidation of methane (POM)

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Introduction

Since the industrial revolution, methane is responsible for the 30% of the temperature rise.[1] On the other hand, methane is a precious resource and can be used to obtain added value products, and catalytic partial oxidation of methane (POM) is widely studied.[2] Due to the strength of the C-H bonds, and the complexity of the reaction, the activation of methane at low temperatures with high selectivity towards the product remains a challenge.[3] It has been shown that the controlled oxidation of iridium leads to the coexistence of (100), (101), and (110) oriented epitaxies of the iridium oxide.[4] To date, an investigation of the structure-activity correlation of these different epitaxies under realistic conditions for the POM is still missing but would result in valuable insight for the design of improved POM catalysts.

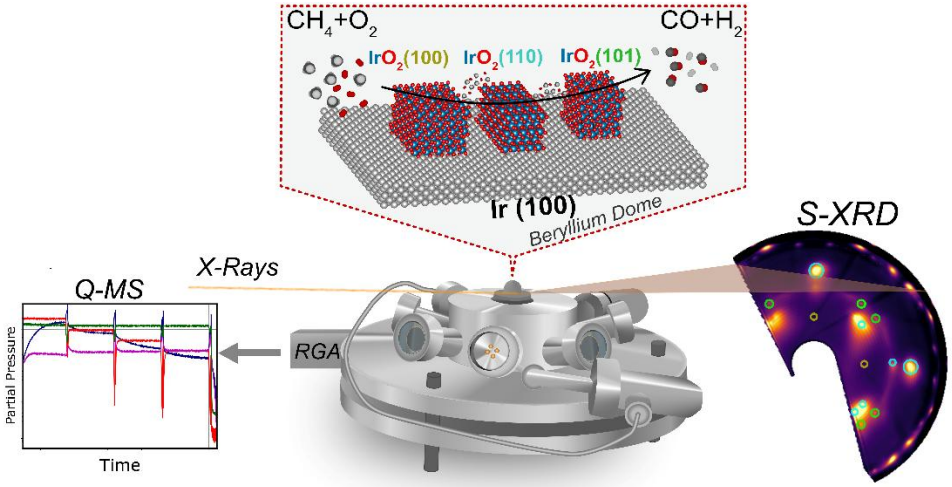

***Figure 1**:Illustration of the experimental set-up combining SXRD and QMS.*

Results and Discussion

By combining synchrotron-based Surface X-Ray Diffraction (SXRD) at beamline SixS (Synchrotron SOLEIL) with online Quadrupole Mass Spectroscopy (Q-MS) we could perfom an *operando* investigation of the Ir(001) surface structural dynamics during POM as a function of the feed gas composition. We observed the three different iridium oxide epitaxies, where our data indicate that the presence of IrO_2(110) might be beneficial for CH_4 activation and CO production likely due to the (110) facets' coordinatively unsaturated sites (CUS) as discussed in the literature.[5]

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Operando High Energy Surface X-ray Diffraction study of Fe doping on Co(0001) during OER

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Introduction

The oxygen evolution reaction (OER) is a key reaction in several energy-related applications, including water splitting. However, OER suffers from sluggish reaction kinetics which necessitates the use of a suitable catalyst. In the field of alkaline electrolytes, research has reported that cobalt (Co) based electrocatalysts and its oxide (CoO, Co_3O_4) and (oxy)hydroxide ($Co(OH)_2$, CoOOH) phases exhibit promising catalytic properties [1]. In combination with iron (Fe), which is known to enhance the catalytic activity of transition metals, Fe-Co electrocatalysts have emerged as a promising alternative to noble metal electrocatalysts in OER anode materials [2,3]. However, several aspects are still under debate and a better understanding of their time-resolved atomic structure and chemical composition under reaction conditions is needed.

Results and Discussion

Our synchrotron studies on a Co(0001) single crystal model catalyst, performed at Petra III/P07-DESY in an electrochemical cell, allowed the combination of Surface Optical Reflectance (SOR) [4] and High Energy Surface X-ray Diffraction (HESXRD) [5,6] (Fig 1.a). We followed the *in-situ* Fe-electrodeposition on the Co(0001) single crystal (Fig 1.b) and could elucidate the Fe effect on the complex Co(0001) surface structure and its catalytic activity. Further studies using ex-situ X-ray photoelectron spectroscopy (XPS) surprisingly revealed an Fe-ED gradient with a higher amount of Fe in the bulk, which correlates with the Co(0001) crystal truncation rod (CTR) positions for different Fe doping levels (Fig 1.c).

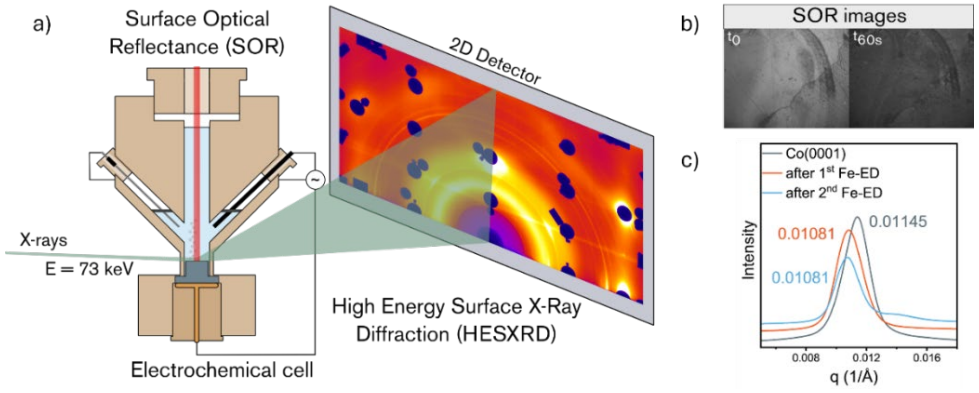

Figure 1. a) Experimental setup, b) SOR images before/after Fe-ED, c) in-plane CTR positions for various Fe doping levels.

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VWTi NH3-SCR catalyst applied to Hydrogen Internal Combustion Engines (HICE)

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Introduction

Motivated by the urgent need to accelerate the transition toward sustainable and near-zero-emission transportation [1], the use of hydrogen as a fuel in internal combustion engines can be considered a viable source to address this challenge in the heavy-duty transport sector. Although there are advantages to use hydrogen as a fuel, such as zero carbon emissions and superior combustion properties [2], one drawback is the production of NOx, that can be similar to traditional fuels, due to operational factor such as engine load, speed, combustion-system design and injection design [3,4].

In order to mitigate nitrogen oxides (NOx) emissions, this project aims to study the application of one of the most established abatement technologies currently applied in engine aftertreatment: ammonia-based selective catalytic reduction (NH_3-SCR) [5]. The NH_3-SCR catalyst investigated for this application is vanadia-tungsta supported on titania (V_2O_5-WO_3-TiO_2), one of the the most commonly used in the heavy transportation sector, due to high activity, thermal stability, and resistance to poisoning by SO_2.

Results and Discussion

In this work, 2 wt% V_2O_5 7 wt% WO_3 on TiO_2 catalysts are synthesized via incipient wetness impregnation (IWI) method. The powder catalyst is used to washcoat cordierite monoliths.

The denitrification activity of the washcoated monolith is tested using a synthetic gas bench (SGB) reactor to emulate the potential engine-out gas composition of hydrogen internal combustion engine (HICE), with relevant NOx level and high water content. The comparison between dry and various water concentrations in the exhaust gas is assessed at low and high temperatures. Further, the effect of variations of alpha (NH_3/NO_x) on SCR reaction is also assessed.

The impact on the catalyst material of exposure to high humidity will be conducted using BET, XRD, CO chemisorption and NH_3-TPD measurements.

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A Computational Study of Dilute Alloy Cu–Pd Nanoparticles for Selective CO_2 Electroreduction

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Introduction

Electrocatalytic CO_2 reduction (eCO_2R) provides a potential pathway for storing renewable electricity in chemical bonds while producing value-added fuels and chemicals. Using density functional theory calculations under electrochemical conditions, this work investigates the catalytic performance of dilute Cu–Pd alloy nanoparticles (1–5% Pd) for eCO_2R toward multicarbon products such as ethanol and ethylene. The results are compared with experimental data from the Luneau research group, revealing atomic-scale reactivity trends that support the experimentally observed Pd concentration optimum for high multicarbon selectivity.

Results and Discussion

Reactivity trends for model Cu–Pd alloy structures were investigated by computing adsorption energies of key eCO_2R intermediates (CO, C, and OH) on surfaces with varying structures and compositions. These adsorption energies were mapped onto established selectivity maps (Figure 1),[1] indicating that lower Pd contents shift multicarbon selectivity into an overpotential window consistent with typical eCO_2R operating conditions at technologically relevant current densities.[2] These conclusions compare well with experimental trends and are consistent with calculated reaction barriers for selectivity-governing reaction steps, including: (1) $CO_2 + (H^+ + e^-) \rightarrow$ COOH or HCOO, and (2) $CO + (H^+ + e^-) \rightarrow$ COH or HCO. These findings highlight the potential of dilute alloy design strategies for improving selectivity in electrochemical CO_2 reduction.

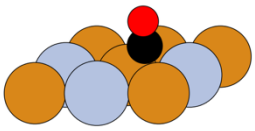

Figure 1a: Random alloy surface with an adsorbed CO molecule.

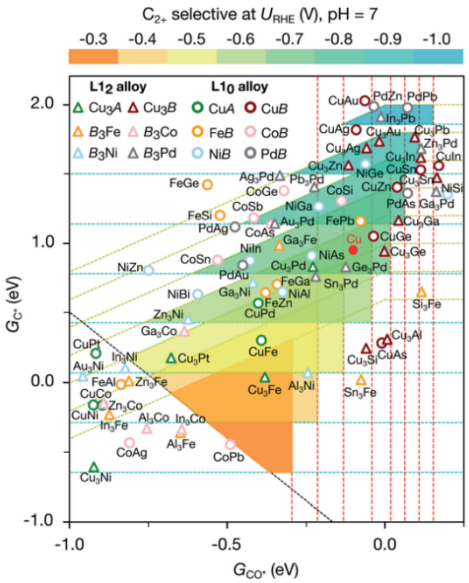

Figure 1b: Selectivity map toward multicarbon products for eCO_2R based on CO and C adsorption energies.[1] Alloy compounds are placed on the map based on computed adsorption energies. The coloured selectivity region changes with applied overpotential (top-most colour scale).

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Direct oxidation of methane to methanol over Cu-ZSM-5 catalysts

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Introduction

The selective direct oxidation of methane to methanol (DOMTM) remains a major challenge in heterogeneous catalysis. Methane has a strong C-H bond (439 kJ mol^{-1}), which makes its activation under mild conditions difficult [1]. At the same time, methanol is more reactive than methane and is easily overoxidized. As a result, achieving both high methanol productivity and high selectivity is still demanding. Despite many studies on this reaction, there is a limited systematic analysis of how key parameters such as copper speciation and dispersion, and Brønsted and Lewis acidity balance, simultaneously affect catalytic performance. Most reports evaluate these factors separately, making it difficult to establish clear structure-activity relationships. In this work, Cu-ZSM-5 was used as a model catalyst to quantitatively assess these effects in DOMTM using H_2O_2 as an oxidant at 50 ºC. Catalysts with different SiO_2/Al_2O_3 ratios and copper incorporation methods were prepared to vary copper dispersion and acidity.

Results and Discussion

The relationships observed in Fig. 1 support the existence of a positive effect between Brønsted acid sites (Al–OH–Si) and Lewis acid sites associated with isolated Cu^{2+} species (identified from UV-Vis-DRS and H_2-TPR). Catalysts exhibiting well-dispersed Cu species as 0.6Cu-ZSM-5-30 (Fig. 1a) and a balanced acidity with a BAS/LAS ratio between 1.2 and 1.7 (Fig. 1b), maximize the methanol productivity. This indicates that neither type of acid site alone is sufficient for effective methanol synthesis. Notably, catalysts dominated by acid sites (BAS/LAS > 10) or only Lewis acid sites (BAS/LAS → 0) show negligible methanol productivity.

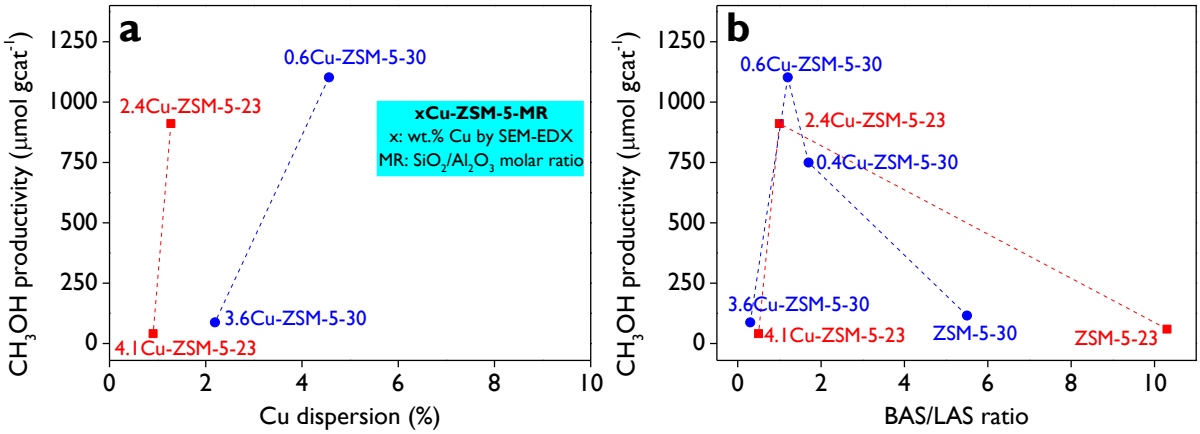

Fig. 1. CH_3OH productivity as a function of **a)** Cu dispersion and **b)** Brønsted to Lewis acidity ratio. **Reaction conditions:** 30 bar CH_4 at room temperature, 0.5 mol L^{-1} H_2O_2 in deionized water, 70 mL total volume, 150 mg catalyst, 50 ºC, 1000 rpm.

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Acknowledgments: The authors acknowledge the Research Council of Finland for funding through the project No. 361444.

Elucidating adsorbate-surface electronic coupling with ultrafast spectroscopy and a first-principles hybridization function

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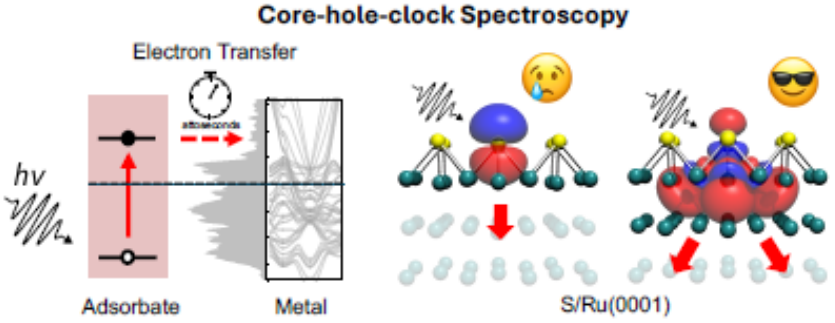
Introduction

Ultrafast spectroscopies provide a unique way of understanding the electronic coupling between adsorbate and surface. In the core-hole-clock method, soft x-rays promote an adsorbate core electron to a valence state above the Fermi level. The electron then delocalizes into the surface with a measurable lifetime, determined by the strength of coupling between adsorbate and surface orbitals. While lifetimes have been measured in the attosecond domain[1], aspects of these measurements remain unresolved, such as the origin of energy dependence in their spectra.

In this work we present a first-principles approach, based on Density Functional Theory, to calculate the ultrafast electron transfer from core-excited adsorbates to surfaces. A key aspect of our approach is the hybridization function, a weighted density of states which gives the coupling between adsorbate frontier orbitals and the surface over the energy scale[2].

Results and Discussion

Upon careful benchmarking of our scheme, we find quantitative agreement with experimental lifetimes in the attosecond domain, comparing to prior measurements in Ar, CO, S/Ru(0001) and Black Phosphorous. The approach allows us to infer the nature of the excited state preprared in these measurements, which, for S/Ru(0001), is delocalized and not atomic as was previously supposed. The method elucidates the origin of energy dependence in these measurements, and offers a means of quantifying the electronic coupling between adsorbate and surface, as well as between neighboring adsorbates.



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Effect of Pretreatment on Active Fe-phase in K-Fe/C Catalysts for CO_2 Hydrogenation

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Introduction

To convert CO_2 and H_2 into higher hydrocarbons via CO_2 hydrogenation through the consecutive reactions reverse Water-Gas Shift (rWGS) and Fischer-Tropsch Synthesis (FTS) with an iron catalyst, literature suggest that χ-Fe_5C_2 is the active phase responsible for chain growth[1]. The K-Fe/C catalyst for this studies, inspired by Tafjord et. al. [2], has a carbon-support derived from alginate and has Fe_3O_4 as Fe-phase in the fresh catalyst. The objective of this study is to form higher hydrocarbons, which we aim to achieve by pretreating the catalyst in various environments to produce χ-Fe_5C_2.

Results and Discussion

The catalyst was *in-situ* exposed to four different pretreatments followed by CO_2 hydrogenation in the *In-Situ* Mass Analyzer [3]. During pretreatment in H_2, the catalyst mass decreases, while the mass increases when exposed to CO. These phenomena are interpreted to relate to Fe_3O_4 reduction, and Fe-carburization, respectively. During the reaction, catalyst mass increase was observed indicating coke formation or carburization. However, during 110 hours time on stream CO_2 conversion and FTS activity increased for H2-350, H2-400 and H2-CO, showing that carburization slowly continues during reaction. Figure 1 shows the results of *in-situ* Mössbauer Spectroscopy where the catalyst was exposed to the same pretreatments and reaction conditions as in the ISMA. After reduction in H_2 the catalyst is not fully reduced and contains a mixture of Fe and Fe-oxides. In contrast, pretreatment in CO forms a significant amount of Fe-carbide. After reaction at 280 °C it can be observed that Fe-carbide species develop for H2-400, while for H2-350 this occurs at 340 °C. These results align with the CO_2 conversion and selectivity towards FTS products. At 340 °C, the lowest conversion (16%) and selectivity towards C_{2+} (4.6%) was observed for H2-350. While the highest conversion was observed for CO-270 (26%) and H2-CO (24%), with a selectivity towards C_{2+} of 32% and 36%, respectively. However, CO-270 showed a selectivity of 30% towards undesirable CH_4.

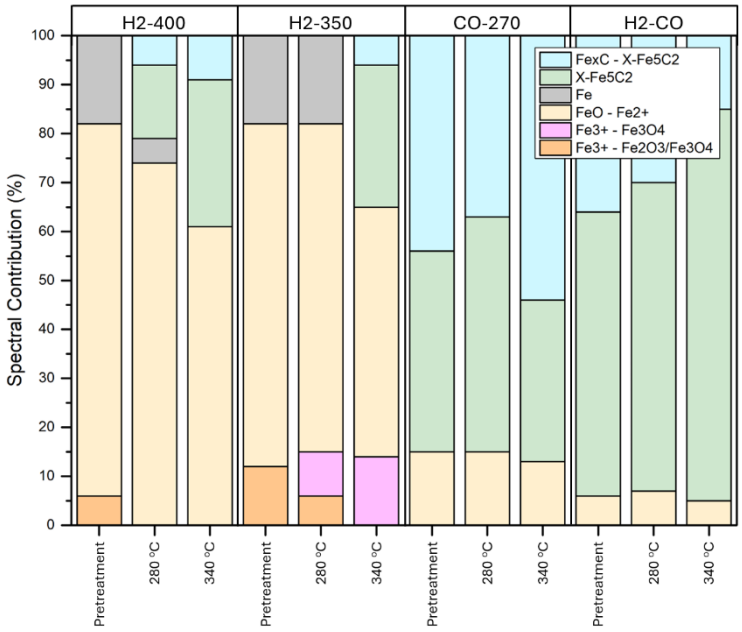

Figure 1. In-situ Mössbauer spectroscopy data after four different pretreatments (H_2, 400 °C, 3 bar and 4 hours), H2-350 (H_2, 350 °C, 3 bar and 4 hours), CO-270 (CO, 270 °C, 10 bar and 20 hours) and H2-CO (H_2, 400 °C, 3 bar and 4 hours) and after exposure to reaction conditions (H_2:CO_2 = 3:1, 280-340 °C, 15 bar and 20 hours).

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Carbon footprint of hydrogen trucks in a life cycle perspective

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Introduction

To keep global warming below 2ºC, a substantial decarbonization of all economic sectors is necessary [1]. Road freight transport is a growing area of focus for reducing transportation-related greenhouse gas (GHG) emissions as this accounts for approximately 40% of global transportation carbon dioxide (CO_2) emissions [2]. Between 2000 and 2020, GHG emissions from global road freight transport increased by over 50%, driven by economic growth, increased freight demand, and predominantly reliance on fossil diesel [3]. Hydrogen trucks are an alternative for decarbonizing the long-haul segment. However, the environmental footprint depend on how hydrogen is produced, transported, stored, and used but also in the production of the truck. We conduct life cycle assessment to quantify the impacts per ton-km (tkm), including also the effect from potential hydrogen leakages.

Results and Discussion

The carbon footprint from the truck first and foremost origin from the carbon fiber hydrogen onboard storage system, followed by producing the chassi-steel, fuel cell system, and batteries. Lowest total climate impact is shown for trucks having a 300 kW fuel cell and 40 kWh Li-battery, using liquid hydrogen (in steel tanks). Highest impact is shown for trucks having a 200 kW fuel cell and 140 kWh Li-battery, using compressed hydrogen (in 700 bars carbon fibre tanks). The carbon footprint can be substantially reduced if substituting to green steel (DRI) and carbon fiber recycled via pyrolysis (around 15% and 25-40% reduction, respectively).

Lowest carbon footprint for the entire pathways, is seen for the case where hydrogen is large-scale produced in central plants, powered by green electricity, liquefied and distributed by trailers for 150 km, and used in fuel cell trucks having a steel tank for liquid hydrogen. Also the scenario “onsite” where hydrogen is produced from green electricity, at the refueling station, and used in fuel cell trucks having either a 350 bar or 700 bar storage tank. All three options have around 10 gCO_{2e}/tkm. Highest carbon footprint is seen from all options assessing blue hydrogen, around 30 gCO_{2e}/tkm. In general, the carbon footprint is slightly higher for internal combustion engines compared to fuel cells. All hydrogen pathways are, however, below the carbon footprint of fossil diesel (which is 55-150 gCO_{2eq}/tkm). The impact from potential hydrogen leakages may double the entire carbon footprint.

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Product Selectivity in Fischer-Tropsch Synthesis

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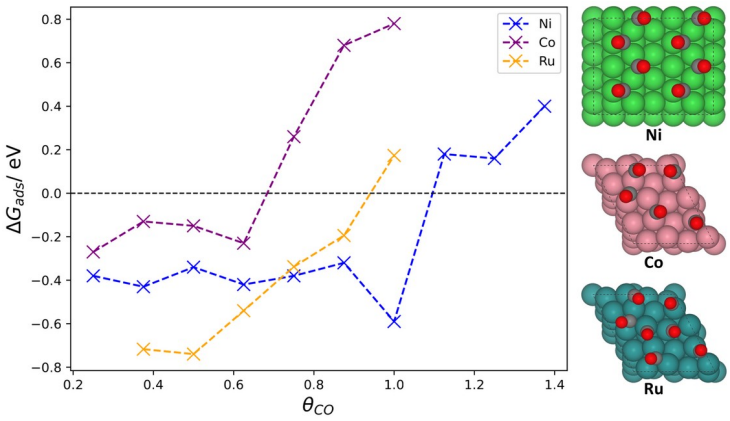
Introduction

The product selectivity and activity of Fischer-Tropsch synthesis (FTS) is important for producing synthetic fuels and chemicals from natural gas, coal, or biomass. Some catalysts generate mainly undesired methane, whereas others show higher selectivity toward longer hydrocarbons. In this study, density functional theory (DFT) and microkinetic modelling is employed to calculate the activity- and selectivity-determining reaction steps and energy barriers of FTS on typical catalysts.

Results and Discussion

Reaction rates and product selectivities are evaluated using a microkinetic model that incorporates the rate- and selectivity-determining steps of the FTS mechanism. To describe the catalyst as realistically as possible, the adsorption energies and barriers are computed at high CO coverage.



A simplified model is compared with a detailed microkinetic model, showing that a few simple descriptors are enough to qualitatively predict reaction rates and selectivities. Finally the dependence of the product selectivities from temperature and reactant pressures is discussed.

Fe, Co, and Mo based unsupported catalysts for low temperature ammonia decomposition

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Introduction

Although hydrogen has been pointed out as a potential energy storage solution, challenges concerning transportation and storage are hampering the commercial development [1]. A solution to circumvent the problems associated with compressed and liquefied hydrogen is to use hydrogen vectors such as ammonia. Ammonia can be used directly as a fuel, but its combustion properties can be improved by the addition of hydrogen through partial decomposition [2]. Ruthenium-based catalysts are considered the most active for ammonia decomposition, but a possible cheaper and more abundant alternative could be catalysts based on transition metals such as Fe, Co, and Mo. Oxides based on these metals forms nitrides in an ammonia atmosphere at elevated temperatures, the active phase of these catalysts are therefore often nitrides. Carbides based on transition metals are also studied for ammonia decomposition, but these catalysts also commonly form nitrides at ammonia decomposition conditions. The phase transitions of binary and ternary oxides and carbides in contact with ammonia were explored to determine the catalysts' active phase. This was subsequently related to their catalytic activity for ammonia decomposition.

Results and Discussion

Combined in-situ XAS and XRD were carried out to study the influence of gas composition on catalyst structure for the transition metal oxides. In the case of carbides, the transition metal oxides were carburized in a gas mixture of CH_4, H_2, and He, before being subjected to ammonia. Figure 1 shows an example of subsequent catalyst activation and ammonia decomposition where Fe_2O_3 was carburized followed by exposure to ammonia. Fe_3N starts forming at 450°C, and is the dominating phase until the temperature reaches 600°C. The fraction of Fe_4N increases throughout the isothermal step at 600°C, indicating a depletion of nitrogen in the lattice at ammonia decomposition conditions. The nitridation directly from oxides was also studied, where oxides were exposed to ammonia at different concentrations and temperatures. The relative intrinsic activity of the phases will be discussed in light of phase composition and activity measurements.

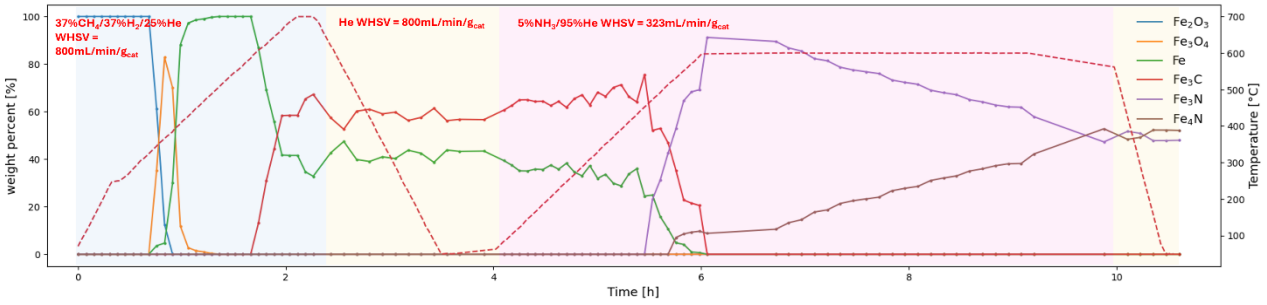

Figure 1 Rietveld refinement of in situ XRD measurements showing an initial activation of the oxide to form a mix of Fe and Fe_3C, before performing ammonia decomposition over the catalyst. Upon exposure to ammonia the catalyst start to form a nitride at 450°C.

Acknowledgements

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Reaction and improved ordering of steps on Rh in NO and CO

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Introduction

While surface science is often used to describe catalytic processes on atomic level, there has recently been significant discussion about high mobility of surfaces during reactions, questioning how useful surface science is for understanding real processes. As an example, steps at Cu surfaces are known to move and become less well-defined during exposure to CO [1]. We have studied stepped and curved Rh surfaces in NO [2] or NO + CO atmospheres using Surface XRD and Ambient-Pressure XPS. In contrast to the Cu case, we find an increased step order during reaction, suggesting that this is a very well suited system for surface-science based catalysis studies. We also find intriguing effects of varying step density.

Results and Discussion

Figure 1a) and b) show SXRD patterns around the (012) Bragg reflection of Rh(553) in 0.3 mbar CO + NO at 100 and 300 °C, respectively. The vertical rod extending from the shadowed Bragg reflection corresponds to the (553) surface. The weaker diffraction rods marked (111) and $(11\bar{1})$ in a) shows that the surface is facetted with varying step distance at 100 °C, while their absence and the sharper diffraction in b) shows that the surface order increases during reaction at 300 °C. Figure 1c) shows APXPS of a curved Rh(111) surface in 0.1 mbar CO +NO at 150 °C. $\alpha = 0$ corresponds to the flat (111) surface, while the step density increases when moving away from 0. The step density has a significant effect on the dissociations and reactions on the surface. We will discuss what this means during the presentation.

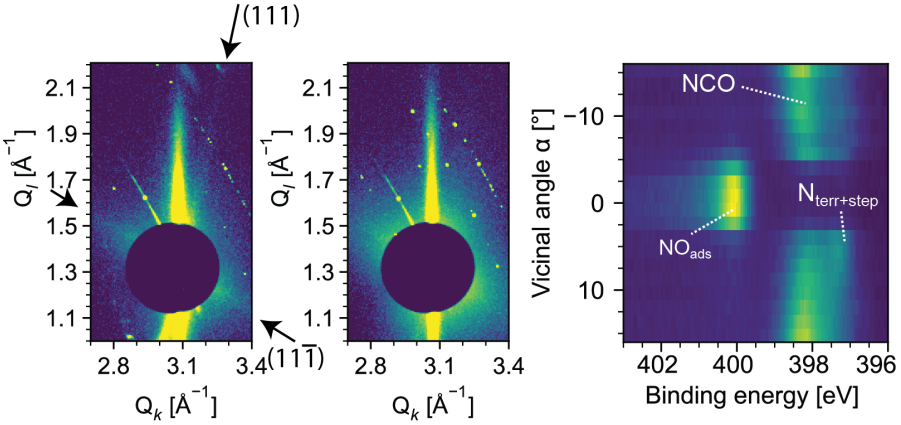

Figure 1: a-b) SXRD of Rh(553) in 0.3 mbar CO + NO at 100 and 300 °C, respectively. c) APXPS of a curved Rh(111) in 0.1 mbar CO + NO at 150 °C.

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Seaborne Imports or Domestic Production? A Techno-Economic Assessment of Hydrogen-based Energy Carriers

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Introduction

Hydrogen and electro-fuels play a crucial role in decarbonizing hard-to-abate sectors, while the comprehensive cost-effectiveness of their global trade driven by regional cost variations remains underexplored [1]. The aim of this study is to evaluate the cost of importing hydrogen carriers (liquid hydrogen, liquid methane, methanol, ammonia, and LOHCs) from China to Sweden via deep-sea shipping, in comparison to domestic production in Sweden, across multiple time horizons. This study advances techno-economic assess-ments of global electro-fuel and hydrogen trade by introducing two novel contributions: (1) accounting for country-specific CAPEX and weighted average cost of capital (WACC) for renewables and electrolyzer systems to capture regional cost differences, and (2) incorporating ship selection covering a comprehensive range of ship types and size categories into the techno-economic assessment to estimate transportation costs. This study addresses two key questions: when importing electro-fuels and hydrogen is econom-ically feasible over domestic production, and which hydrogen carrier pathway should be prior-itized under different conditions.

Results and Discussion

The study shows that, although Sweden holds superior wind potential and lower electricity prices, the production costs of all electro-fuels in China are lower than those in Sweden across all time horizons. This is primarily due to higher country-specific CAPEX and WACC for Sweden. Thus, this study highlights that the region-al differences in renewable energy potential and electricity price alone are not decisive in deter-mining hydrogen production costs, while country-specific CAPEX and WACC for renewable and electrolyzer systems are equally critical.

Including transport costs, importing ammonia, methane, and methanol from China for direct use is more cost-effective than domestic produc-tion in Sweden, indicating that China's production cost advantages are sufficient to offset long-distance shipping costs. In contrast, due to the low volumetric energy density and costly cryo-genic storage conditions for liquid hydrogen, importing liquid hydrogen results in higher costs than domestic production in Sweden. Among the electro-fuel options, ammonia exhibits the lowest import cost.

For hydrogen carrier scenarios where all electro-fuels need to be reconverted to hydrogen, all import options in base cases are more expensive than domestic production, due to the high addi-tional costs and hydrogen losses associated with reconversion, suggesting that importing electro-fuels for direct use is more economically attrac-tive than importing hydrogen.

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Density functional theory investigations of gas leakage from graphene-sealed SiO_2 cavities

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Introduction

Graphene-sealed SiO_2 cavities have previously been investigated as a gas seal for visualizing single nanoparticles in reactive gases under an electron microscope[1]. Graphene-sealed SiO_2 devices experience a leakage of gas, which is ascribed diffusion through the graphene/SiO_2 interface[2]. While experiments have characterized the dependence of gas species[2] and temperature[3] on the leak rates, no study so far has has established whether the graphene/SiO_2 interface is leak tight in the ideal case of flat, defect-free graphene on top of crystalline SiO_2.

Results and Discussion

Intercalation energies of 10 different molecules in the graphene/α-quartz interface were calculated using DFT for four different unit cell sizes. The effect of graphene bulging around the intercalate is accurately estimated using an α-quartz supercell size of 3x3x1, due to nearly identical intercalation energies for the 3x3x1 and 4x4x1 supercells. All calculated intercalation energies are significantly above 0 eV suggesting it is unfeasable within reasonable temperatures and pressures for the gases to pass through the interface. Diffusion of a He atom from one intercalation site to an adjacent site was calculated and found to be 0.4 eV, which together with a high energy of intercalation suggests that diffusion in the interface is unfeasible.

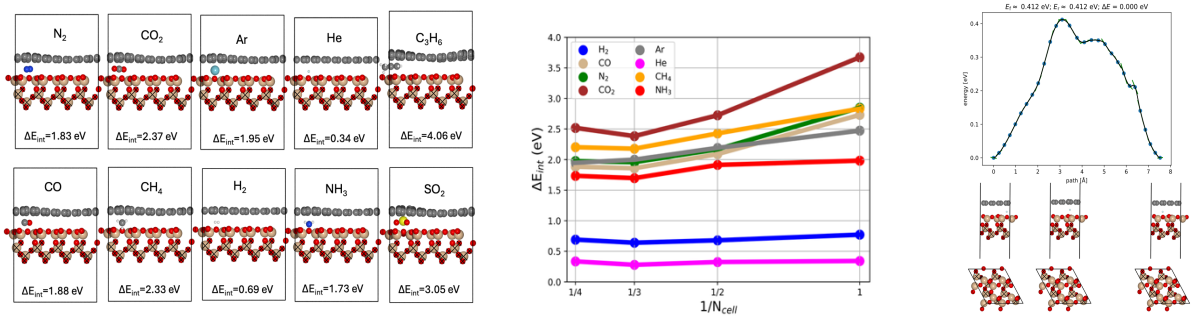

Figure 1 a) Intercalation energies and geometries of 10 gases in the graphene/α-quartz interface. b) intercalation energy as a function of unit cell size. c) diffusion barrier of a helium atom from an intercalation site to an adjacent site.

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Glycerol upgrading via acidic solid catalysts

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Introduction

Glycerol can be upgraded into higher-value products through esterification with valeric acid, yielding esters with potential applications as renewable fuel additives, solvents and lubricants. Common commercial acid catalysts for such reactions include zeolites and tungsten zirconia WO_3/ZrO_2. Although these catalysts are well established in various solid acid-catalyzed reactions, their behavior under solvent-free valeric acid and glycerol esterification conditions remains largely underexplored. This work examines how acidity, pore morphology and Si/Al ratios in zeolites (BEA, FAU, and MFI types) affects conversion and selectivity toward mono- (MV), di- (DV), and trivalerin (TV) esters, and compares their behavor with that of acidic WO_3/ZrO_2. Commercial zeolites were purchased from Zeolyst and activated by calcination. WO_3/ZrO_2 catalysts containing a nominal tungsten oxide loading of 10% (w/w) were synthesized via an incipient wetness impregnation method from $Zr(OH)_4$, denoted as WZrOH and commercial m-ZrO2 (DKKK), denoted as $WZrO_2$. Reactions were conducted in a 100 mL three-neck flask under nitrogen flow without reflux. The reaction mixture (60 mL) contained valeric acid and glycerol at a molar ratio of 5:1. Catalyst loading was 4-10 wt% relative to the feed mass, and reactions were conducted at 140 °C for 6 h. Liquid sample were analyzed by GC-MS/FID to quantify MV, DV, and TV yields, as well as glycerol conversion.

Results and Discussion

Catalyst performance depended strongly on the balance between acid strength and pore morphorlogy. Among the 11 zeolites examined, HZSM-5-80, HY-80, and HBEA-38 (with numbers indicating their SiO_2/Al_2O_2 atomic ratios) gave the most favorable results, attributable to their combination of accessible porosity and intermediate acidity. In contrast, zeolites with lower Si/Al ratios were less effective, likely because their stronger acidity, higher hydrophilicity, and more confined pore structures promoted deactivation and limited ester formation. HY-80 emerged as the best-performing catalyst, reaching 99% glycerol conversion after 2 h with only 4 wt% catalyst loading, along with 82% combined selectivity to the di- and triesters (Figure 1). Its performance surpassed that of both WZrOH and $WzrO_2$ under 4 wt% loading, consistent with its larger surface area and higher acidity. Recycling tests further demonstrated that HY-80 retained high activity, with only a 2% drop in glycerol conversion after 4 cycles. Full performance was restored after calcination in air at 500 °C for 6 h.

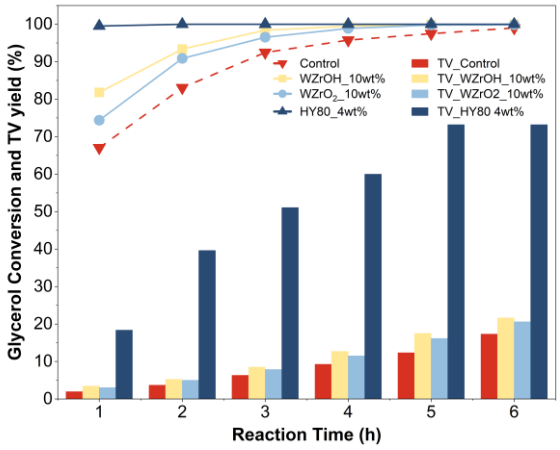

Figure.1 Glycerol conversion over HY-80, WZrOH, and $WZrO_2$ catalysts at 140 °C under a 5:1 acid-to-glycerol molar ratio, 500 rpm stirring, and continuous water removal. Catalyst loadings are shown in the legend.

On the acidity characterization of pristine and zinc-modified H-ZSM-5 zeolites: Comparison of adsorption-based characterization methods

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Introduction

In contrast with temperature-programmed desorption of ammonia (NH_3-TPD) and Fourier-transform infrared spectroscopy of adsorbed pyridine (pyridine-FTIR), where ammonia and pyridine do not react, TPD of isopropylamine (IPAm-TPD) utilizes a Brønsted-acid-catalyzed decomposition of isopropylamine to propylene and ammonia to selectively probe Brønsted acidity. Prior studies report altered IPAm-TPD responses for metals-modified zeolites relative to pristine zeolites [1–4], but explanations for the cause diverge [1–4]. This work compared the IPAm-TPD results of pristine and zinc-modified H-ZSM-5 with those of NH_3-TPD and pyridine-FTIR for added insight [5].

Results and Discussion

For pristine zeolites, IPAm-TPD showed the expected Brønsted-site-related propylene desorption, with propylene amounts proportional to framework aluminium, strongly adsorbed ammonia in NH_3-TPD, and Brønsted-bound pyridine in pyridine-FTIR. For zinc-modified zeolites, IPAm-TPD traces became multi-featured. Combined results from mass spectrometry (MS), NH_3-TPD, and pyridine-FTIR indicated contributions from a Brønsted-site-related propylene release, an additional, likely Lewis-site-related propylene release, and side products overlapping with propylene signals, possibly from dehydrogenation and aromatization. Quantifying only the Brønsted-related propylene release and comparing it to Brønsted-associated pyridine suggested that IPAm-TPD results may still represent Brønsted acidity despite the side reactions.

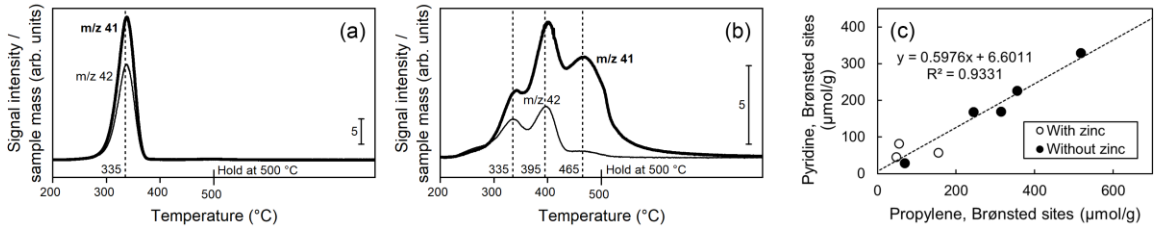

Figure 1. The MS IPAm-TPD traces of H-ZSM-5-80 (a) and Zn/H-ZSM-80 (b), and propylene desorbed from Brønsted sites in IPAm-TPD displayed against pyridine adsorbed on Brønsted sites in pyridine-FTIR (c).

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Glycerol aromatization to benzene, toluene, and xylenes over pristine, zinc-modified, and gallium-modified H-ZSM-5 catalysts

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Introduction

Benzene, toluene, and xylenes (BTX) total 30 wt.% of all petrochemicals produced [1] with few commercial renewable alternatives [2]. Catalytic glycerol aromatization offers a renewable route to BTX [2]. The industrial green transition supports the use of glycerol in chemicals production, as the availability of crude glycerol has increased with increases in biodiesel production by transesterification [2,3]. This study examined pristine, zinc-modified, and gallium-modified H-ZSM-5 catalysts in glycerol aromatization. For the pristine zeolites, SiO_2/Al_2O_3 ratio was varied. Additionally for zinc, the effect of the metal loading and the introduction method of the metal (ion exchange, atomic layer deposition (ALD), and evaporation impregnation) was examined.

Results and Discussion

In catalytic tests in a fixed bed flow reactor (450 °C, 1 bar, 40 wt.% glycerol/H_2O liquid feed, 0.71 h^{-1} $WHSV_{glycerol}$, 20 sccm N_2 carrier gas, 8 h total time-on-stream), complete glycerol conversion was obtained for all catalysts. For most of the pristine zeolite catalysts, the molar yield of BTX at ca. 2 h was between 15–25 %, with deactivation evident at ca. 7 h. While the Ga/H-ZSM-5-80 catalyst resembled the corresponding pristine zeolite in performance, the Zn/H-ZSM-5-80 catalysts with 2–3 wt.% zinc loading maintained activity and BTX yields of 15–25 % at ca. 7 h. Acidity characterizations by temperature-programmed desorption of ammonia (NH_3-TPD) and isopropylamine (IPAm-TPD) showed a decrease in Brønsted acidity with the introduction of the metals. The performance of Zn/H-ZSM-5-80 catalysts prepared by ion exchange and ALD resembled the performance of Zn/H-ZSM-80 catalysts with similar metal loading prepared by evaporation impregnation. Scanning transmission electron microscopy (STEM) and energy-dispersive X-ray spectroscopy (EDS) analysis of a spent 3 wt.% Zn/H-ZSM-5-80 zeolite prepared by evaporation impregnation indicated zinc migration after exposure to the reaction conditions. Our results suggest that the addition of zinc improves catalyst stability, while the addition of gallium showed no difference. The improved performance appeared connected to decreased Brønsted acidity and the contribution of zinc sites to the overall reaction from glycerol to BTX. Additionally, the zinc loading appeared more significant than the zinc introduction method.

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Catalytic hydropyrolysis of polyethylene in a fluidized bed with Ni-based catalysts

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Introduction

To reduce the pollution from plastic waste, there is a strong demand for improvements to plastic recycling efficiency. Catalytic hydropyrolysis can turn plastics into short-medium chain length hydrocarbons with a low heteroatom content. Such products can be used in various industrial applications, from fuels to raw materials for new plastics.

This work investigated two-step catalytic hydropyrolysis of LDPE using Ni-based catalysts in a fluidized bed system coupled with a downstream fixed bed reactor for secondary catalytic hydrocracking. The fluid bed (mixed sand and catalyst) and fixed bed (catalyst only) were operated at 530-580 ºC and around 300ºC respectively, 10-15 barg and 70% H_2. The aim was to maximize the yield of n-paraffinic condensable hydrocarbons (C_{4+} excluding wax) for fuel and input to steam crackers.

Results and Discussion

It was found that using a pure sand fluid bed led to under-cracking (high wax yield), while a fluid bed with catalyst only led to over-cracking (high C_{1-3} yield). Employing a mixture of sand and 5-10 wt.% catalyst in the fluid bed provided a vapor product well suited for downstream fixed bed upgrading. Fig. 1 presents the oil yield and oil composition of two experiments using a Topsoe hydrocracking catalyst and a synthesized Ni/Al_2O_3 catalyst (7 wt.% Ni loading).

Both experiments obtained oil yields above 30 wt.% but produced oils with different properties. While the hydrocracking catalyst oil was highly iso-paraffinic (> 60 wt.%), the Ni/Al_2O_3 catalyst oil consisted of 57 wt.% n-paraffins. The isomer-rich oil is favorable for jet fuel applications while the n-paraffinic oil seems suitable as feed to stream crackers.

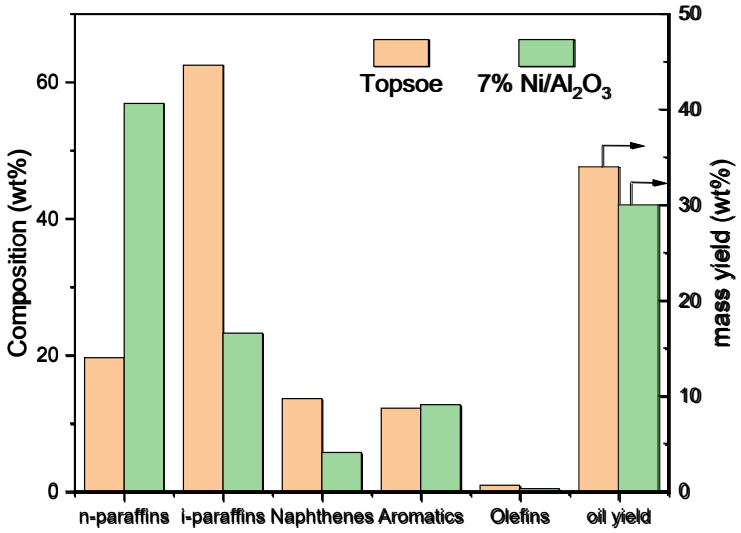

Figure 1. Oil yield and hydrocarbon distributions in oil from different catalysts.

Operando Soft X-ray Spectroscopy Infrastructure at MAX IV Laboratory

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Introduction

The ambient pressure soft X-ray photoemission spectroscopy/X-ray absorption spectroscopy (APXPS/APXAS) beamlines HIPPIE and SPECIES at MAX IV Laboratory offer a versatile platform for a broad range of research communities. Designed for flexibility, the APXPS endstations support experiments in electrochemistry, catalysis, thin film deposition, sulphur chemistry and advanced material characterization. The setups enable measurements under both AP and UHV conditions and include surface preparation tools for precise studies on model systems. A new capability for XAS measurements at 1 bar has also been developed recently.

Results and Discussion

The electrochemistry setup enables photoemission studies of solid-liquid and liquid-gas interfaces using a dip-and-pull geometry with a three-electrode configuration. This forms a thin, electrochemically active film that can be probed with APXPS/APXAS.

Solid-gas endstations are available for users and include three ambient pressure cells: the standard or catalysis cell, supporting up to 20 mbar and 1000°C heating, the atomic layer deposition (ALD) cell, supporting up to 20 mbar and 500°C heating, and the new sulphur cell, supporting up to 20 mbar and 500°C heating.

The atomic layer deposition (ALD) cell enables real-time XPS monitoring of layer growth, allowing *in situ/operando* studies that reveal detailed reaction mechanisms during film formation. The standard (catalysis) cell is designed for heterogeneous catalysis experiments. Photocatalysis is now part of baseline operations; a solar simulator and pulsed Xe lamp are available on request and have been effectively used at both beamlines alongside synchrotron radiation [1]. The sulphur cell, commissioned in December 2025, enables H_2S dosing and *in situ/operando* studies of sulphur chemistry.

Time-resolved APXPS has been implemented. Highly repeatable signals have been generated using piezo-driven valves in the gas supply, and these signals are analyzed using event-averaging or Fourier-transform techniques. Knudsen et al.'s measurements [2] are an example of this data acquisition approach. Direct synchronization is also possible, allowing the detector electrons to be referenced to an external signal.

A new ambient pressure X-ray absorption spectroscopy (1-bar XAS) cell was installed at the the SPECIES beamline in spring 2025. In contrast to hard XAS, 1-bar XAS is surface sensitive due to the beamline photon energy range. *In situ/operando* XAS investigations at 1 bar provide information on light elements (K-edges) as well as metals (L- and M-edges), bridging the pressure gap between the mbar range and ambient pressure and the materials gap between model and real catalysts or practical devices.

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Potassium-modified biochar for catalytic methane decomposition

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Introduction

In the recent times, where the green transition is a major topic in combating climate change, hydrogen has emerged as a key resource. However, the modern hydrogen production technologies are either costly or results in inherent greenhouse gas emissions. Therefore, it is necessary to find alternative hydrogen production routes, to close the gap between the economic and environmental impact. Methane decomposition is such an alternative, where methane is decomposed to hydrogen and solid carbon:

$$\mathrm{CH}_{4\,(g)} \rightleftharpoons 2\mathrm{H}_{2(g)} + \mathrm{C}_s, \quad \Delta H^{\circ}_{298\,K} = 74.5\ \mathrm{kJ/mol}$$

Due to the endothermic nature of the reaction, high temperatures (>1200 °C) are required to obtain satisfactory conversion and reaction rate [1]. To improve the reaction rate, catalysts are often employed, thereby reducing the required temperature. Catalyst materials vary broadly ranging from solid metals and carbon materials to molten salts [2]. However, the inevitable formation of solid carbon results in detrimental catalyst deactivation. Thus, challenges remain with finding stable catalyst materials that can maintain high activity. Carbon materials have gained increased interest due to their high tunability and favorable surface properties, in addition to the similar nature to the carbon byproduct [3]. Biochar is a carbon material that can be produced from biomass through pyrolysis. While biochar exhibits catalytic properties comparable to activated carbon and carbon black, utilizing agricultural waste as a precursor facilitates a circular, potentially carbon-negative pathway for hydrogen production. By varying the feedstock and pyrolysis conditions, in addition to pre-treatment of the precursor, active biochar for methane decomposition can be produced.

Results and Discussion

Preliminary results indicate that biochar produced at 850 °C and tested at the same temperature can obtain initial methane conversions up to 30%. However, the activity is close to zero after 45 min of time-on-stream, owing to the deactivation of the catalyst. Therefore, measures have to be taken to improve the catalytic properties to maintain the activity of biochar. Literature reports that activation of the biochar through chemical treatment or gasification processes can increase the activity and stability. Particularly, KOH is known to result in a highly porous carbon material, that can achieve high activity [4]. This is primarily due to the reactions between KOH and oxygenated surface groups on the carbon, resulting in carbon edging and pore opening. However, limited knowledge has been presented on the mechanisms behind the activation with KOH in relation to methane activation during the decomposition reaction. This work aims to unveil how biochar modified with potassium can improve the activity in methane decomposition to obtain a more active and stable catalyst.

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Ru-based Catalysts for Ammonia Cracking

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Introduction

In tackling climate change, hydrogen is handled as a key energy vector in the replacement of fossil fuels by renewable energy sources. Among the many potential hydrogen carriers, ammonia is particularly promising and can be stored and transported relatively easily. After transportation, the stored hydrogen can be released using the ammonia cracking reaction, for which ruthenium has been found to be the most active metal [1,2]. In the present work, various Ru based catalysts were prepared, characterized and tested. Support choice and metal deposition method were shown to have a significant impact on Ru catalyst performance. Several catalyst formulations were identified which not only show high activity, but also long-term stability and high-temperature stability, supporting the choice of Ru for industrial ammonia cracking processes.

Results and Discussion

Various Ru based catalysts using different supports, dopants and deposition methods were prepared and tested in this work. Initially a broad activity screening of different catalyst types was performed. In a second stage, the most promising candidates were tested in more detail regarding long-term activity and stability. This further included exposure to harsher conditions such as high temperature ageing and high operating pressures, as well as resilience to water impurities. The aim here was to assess different industrially relevant conditions.

The initial activity screening was performed at ambient pressure in ammonia at temperatures between 350-600°C. Follow-up ageing tests included ageing in forming gas at temperatures up to 900°C, with activity and stability testing afterwards. Testing here was done in pressure and temperature cycle experiments between 1 and 30 bar and temperatures between 450-700°C, as shown for example in Figure 1.

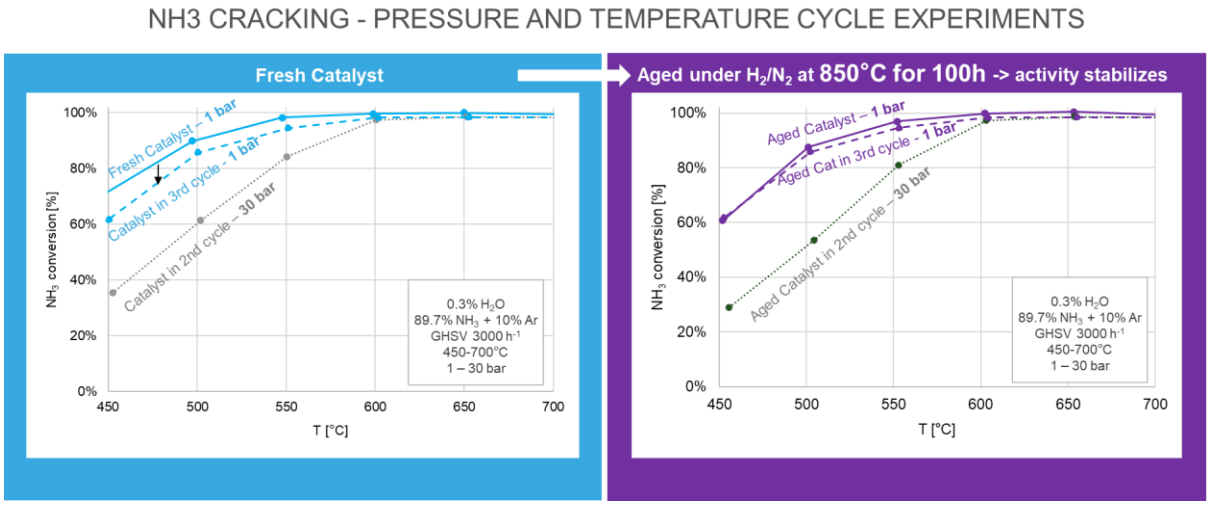

Figure 1 shows ammonia conversion in pressure and temperature cycle experiments with a fresh vs high-temperature aged catalyst. For cycling, pressures of 1 and 30 bar over a temperature range of 450-700°C were used, with 0.3% H_2O impurity in ammonia.

Performance-testing was supplemented by reaction modelling to get a better understanding of how different catalyst formulations and ageing conditions affect activation energy and frequency factor.

Some promising Ru catalysts showed high initial activity, which stabilized after a short degreening period, and which could further be shown to stabilize under high temperature pre-treatment. Catalyst characterization and catalyst up-scaling of the most resilient types is now in focus on the way to commercialization.

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Electrically heated and advanced substrate alternatives for fast TWC cold start

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Introduction

The future of the internal combustion engine (ICE) is closely tied to its ability to achieve life cycle emissions comparable to those of pure battery electric vehicles (BEVs). To reach this goal, it is essential not only to utilize carbon-free fuels but also to enhance the hybridization of the powertrain to reduce fuel consumption. Additionally, it is crucial to minimize pollutant emissions to near-zero levels, necessitating the development of highly sophisticated exhaust aftertreatment systems. For Plug-In Hybrid Electric Vehicles (PHEVs), one challenging use case is the High-Power Cold Start (HPCS). This scenario occurs when the transition from pure electric drive to ICE-assisted drive happens during a high load request, such as accelerating on a freeway ramp. This use-case has been evaluated by legislators and in numerous studies. The authors aim to investigate which metallic substrate technology performs best during an HPCS. This condition differs significantly from a normal cold start: the exhaust gas flow, pollutant concentration, and the available energy are much higher. The catalyst must heat up quicker (than in a conventional cold start), but the required volume above the light-off temperature must be much larger to convert a higher quantity of pollutants. Simulation tools are used to visualize quantification of system cold start improvements.

Results and Discussion

Electrically Heated Catalyst (EHC) or Electrically Heated Disk (EHD) can help to overcome challenging conditions. PHEVs (e.g. passenger cars) represent one of the solutions to reduce CO_2 and with increased battery capacity are also enabling the usage of an electrical heated catalyst. EHC tests from real PHEV vehicle conditions will be showed and quantified as real benefits.

An alternative catalyst upgrade is a more advanced substrate. A 1D tool was used to quickly identify and select the best substrate technology to meet specific light-off time requirements, assuming ideal gas distribution at the inlet and simplified chemistry. The upgraded substrate improved emissions during testing that verified the 1D predictions.

If detailed simulation during cold start including e.g. water condensation is desired then a more sophisticated model is needed. Therefore, the test cycle was simulated with a 1D code that accounts for this detailed chemistry in the catalyst, allowing to examine even the effects of washcoat loading and PGM composition. A more exact distribution of temperatures is needed to reach good predictions. This is discussed with a 3D approach.

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Activity of NiMo/Al_2O_3 catalyst in waste tire pyrolysis oil upgrading: the effect of sulfidation degree

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Introduction

The accumulation of end-of-life (EOL) tires, driven by the rapid growth of the automobile industry, has led to serious environmental and public health concerns. Pyrolysis enables the valorization of waste tires by producing waste tire pyrolysis oil (WTPO). This oil contains high concentrations of hydrocarbons and possesses a high calorific value, making it a promising alternative to fossil oils for fuel production [1]. However, WTPO also contains high levels of impurities, particularly sulfur compounds, olefins and polycyclic aromatic hydrocarbons. These contaminants lead to pollutant emissions, engine damage, and instability during storage [2]. Catalytic hydrotreatment offers an effective route for upgrading WTPO, enabling its use in fuel production while also enhancing its storage stability. In this study, the effects of catalyst sulfidation degree on catalyst structure and WTPO upgrading performance were investigated.

Results and Discussion

Varying the amount of sulfidating agent (DMDS) produces catalysts with different sulfidation degrees. Catalysts with lower sulfidation degrees exhibited similar GC-detectable liquid product yields, whereas higher GC yields were achieved with highly-sulfided catalysts (**Figure 1**). The increasing trend in GC-detectable yield corresponded to a progressive rise in saturated species and a reduction in olefins. Compared with reduced mixed oxides, the sulfided catalysts exhibited superior hydrodesulfurization (HDS) performance (**Table 1**). This observation suggests that sulfidation generated metal sulfides (MoS_2 and NiMoS) on the catalyst surface, which enhances hydrogenation, cracking activities, and HDS. For high sulfidation degree, the HDS efficiency remained similar.

Figure1. GCxGC-MS composition of oil products.

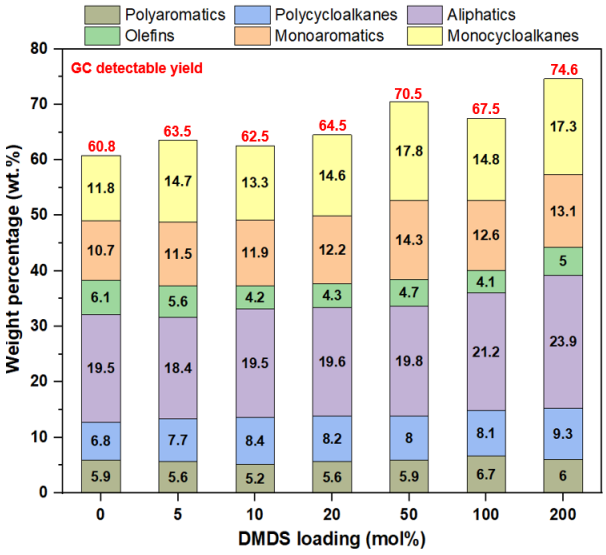

Table 1. HDS performance of catalyst with varying sulfidation degrees.

DMDS amount (mol%)	HDS efficiency (%)	DMDS amount (mol%)	HDS efficiency (%)
0	72.1	50	82.9
5	76.9	100	86.4
10	76.9	200	87.2
20	78.6		

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Effect of Copper Doping on the Catalytic Performance of Cryptomelane in Simultaneous Soot and VOC Oxidation

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Introduction

Air pollution remains one of the most critical challenges worldwide. In Europe, particulate matter – often containing soot – is estimated to contribute to a significant number of premature deaths every year [1]. Catalytic oxidation belongs to the most effective methods applied to remove jointly soot and volatile organic compounds (VOCs) from exhaust streams. Over the past decade, cryptomelane (K-OMS-2), an inexpensive and easily synthesized manganese oxide, has been shown to be active in these oxidation reactions. Moreover, doping of cryptomelane with selected metals can further enhance its functional properties [2,3]. This study investigates the influence of copper doping, introduced at various concentrations, on the catalytic activity of cryptomelane in the oxidation of model soot, ethene, and methane, as well as the potential route for simultaneous removal of soot and VOCs.

Results and Discussion

A series of Cu-doped K-OMS-2 samples was synthesized via dry impregnation using copper nitrate solution as dopant precursor. Structural characterization (XRD, RS, FTIR) confirmed the preservation of the cryptomelane framework after doping and revealed the presence of CuO nanocrystallites therein. This finding was supported by TEM analysis, which clearly showed nanodomains of copper oxide alongside cryptomelane nanorods. Temperature-programmed oxidation of soot, CH_4, and C_2H_4 demonstrated that appropriate copper doping enhances the catalytic activity of cryptomelane (Fig. 1). The optimal Cu content – corresponding to the highest activity expressed as T_{50} – varied depending on the oxidized pollutant, most probably indicating different mechanistic scenarios for soot, ethene, and methane oxidation. These results also highlight the complexity of designing a catalyst capable of removing soot and VOC simultaneously. Nevertheless, the study confirms that achieving such a dual functionality can be achieved in the case of Cu-modified cryptomelane systems.

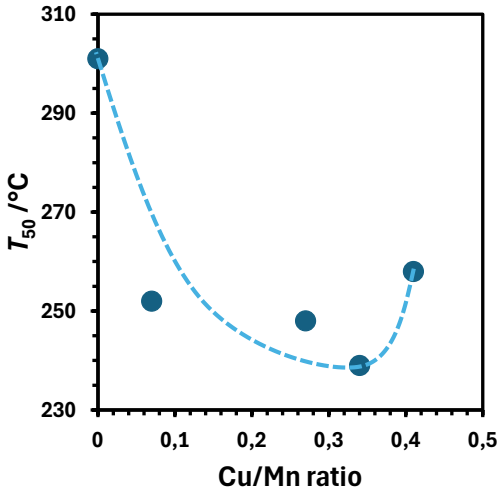

Fig. 1. Catalytic activity in ethylene combsution (expressed as temperature of 50% conversion) vs. composition of the catalyst

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Acknowledgement

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Redox-Metal-Doped Potassium Silicate Glasses for Simultaneous Soot and VOC Abatement

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Introduction

Despite numerous regulations and technological solutions implemented in recent years, further efforts are necessary to meet strict air-quality standards. Catalytic oxidation remains one of the most promising methods for removing carbon-based pollutants such as soot and volatile organic compounds (VOCs). While numerous metal oxides (including mixed oxides) have been investigated, noble-metal-free potassium silicate glasses doped with redox-active metals represent an emerging and largely unexplored class of catalytic materials [1]. Their amorphous nature offers unique opportunities for tailoring metal dispersion and for controlling redox properties. This work examines how different redox-active dopants and preparation routes influence the performance of potassium silicate glasses in the simultaneous oxidation of soot and VOCs.

Results and Discussion

As confirmed by XRD, RS, and FTIR, all synthesized doped glasses exhibit an amorphous structure. Spectroscopic analysis (UV/Vis-DR, XPS) and H_2-TPR demonstrated that the oxidation state and accessibility of dopants were strongly dependent on the way of their introduction. Dry impregnation is more efficient at providing available redox-active sites than remelting, which resulted in higher activity in both soot and ethylene oxidation for impregnated glasses. All investigated samples were active in the simultaneous oxidation of both studied pollutants, however, in slightly shifted temperature windows, i.e., at 350–450 °C for soot combustion and above 500 °C for ethylene combustion. These results reveal how the amorphous glass can be engineered to tune dopant redox behavior, enabling multifunctional catalytic performance without noble metals.

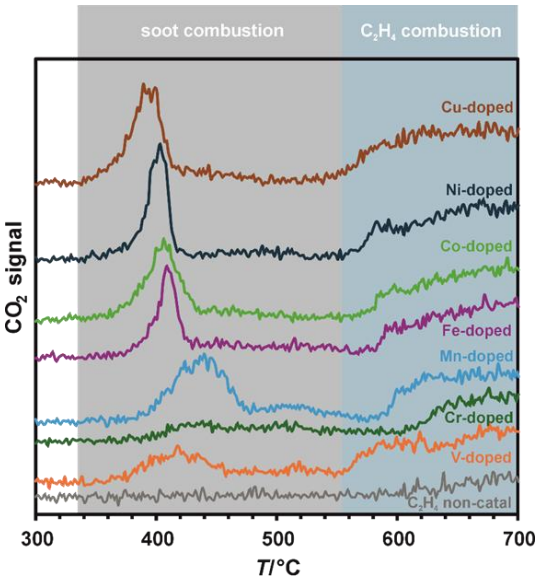

Fig. 1. Temperature evolution of the CO_2 signal intensity accompanying simultaneous oxidation of soot and ethylene on metal-doped glasses

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Acknowledgement

This work has been supported from the Anthropocene Priority Research Area budget under the program "Excellence Initiative – Research University" at the Jagiellonian University

Controlling Catalyst Layer properties with Ink Formulation for Proton Exchange Membrane Fuel Cells

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Introduction

Fuel cells are important part of the transition from fossil fuels to renewable alternatives, such as hydrogen. The performance and durability of proton exchange membrane fuel cells are strongly governed by the microstructure of the catalyst layer, which in turn is determined by the properties and processing of the catalyst ink. This work focuses on understanding how ink formulation control the resulting catalyst layer structure and thereby the electrochemical behaviour of the cell.

Rheological methods, such as oscillatory frequency sweeps and thixotropy can be used to characterize the catalyst ink. The catalyst ink is a complex viscoelastic liquid and the properties of it will be strongly affected by components, concentrations and preparation methods.[1]

Nitrogen physisorption isotherms can be studied to get an understanding of the surface area and pore size distribution in the catalyst layer.[2]

Results and Discussion

Experiments have been performed on catalyst inks using Vulcan XC-72 based carbon support and Aquivion N+ 125D. The inks have been dispersed using a bead mill with beads of 1 mm.

The rheological investigations have shown a stronger network in the catalyst ink for undispersed samples. The linear viscoelastic region has been observed to become lower with the time of the dispersion in the bead mill.

Nitrogen physisorption has been used to characterize the surface area and pore size distribution. BET calculations show that a decreased surface area is measured for more dispersed inks

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Composition-Gradient Libraries Prepared by an Automated Hull-Cell Platform for Electrocatalyst Discovery

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Introduction

Green transition requires the rapid development of efficient and sustainable electrochemical materials for energy conversion technologies. However, conventional electrocatalyst discovery remains largely dependent on time-consuming trial-and-error experimentation, limiting the exploration of vast compositional design spaces. To address this challenge, we present an automated platform for generating and screening composition-gradient electrocatalyst libraries. The system integrates a programmable 3D printer with a potentiostat, enabling reproducible and spatially resolved metallic electrodeposition in a Hull cell configuration. The nonuniform current distribution intrinsic to the Hull cell geometry produces continuous gradients in composition and thickness across a single substrate. Unlike conventional combinatorial approaches that require fabrication of numerous discrete samples, this strategy enables screening of continuous compositional ratios within a single material library.

Results and Discussion

The platform can operate an array of 3 x 4 Hull cells in parallel, substantially increasing experimental throughput while maintaining low material consumption. Deposition time, electrode trajectory, and immersion depth are precisely controlled, ensuring reproducibility and enabling scalable library generation. This approach reduces synthesis redundancy and improves experimental sustainability by minimizing reagent consumption. Energy-dispersive X-ray spectroscopy (EDS) and scanning electron microscopy (SEM) are used for compositional and structural characterization, whereas local mapping of catalytic performance as a function of catalyst composition is obtained using scanning electrochemical cell microscopy (SECCM). This integrated approach can accelerate the identification of optimal electrocatalyst compositions for diverse reactions relevant to electrochemistry.

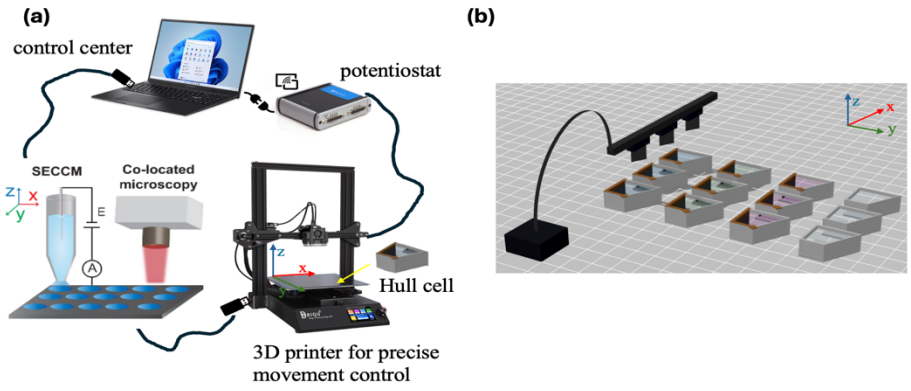

Figure 1(a) Schematic of the full approach from catalyst preparation to screening. (b) Schematic showing series of hull cells on a custom 3D printer for sequential preparation of metallic composition gradients by electrodeposition.

Biogas tri-reforming over $NiTiO_3$ catalysts: Effect of La/Ce doping

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Introduction

Hydrogen (H_2) production from renewable sources can reduce the emissions of greenhouse gases offering an alternative route for sustainable energy system in the near future. Biogas produced from biomass is composed mainly of methane (CH_4) at 40–70% and carbon dioxide (CO_2) at 30–50%, nitrogen (N_2) <1–15%, and hydrogen sulfide (H_2S) at 0–10 000 ppm[1]. In this study, hydrogen is obtained from biogas via catalytic tri-reforming reaction which consists from simultaneous dry reforming of methane, steam methane reforming, and partial oxidation of methane. In catalytic tri-reforming reaction biomethane is converted to syngas which is a mixture of biohydrogen and carbon monoxide (CO). A series of nickel titanate ($NiTiO_3$) catalysts with different lathanum (La) and cerium (Ce) loadings [2], were synthesised using a sol-gel process (the Pechini process) and tested as catalysts in the tri-reforming reaction at 850°C, 1 bar pressure and a gas hourly space velocity (GHSV) of 37 700 h^{-1}.

Results and Discussion

X-ray diffraction characterization results showed the characteristic peaks of the ilmenite-type $NiTiO_3$ structure in all compositions. Only the sample with a 10% Ce loading had a peak corresponding to CeO_2; Ce/La oxide peaks were not found in the other samples. Therefore, it can be concluded that Ce/La have replaced Ni or Ti in its crystal structure.The Raman and FTIR test results confirm that the ilmenite-type ($NiTiO_3$) structure remains stable after doping with Ce and La; the absence of secondary peaks indicates high dopant dispersion.

The tri-reforming results for the undoped catalyst showed CH_4 and CO_2 conversions of 92% and 58%, respectively. For the catalysts doped with La, higher conversions of CH_4 (96–98%) and CO_2 (60–68%) were obtained, and the 5% La catalyst achieved the highest conversion of CH_4, and the 1% La catalyst the highest conversion of CO_2. For the catalysts doped with Ce, conversions of 95–98% for CH_4 and 62–67% for CO_2 were obtained, with the 10% Ce catalyst achieving the highest conversions for both CH_4 and CO_2. The results show that doping increases the conversions of CH_4 and CO_2 over the $NiTiO_3$ catalyst, but a greater amount of doping within the catalyst does not always represent better conversion values.

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Characterization of Pt Electro-oxidation with XPS and DFT

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Introduction

Due to its stability and efficiency, platinum (Pt) is widely used as a catalyst for commercial applications, including in fuel cells and electrolyzers [1]. In processes like these, the Oxygen Reduction Reaction (ORR) [2] and the Oxygen Evolution Reaction (OER) [3] serve as bottlenecks due to their slow kinetics. These mechanisms are linked to Pt electro-oxidation. The presence of Pt oxide has been shown to hinder ORR onset on poly-crystalline Pt and Pt dissolution occurs with oxidation [4], leading to reduced catalyst efficiency, activity, and longevity. Surface-sensitive studies of Pt electro-oxidation are essential to characterize the structure-function relationships underlying these processes.

Results and Discussion

Data was collected ex situ using an Ar-pressurized to UHV transfer cell [5] at the FlexPES beamline at MAX IV. A Pt(111) sample was studied with x-ray photoelectron spectroscopy (XPS) after electrochemical (EC) treatments at OCP, 1.4, 1.6, and 1.8 V_{RHE}. These treatments consisted of forming a meniscus between the surface of the sample and the 0.05M KOH electrolyte, running a cyclic voltammogram (CV) between 0.2 V_{RHE} and the desired upper potential. While still held at that potential, contact between the sample and the electrolyte was broken, preserving the state of the surface, and the sample was placed back in a vacuum environment using the transfer cell. Once the chamber pressure returned to UHV, the sample was moved to the analysis chamber and XPS spectra were recorded from the Pt 4f, O 1s, C 1s, and K 2p binding energy regions. Shirley backgrounds were subtracted from the Pt 4f and O 1s XPS spectra and deconvoluted for each set of measurements. The components were identified as surface Pt, bulk Pt, chemisorbed species, or Pt oxide based on the onset potentials of OH adsorption and Pt oxidation peaks in the CV in combination with DFT modelling. Theoretical chemical shifts based on several models were compared to the experimental shifts. The O 1s binding energy from the known p(2x2) oxygen peak was used as an anchor to calculate O 1s chemical shifts. Good agreement was found between the Pt 4f XPS measured and calculated shifts. The O 1s agreement is currently less satisfactory, and will be discussed during the presentation.

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The influence of potassium on pre-carbided iron catalysts for CO_2 hydrogenation

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Introduction

The conversion of CO_2 to long chain hydrocarbons is viewed as a possible pathway for the chemical storage of green hydrogen, which allows for easy H_2 transport whilst also enabling the use of waste CO_2 as a storage medium for a green energy vector (i.e. H_2). Iron catalysts have received increasing attention for this reaction due to their success as catalysts for both CO_2-activation and the Fischer-Tropsch (FT) synthesis. It has been reported [1] that the formation of long chain hydrocarbons occurs on the iron carbide phases, whose selectivity is enhanced upon promotion of the catalysts with potassium (K). This is accompanied with an increase in the catalytic activity. However, iron-based catalysts tend to deactivate in CO_2-hydrogenation through oxidation of the carbide phase. Here we report on a detailed study on the effect of varying K-promotion of iron-based catalysts on the catalytic activity, hydrocarbon selectivity and carbide stability.

Results and Discussion

The catalysts were activated by reduction in hydrogen, followed by carburization in syngas (H_2/CO = 2) at 300˚C, which resulted in the formation of cementite (Fe_3C) and Hägg carbide (χ-Fe_5C_2) for the unpromoted catalyst; K-promotion resulted in the formation of predominantly Hägg carbide as confirmed by powder X-ray diffraction and Mössbauer spectroscopy. CO_2 chemisorption showed an increasing CO_2 uptake with increasing potassium loading. The CO_2 conversion at 300˚C and 20 bar pressure remained largely similar for all catalysts, not showing the expected trend of potassium promotion increasing conversion. The CO_2-conversion over the unpromoted catalyst yielded a methane selectivity of ca. 35 C-% and a C_{5+} selectivity of 50 C-%. The potassium promotion did not significantly increase the CO_2 conversion (which was maintained between 36-39%) but notably decreased the methane selectivity to ca. 7 C-% and increased the C_{5+} selectivity to above 75 C-%. Post-reaction characterisation showed evidence of partial carbide oxidation to magnetite and the extent of oxidation decreased with increasing potassium loading. In the spent catalysts, amorphous carbon was detected in addition to magnetite for the unpromoted catalyst and the catalysts with a low potassium loading. At a high potassium loading, the spent catalyst showed evidence of filamentous carbon which is typically observed for high temperature FT catalysts. Ultimately, here we find that promotion with potassium does not increase the activity for CO_2 conversion but does increase the selectivity for the formation of long chain hydrocarbons and the extent of carbon laydown during the reaction.

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Highly stable Mg-modified Ni-based catalyst prepared by the solution combustion synthesis for dry reforming of methane

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Introduction

For production of synthesis gas one method is to utilize CO_2 and methane, which could promote sustainability. Due to the endothermicity of the process:

$$CH_4 + CO_2 \longrightarrow 2\,CO + 2\,H_2,\ \Delta H_0^{298} = +248\ \text{kJ/mol}$$

high temperatures are required. Typically, Ni-based catalysts are used, however, they are very prone to catalyst deactivation. To suppress catalyst coking, a trimetallic Ni-Mg-Al catalyst was prepared by solution combustion method (SCS) facilitating formation of a thermostable $MgAl_2O_4$ spinel with high basicity. The aim was to study the effect of catalyst composition, i.e. Ni-Al, Ni-Mg, Ni-Mg-Al, prepared by SCS method and Ni-Mg/γ-Al_2O_3 prepared by impregnation. Furthermore, the effects of temperature, catalyst stability and coking were studied.

Results and Discussion

Among the four studied catalysts, the best results were obtained with Ni-Mg-Al prepared by SCS method showing the stable performance in 200 h time-on-stream at 850ºC (Fig. 1) The molar ratio of H_2/CO was 1.2 indicating the minimal reverse water gas shift reaction. Coke formation rate decreased with increasing time-on-stream due to presence of $MgAl_2O_4$ and the catalyst retained its activity in the presence of metallic nickel. In the final work catalyst properties will be correlated with their performance.

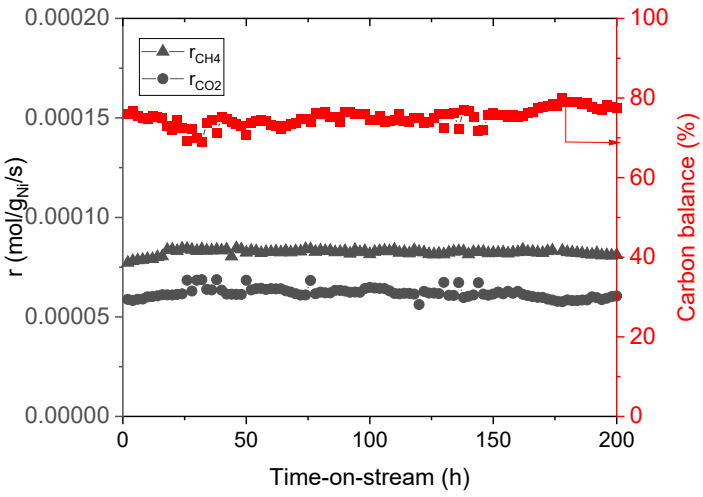

Fig. 1. a) Reaction scheme and b) methane formation rate and carbon balance in dry methane reforming at 850 ºC using gas hourly space velocity of 3000 h^{-1}.

Life cycle assessment of Methane Production through CO2 Hydrogenation: A comparative analysis

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Introduction

Methane synthesis through CO_2 hydrogenation represents a promising route for carbon recycling and renewable energy storage [1,2]. H_2 and CH_4 production through power-to-methane with electricity from renewable sources, such as wind power or solar, offers substantial potential to reduce GWP and primary energy demand [3]. Ni/Al_2O_3 catalysts are widely studied for their efficiency and cost-effectiveness in methanation reactions [4,5], as they increase activity at lower temperatures and provide high selectivity and stability for CH_4 [6]. Consequently, the transition to sustainable methane requires evaluating environmental performance from early stages of technological development. Life Cycle Assessment (LCA) offers a systematic method to quantify environmental burdens; however, in practice, data scarcity often limits early-stage evaluation [3,7]. This study presents the development of an early-stage evaluation framework for methane production over Ni/Al_2O_3 -catalyzed CO_2 hydrogenation. Scenario-driven LCA modeling approach combined with a custom equation in MATLAB is used to build a model that provides an initial perspective for evaluating environmental impacts when dealing with limited data. The framework integrates synthetic data derived from stoichiometric reactions and previous studies. Different variables were used to generate 27 scenarios for performing the LCA. The LCA was carried out for 1 kg of methane produced, with CO_2 generated from biogas production, and hydrogen obtained via wind-based electrolysis. SimaPro software with Ecoinvent database (v3.10) was used for impact characterization.

Results and Discussion

LCA results of CO_2 methanation over Ni/Al_2O_3 catalyst showed the influence of energy demand on overall environmental performance, as approximately 90% of the global warming potential (GWP) is attributed to the electricity supply for electrolysis, which aligns with values reported by other authors [2,3,8]. The environmental damage occurs in the category of human health, followed by ecosystem quality, while resource scarcity presents the lowest contribution, being associated with the electricity demand in the methanation process. The production of the Ni/Al_2O_3 catalyst contributes to human toxicity (nickel-related). Future work may apply the framework to C1-based chemical production case studies for assessing future scenarios.

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Mind the coverage gap: How does the potential-dependent surface coverage control the mechanism, activity, and selectivity of the oxygen reduction reaction?

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Introduction

Computational electrocatalysis has become an essential tool for elucidating the atomic-scale mechanisms of electrochemical reactions. However, significant discrepancies often remain between theoretical predictions and experimental observations. Bridging this gap requires not only treating the electrode potential as a fundamental thermodynamic variable but also explicitly accounting for the complex interfacial environment present under realistic electrochemical conditions. Among these factors, the surface coverage of adsorbed species plays a key role in determining catalytic activity and selectivity, yet it is often neglected or oversimplified in computational studies. [1–4] In here, we employ a grand canonical density functional theory (GC-DFT) framework to investigate how potential-dependent surface coverage influences the oxygen reduction reaction (ORR) on gold electrodes. By explicitly considering electrode potential, surface coverage, and interfacial water molecules, we aim to provide a more realistic description of the electrochemical interface and its influence on ORR pathways under alkaline conditions.

Results and Discussion

Our results show that under ORR operating conditions gold surfaces stabilize moderate hydroxyl coverages (≈1/3–2/3 ML OH*) together with interfacial water molecules, forming a dynamically structured electrochemical interface. The combined effects of pH and OH* coverage significantly influence the surface charge and shift the potential of zero charge, leading to negatively charged electrode surfaces under alkaline conditions. [3, 4]

Surface coverage is found to strongly influence both the activity and selectivity of ORR on different gold facets. On Au(111), the OOH* intermediate becomes thermodynamically unstable under realistic surface coverage, favoring the two-electron ($2e^-$) ORR pathway toward H_2O_2 formation. In contrast, on Au(100), interfacial water stabilizes key intermediates and modifies the reaction landscape. [3, 4] Furthermore, our simulations indicate that potential-dependent surface coverage alters the reaction mechanism on Au(100), redirecting the four-electron ($4e^-$) ORR pathway toward peroxide disproportionation rather than direct O–O bond cleavage, as previously suggested [4].

Our results highlight the importance of explicitly accounting for potential-dependent surface coverage and realistic interfacial environments in computational electrocatalysis, providing key insights that help bridge the gap between theoretical modeling and experimental observations.

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Influence of Gas Temperature and Water Content on NOx Reduction in SCR Catalysts for Hydrogen Engines

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Introduction

The transport sector accounts for 25% of Europe's total greenhouse gas emissions in 2023 [1]. Cutting GHG emissions from transport is essential. Lowering emissions from fuel production and vehicles reduces overall transport sector emissions [2]. Green hydrogen combustion engines, fuel cells, battery electrification, and other renewable fuels help create carbon-neutral propulsion. Carbon-neutral fuels are projected to power 50% of heavy-duty vehicles by 2050. Hydrogen lean-burn combustion produces lower (40-500 times) nitrogen oxide (NOx) emissions than diesel engines [3]. A Selective Catalytic Reduction (SCR) catalyst helps reduce NOx emissions to nearly zero. Hydrogen engines typically operate with lower exhaust-gas temperatures and higher water content than diesel engines, which can limit the performance of conventional urea-SCR systems [4]. Therefore, developing an appropriate SCR catalyst for hydrogen engines is necessary. For instance, Shao et al. [5] reported that the $Pd/MnTiO_2$ catalyst H_2-SCR showed 50% NO conversion at 200°C, 12% H_2O and 20000 h^{-1} space velocity. However, the exhaust from hydrogen engines has higher water content and temperature, and their effects on NOx reduction need further evaluation. Therefore, more research is necessary.

Results and Discussion

A spark-ignition hydrogen engine with an exhaust aftertreatment system (EATS) is used in this study. EATS comprises water injection, an electric heater, urea injection, and SCR. This system allows independent investigation of how variations in water content (16-30%), gas hourly space velocity (70000-140000 h^{-1}), and gas temperature (200-400°C) influence the SCR performance. This study compares conventional urea Cu-zeolite SCR [6] and $Pd/MnTiO_2$ H_2-SCR [5] in NOx conversion. It aims to develop an effective SCR system for hydrogen engines operating under lean-burn conditions (1.0-2.4 lambda). The impact of water content, temperature, and gas hourly space velocity on SCR performance will be presented.

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Novel Al_2O_3 supports with homogeneously distributed amorphous $AlPO_4$ entities for the conversion of renewable feedstocks

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Introduction

The conversion of renewable feedstocks, such as biomass and plastic waste, into platform molecules and fuels is very important for the de-fossilization of the chemical industry. Several related processes call for the development of novel heterogeneous catalysts, which exhibit improved chemical and thermal stability. It has been shown that mildly acidic support materials with adjusted mesoporosity play a pivotal role in catalytic pyrolysis and upgrading of pyrolysis oils as these can efficiently facilitate pre-cracking of large molecules into small entities allowing for better accessibility of the micropores present in zeolites thus reducing the formation of coke and preventing the deactivation of the catalysts [1–3]. In this study, we present a novel class of catalyst support materials as an alternative to conventional aluminas or amorphous silica-aluminas. $AlPO_4$ /Alumina materials are available from Sasol and were prepared by a proprietary, alkoxide based process. The samples with different $AlPO_4$ loadings were analyzed via SEM-EDX, NH_3 -TPD and PXRD of fresh and aged samples

Results and Discussion

The different $AlPO_4$ /Al_2O_3 samples with up to 15% "P_2O_5" are characterized by high surface areas, and high pore mesopore volume. As seen from SEM/EDX analysis a very homogenous distribution $AlPO_4$ /Al_2O_3 was achieved. The absence of crystalline phases of Aluminium Phosphate XRD confirm the presence of non-zeotypic, amorphous $AlPO_4$ entities The concentration of acidic centers increases with $AlPO_4$ content and is markedly higher than that of a commercial silica-alumina (SIRALOX 5/320). In addition, an exceptionally high thermal stability was found. These features illustrate that the presented $AlPO_4$ /Al_2O_3 compositions are ideal support materials for any application requiring high concentration of acidic centers with moderate strengths, high mesopore volume such as thermal durability.

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Electroreduction of CO_2 over Copper-Based Dilute Alloy Catalysts in Zero-Gap Electrolysers

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An important challenge in the transition to a sustainable society is the shift to carbon neutral manufacturing methods for major commodity chemicals currently derived from fossil fuel-based hydrocarbons. One such chemical is ethylene, the production of which is currently estimated to give rise to 300 million tons of CO_2 equivalents per year. A promising alternative, sustainable, production pathway is offered by direct electroreduction of CO_2 (CO_2ER) which could be powered using renewable energy. This technology is however currently being held back from large scale industrial implementation due to the lack of efficient and selective catalyst materials, that are stable enough for long term operation.

Copper (Cu)-based catalysts have by far shown the best promise towards the formation of multi-carbon products [1]. Despite their advantages over other metals, Cu catalysts still suffer from poor selectivity, giving rise to a multitude of products, which creates a need for costly separation of products. In addition, fundamental, lab-scale, studies are most often carried out using a H-cell which is limited to low current densities due to the low water solubility of CO_2. This means that these results are not directly transferable to industrial scale application where high current densities are a necessity.

In this work, promising dilute alloys, as shown in Figure 1, are evaluated at high current densities toward ethylene using a gas-fed electrolyser based on a membrane electrode assembly (MEA). Dilute alloys are known to break classical scaling properties of adsorption energies on transition metal surfaces which can lead to higher performance in CO_2ER. As such, dilute alloys composed of Cu as the majority metal and Pd as the minority metal are evaluated and compared to standard, sputtered or electrodeposited, Cu-based catalysts. In contrast to the standard Cu-based cathodes used in most advanced studies of MEA electrolysers toward ethylene, dilute alloys can be synthesised with a high degree of control over the composition and nanoparticle size, which can directly influence their electrocatalytic performance [2].

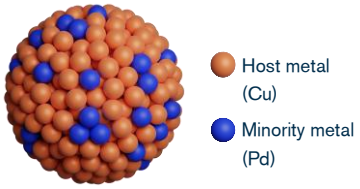

Figure 1: Dilute alloys are promising electrocatalysts with high atomic efficiency of metals and can be synthesised with a high degree of control.

Cu-based catalysts that could be used in an MEA with a high selectivity toward ethylene would open up for industrial upscaling of the system, and by extension potentially provide an industrially relevant, sustainable, method for production of ethylene.

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The Influence of Gel Aging On Mordenite's Structure and Catalytic Activity

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Introduction

While synthesis parameters such as structure-directing agents and aluminum source are known to influence the Al siting in zeolites (MOR), the chemical consequences of precursor gel aging remain insufficiently understood. Aging is traditionally associated with effects on crystallization kinetics and morphology; however, its impact on framework Al incorporation and catalytic functionality has not been systematically explored. Here, we investigate how precursor gel aging time (8, 17, and 24 h) governs the structure, acidity, and catalytic behavior of mordenite (MOR) zeolites in stepwise methane to methanol (MTM) conversion.

Results and discussion

Aging significantly influences crystallinity and morphological development with the 8 h sample exhibiting incomplete crystallization and crystal intergrowth, whereas 17 h and 24 h aging produces highly crystalline, well-faceted MOR crystals. Aging also leads to increase in surface area from 201 $m^2\ g^{-1}$ (8 h) to 546 $m^2\ g^{-1}$ (17 h), accompanied by the development of a well-defined microporous network.

Brøsnted acid sites increase with an increase in aging time from 8 h to 17 h aging, followed by a decrease at 24 h. Copper uptake increases with aging time, with the 24 h sample incorporating the highest Cu content. Catalytic testing reveals that highest intrinsic MTM performance (normalized per Cu) is obtained for Cu-MOR-17h. In situ XAS indicates that under methane exposure, Cu-MOR-17h exhibits a greater extent of reduction than Cu-MOR-24h, correlating with its higher normalized MTM activity.

These findings suggest that optimal catalytic performance arises from a balance between accessible Cu species and residual Brønsted acid sites, governed by aging-induced modifications in framework chemistry.This study establishes precursor gel aging as a decisive yet underexplored design parameter for tuning aluminum incorporation in MOR providing a powerful tool for tuning zeolite catalysts for selective methane oxidation.

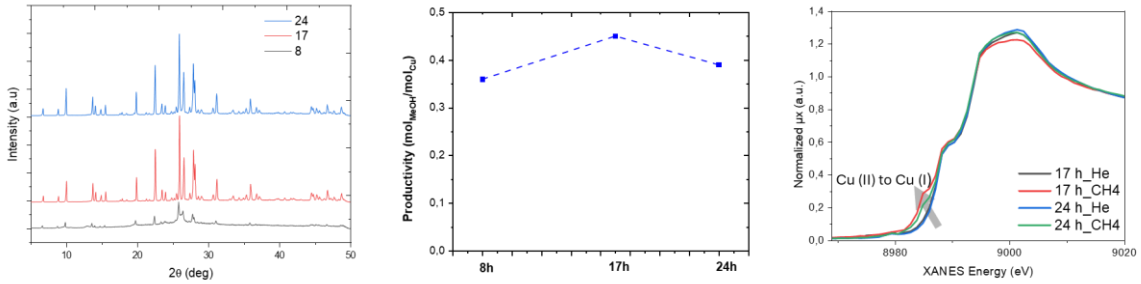

Figure 1: Crystallinity, productivty of aged samples and in-situ XAS during methane activation and He as a reference.

Tunable Superacidity and Sustained Reactivity in Sulfated Anatase TiO_2 via Surface Sulfation and Facet Engineering

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Introduction

Sulfated titanium dioxide (SO_4–TiO_2) has attracted interest as a solid superacid catalyst due to the strong acidity introduced by surface sulfate groups. In this work, we demonstrate a strategy for designing SO_4–TiO_2 catalysts with tunable Brønsted-to-Lewis (BL) acid site distributions and enhanced sustained reactivity through controlled crystal growth and sulfate surface functionalization. Nanocrystalline anatase TiO_2 thin films were deposited by reactive DC magnetron sputtering under conditions yielding either randomly oriented crystallites or preferential <001>-oriented films with an increased fraction of exposed {001} facets.[1] Sulfate groups were subsequently covalently photo-adsorbed on the film surface, forming SO_4–TiO_2 interfaces with enhanced acidity. In parallel, sulfated anatase TiO_2 nanoparticles were prepared by solid-state thermolysis of titanyl sulfate followed by calcination at 550–700 °C, enabling control of sulfate coverage and coordination.

Results and Discussion

Surface characterization by XPS, EPR, Zeta-potential and operando FTIR spectroscopy using pyridine as a probe molecule reveals that sulfate functionalization induces superacidic behavior and allows tuning of the BL acid site ratio via thermal treatment and sulfate coverage.[2] At low calcination temperatures, surfaces saturated with sulfate groups are dominated by Brønsted acid sites, while higher calcination temperatures lead to a predominance of Lewis acid sites with residual bridging coordinated sulfate groups enhancing the Lewis acidity (Fig. 1). Photocatalytic oxidation of acetaldehyde demonstrates that sulfate-functionalized <001>-oriented TiO_2 films exhibit improved sustained activity compared to non-functionalized films, retaining more than 60% of their activity after prolonged illumination. These results are explained by a mechanistic model in which bridging bidentate coordinated sulfate groups,[3] facilitate proton transfer and block defect sites on the oxide surface, preventing the formation of strongly bound carboxylate intermediates that would otherwise deactivate the catalyst. The combined control of crystallographic orientation and sulfate functionalization provides a versatile route to SO_4–TiO_2 catalysts with tunable acidity and durable catalytic performance for photocatalysis and heterogeneous acid catalysis.

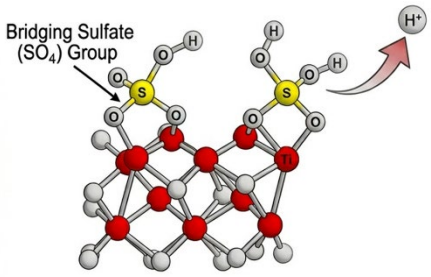

Figure 1 A method is presented for producing sulfate-terminated anatase TiO_2 nanoparticles exhibiting superacidic behavior with a tunable Brønsted-to-Lewis acid site distribution.

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Heterogeneous Copper-Catalyzed Asymmetric Allylic Alkylation

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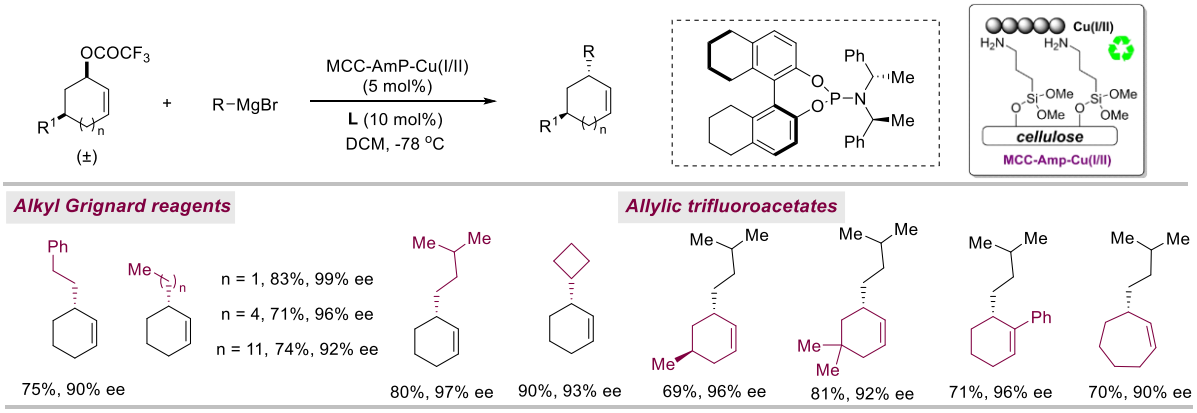
Introduction

Cu-catalyzed asymmetric allylic alkylation (AAA) is a significant and irreplaceable strategy for construction of C-C bonds and synthesis of chiral substituted alkenes.[1] Traditionally, these reactions have predominantly relied on homogeneous catalysis, which leads to copper waste and environmental pollution. As an alternative, heterogeneous catalysis has attracted widespread attention because of its advantages such as facile catalyst recovery, catalyst recyclability, and lower heavy-metal contamination.[2] Immobilization of chiral ligands on solid support is the most reliable methods to heterogenize chiral metal complexes. However, this approach requires additional functionalization of the ligands, complicating synthesis and potentially altering its electronic and structural properties, which may result in lower enantioselectivities. In contrast, metal nanoparticles combined with chiral modifiers provides a simple and direct route to chiral heterogeneous catalysts, although its application is limited due to metal leaching caused by strong ligand interactions.[3]

Results and Discussion

Building on our group's previous studies on heterogeneous copper catalysis,[4,5] we developed a nanocopper MCC-Amp-Cu catalyzed asymmetric allylic alkylation with Grignard reagents in the presence of an external chiral phosphoramidite ligand. The support, bearing sites for metal coordiation, effectively suppresses copper leaching by simultaneously activating and stabilizing the metal particles. Meanwhile, the chiral phosphoramidite ligand significantly accelerates the reaction, enabling the formation of a diverse set of cyclohexenes bearing stereocenters with excellent enantioselectivity (up to 99% ee). Moreover, the efficient nanocopper catalyst can be recovered and reused multiple times without a noticeable loss of yield or enatioselectivity.



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Study of the Meerwein–Ponndorf–Verley Reduction over Sn(Fe)-Mg(Zn)/Al Mixed Oxides

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Introduction

The Meerwein–Ponndorf–Verley (MPV) reaction is a well-established hydrogen transfer process between an alcohol and a carbonyl compound [1]. In heterogeneous catalysis, the reaction proceeds via hydride transfer through a six-membered cyclic transition state formed on paired Lewis acid–base sites. The selective reduction of α,β-unsaturated aldehydes is particularly attractive, as the C=O bond can be reduced under mild conditions without molecular hydrogen. Hydrotalcite-derived Mg–Al mixed oxides belong among the most promising heterogeneous MPV catalysts due to their tunable acid–base properties[2-5]. Surface basicity and acidity can be tailored by varying the Mg/Al ratio, calcination conditions, or incorporation of additional metal cations. However, the relationship between catalyst composition, surface properties, and catalytic performance is not yet fully clarified. In this work, (Sn/Fe)MgAl, (Sn)ZnAl, and (Sn)MgZnAl were prepared and evaluated in the MPV reduction of cinnamaldehyde. The aim was to correlate catalytic activity with surface acid–base properties and specific surface area.

Results and Discussion

Mixed oxides based on (Sn/Fe)MgAl, (Sn)ZnAl, and (Sn)MgZnAl systems were prepared by co-precipitation followed by calcination at 450 °C. Their properties were characterized by different techniques. Sn-modified mixed oxides exhibited slightly higher catalytic activity compared to the corresponding unmodified samples, whereas the incorporation of Fe led to a decrease in catalytic performance. A positive correlation between total basicity and cinnamaldehyde conversion was observed, suggesting that an appropriate balance between Lewis acidic and basic sites is crucial for efficient hydride transfer in the MPV mechanism. This behavior is consistent with the generally accepted mechanism of MPV reduction on calcined hydrotalcite-derived Mg–Al mixed oxide. Moderate Lewis acidity can contribute synergistically by activating the carbonyl group, but the density and strength of Lewis basic sites are considered the primary factor controlling catalytic activity. Increasing Fe content therefore led to a gradual decrease in activity, suggesting that excessive surface acidity may be detrimental to the reaction. Zn-containing mixed oxides showed poor catalytic activity; however, partial substitution with Mg and further modification with Sn improved their performance. An important advantage of heterogeneous catalysts is their potential for reuse. The studied catalyst could be regenerated by calcination and reused in three consecutive catalytic cycles without a significant loss of activity.

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Application of a bifunctional magnetic composite catalyst for valorization of bio-based platform chemicals

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Introduction

In the process of searching for potential renawable technologies which would mitigate the use and reliance on fossil fuels, scientists and engineers alike put enormous effort in the research of novel electrification techniques for various chemical processes. One of the potential methods is the electrification *via* magnetic heating which occurs in ferro- and ferrimagnetic materials, which can be incorporated in the catalyst structure.[1] Important platform chemicals obtained from woody biomass, such as furfural, 5-HMF and levulinic acid can be converted to value-added compounds, finding their use in pharmacy, cosmetics, manufacture of chemicals, and even sustainable aviation fuels (SAFs). In this work, we present a successful synthesis of a bifunctional magnetic nanocomposite ruthenium catalyst and its application in furfural hydrogenation.

Results and Discussion

Iron oxide nanoparticles were synthesized using a combination of co-precipitation and hydrothermal growth, forming magnetite-maghemite solid solution nanoparticles of about 10-20 nm in diameter. The nanoparticles were coated with γ-Al_2O_3 *via* hydrolysis of AlN. Ruthenium was then impregnated onto the γ-Al_2O_3 support (see Figure 1a). The synthesized catalyst was characterized using different characterization techniques, including unique magnetic characterization methods necessary for proving the magnetic heating potential of the material (see Figure 1b and c). Detailed catalytic tests were performed using furfural as a starting compound, as well as using different furfural hydrogenation products in order to investigate the reaction pathways.

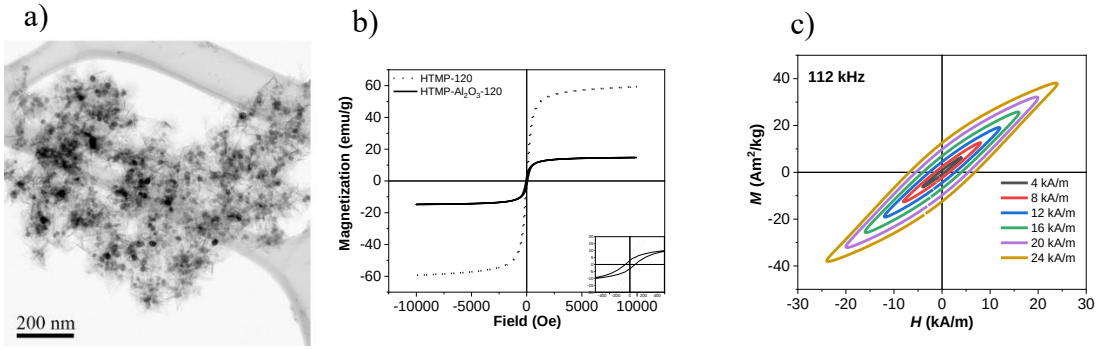

Figure 1: a) STEM image of the Ru/iron oxide-alumina catalyst, b) room temperature magnetization curve, and c) dynamic hysteresis loops of the nanocomposite catalyst

Acknowledgments: We thank the following projects for funding our work: P2-0152, J2-70093, Gravitacija, BioSmart (Grant agreement ID: 101235677), and S4f

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Catalytic Hydrodeoxygenation of Biomass Pyrolysis Oil Model Compounds in a Continuous Slurry Reactor

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Introduction

Biomass derived fast pyrolysis oil requires hydrotreating before it can be used as a fuel. This process has been performed in fixed bed reactors through hydrodeoxygenation at elevated temperatures and hydrogen pressures using various catalysts [1]. However, fixed bed reactors are known to clog when the catalyst is exposed to the very reactive bio-oil [2]. Slurry reactors are a promising alternative, since the catalyst and reaction liquid are vigorously stirred and well mixed, and the fresh, reactive bio-oil is instantaneously diluted into already upgraded oil [3].

In this work, a continuous slurry reactor was employed to hydrotreat a bio-oil model mixture, consisting of 2-ethylhexanol (68 wt%), acetophenone (10 wt%), guaiacol (8 wt%), furfural (6 wt%), diacetone alcohol (6 wt%) and octanoic acid (2 wt%). The 500 ml reactor (Parr) was equipped with continuous liquid/H_2 feed and product removal. The liquid level was 100 ml, kept constant by a dip tube. The pressure was 100 bar of H_2 and the temperatures varied from 200 to 350 °C. The H_2 flow rate was 300 ml_N/min, and the liquid flow rate was 0.5 ml/min. 2 to 6 g of a sulfided NiMo/Al_2O_3 catalyst provided by Topsoe A/S was used, as extrudates, inside catalyst containers. These consisted of 8 perforated cylinders secured between two perforated circular frames. The stirring speeds varied from 300 to 750 rpm. Run times were 50 to 100 h.

Results and Discussion

Experiments at 200 and 250 °C, with 750 rpm and 6 g of catalyst, had very low reactant conversions, which, over time, resulted in catalyst deactivation. At 300 °C, and even more at 350 °C, the reactant conversion and oxygen removal increased substantially, at the cost of slightly lower liquid carbon yield. For experiments with less catalyst, 4 and 2 g, at 300 °C, lower reactant conversion and oxygen removal were achieved, but the liquid carbon yield was slightly higher. Despite the lower conversion, no catalyst deactivation was observed, even after 100 h on stream.

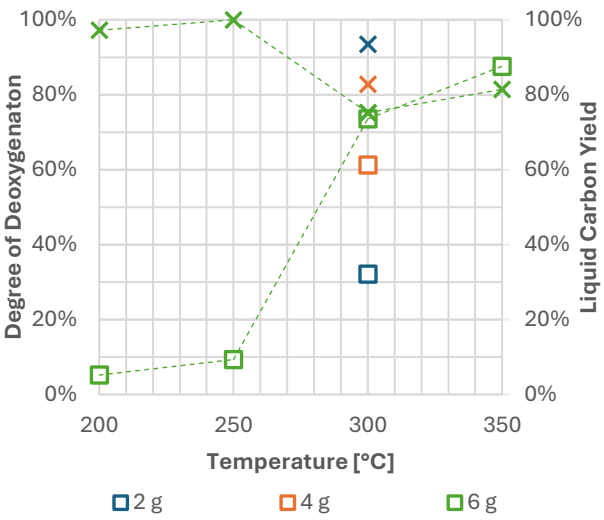

Figure 1 – Degree of Deoxygenation (□) and Liquid Carbon Yield (x) with temperature and catalyst mass

The continuous slurry reactor design appears very promising and bio-oil upgrading will soon be performed.

The authors acknowledge Innovation Fund Denmark for funding this research through the project "HyProFuel" (case # 0224-00029A) and Topsoe A/S for the close cooperation.

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Improving Electrochemical Durability of PEMWE Electrodes with CNF-Enhanced Low Ir Catalysts

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Introduction

To succeed in limiting global warming below 2°C, one of the main keys is fossil-free hydrogen produced from electrolysis [1]. However, the high cost and relatively low efficiency of today's electrolysers remain a bottleneck to reach high volume production of green hydrogen. We aim to develop and characterize new catalysts materials for the oxygen evolution reaction (OER) in proton exchange membrane water electrolyser cells (PEMWEs) based on an active catalyst, here iridium, supported on carbon nanofibers (CNFs) (see Figure 1), forming a structure called porous transport electrode (PTE), to reach a high utilization of iridium as well as a high power density of the electrolyser [2]. The goal of this study is to enhance the performance and the durability of the catalyst material while reducing the platinum group metal (PGM) loading, making a scale-up of PEMWE possible.

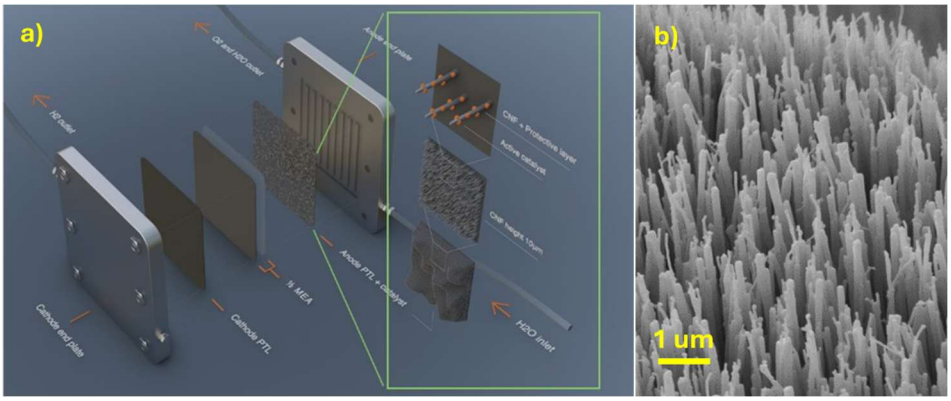

Figure 1: (a) Schematic and (b) SEM pictures of Ir-coated nanofibers from Smoltek Hydrogen

Results and Discussion

In order to improve the PTE structure, and as the performance and durability of the PEMWE cell depends on the stability and activity of the OER catalyst, we thus need to understand better the dissolution and oxidation of iridium [3]. For that we use half-cell test to study the formation of Ir oxides during OER and the electrochemical quartz crystal microbalance with dissipation monitoring (EQCM-D) to characterize the deactivation and activity regeneration of the iridium catalyst.

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Effect of Silver on Ammonia Cracking Activity over Palladium-Silver Alloy Catalysts

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Introduction

The use of H_2 as a fuel faces challenges related to safety and energy consumption during storage. NH_3 is particularly attractive as a H_2 carrier, being carbon-free and producing no emissions upon H_2 release. Pd-Ag membranes are well known for their high permeability and selectivity towards H_2, permitting to obtain pure H_2 [1]. However, exposure to NH_3 can reduce their performances due to competitive adsorption and segregation phenomena [2]. To better understand these effects, Pd-Ag catalysts of different Pd:Ag ratios were synthesized in order to investigate the extent of catalytic activity occurring on the membrane's surface.

Results and Discussion

Pd/γ-Al_2O_3(2 wt%) and Pd-Ag/γ-Al_2O_3 (1.5 wt%-0.5 wt% and 0.5 wt%-1.5 wt%) catalysts were synthesized, and to assess the extent of alloy achieved, the samples were intentionally sintered to increase particle size, enabling XRD analysis. An alloy phase was formed in both catalysts, with the Pd-rich sample showing a Pd-rich alloy and the Ag-rich sample a Ag-rich alloy together with a pure Ag phase (Fig. 1). These observations were supported by a qualitative EDS elemental analysis on the unsintered catalysts: the Pd-rich sample showed a consistent Pd to Ag signal ratio across all the analyzed particles, whereas several particles in the Ag-rich one showed no detectable Pd. The NH_3 (0.5% NH_3 in Ar) cracking activity was then evaluated at a total WHSV of 1000 $mLmin^{-1}g_{cat}^{-1}$. The Pd(2 wt%) catalyst exhibited activity starting at 450 °C, whereas the Pd-rich and Ag-rich catalysts showed activity only above 550 °C and 600 °C, respectively. At 600°C the monometallic Pd catalyst achieved an NH_3 conversion of 40%, decreasing to 10% for Pd-Ag(1.5 wt%-0.5 wt%), and to 4% for Pd-Ag (0.5 wt%-1.5 wt%) (Fig. 2).

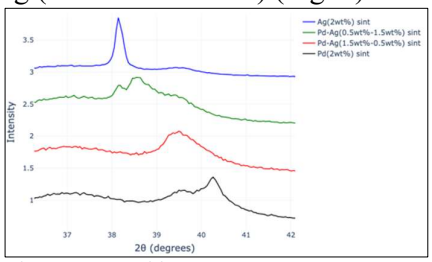

Figure 1. Magnified XRD pattern of [111] reflection of Pd, Ag and Pd-Ag catalysts.

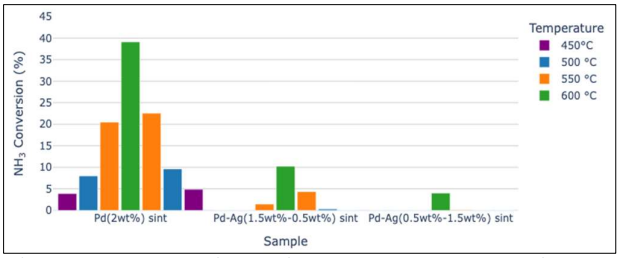

Figure 2. NH_3 conversion achieved by each catalyst at different temperatures.

This trend agrees with CO chemisorption measurements results, which show decreasing CO uptake with decreasing Pd loading, indicating fewer Pd surface sites. STEM analysis revealed similar particle size distribution across all samples, excluding particle size effect and instead suggesting effects related to alloy composition, metal segregation, and electronic effects.

Acknowledgement

Authors acknowledge support of FME HYDROGENi, (#333118) financed by the Research Council of Norway

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Insights into CO_2 and NH_3 Binding at Cu Sites in CuBTC under 1-bar Conditions by soft X-ray Absorption Spectroscopy

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Probing gas–host interactions in metal–organic frameworks under realistic conditions is essential for advancing their use in gas capture and storage. We report in situ Cu $L_{2,3}$-edge soft X-ray absorption spectroscopy of CO_2 and NH_3 adsorption–desorption kinetics in CuBTC (HKUST-1) at 1 bar, performed at the SPECIES beamline of MAX IV Laboratory. The surface sensitivity of soft X-rays enables direct tracking of coordination and electronic-structure changes at the Cu paddle-wheel nodes.

For CO_2, the adsorption and desorption process was found to be reversible, as evidenced by the changes in the Cu^+ absorption feature returning to its initial state after desorption, consistent with physisorption and in agreement with earlier studies [1]. In contrast, NH_3 exposure on hydrated CuBTC induces a rapid shift of the Cu^{2+} absorption edge to higher energy, indicating the formation of a stronger coordination bond. Despite this pronounced response, the spectra partially recover after desorption, demonstrating that NH_3 binding is only partly reversible.

These results highlight the capability of soft X-ray absorption spectroscopy to resolve subtle, reversible and semi-reversible coordination changes in MOFs - features that are often obscured in hard X-ray measurements due to their deeper penetration. The study underscores the value of soft X-ray methods for elucidating gas uptake mechanisms and guiding the design of improved sorbent materials.

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Reactive Water Microdroplet Interfaces for Greenhouse Gases Capture and Activation: Mechanisms and Kinetics

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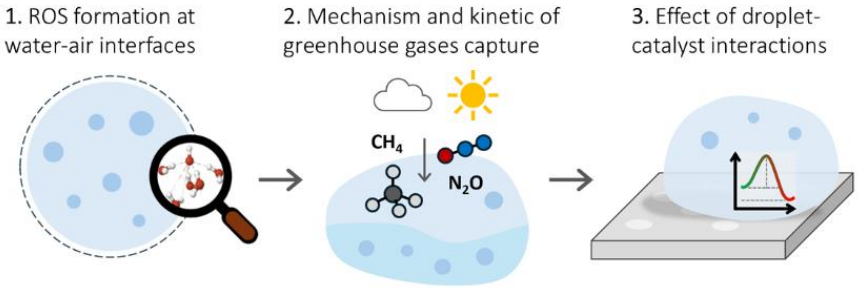
Introduction

Water micro- and nanodroplets exhibit strikingly enhanced chemical reactivity compared to bulk water, a phenomenon increasingly attributed to the unique physicochemical environment present at droplet-air interfaces. In particular, the spontaneous formation of reactive oxygen species (ROS) has been experimentally observed under ambient conditions,[1] yet the fundamental mechanisms driving their generation remain only partially understood. Mounting evidence suggests that intense electric fields arising at confined aqeous interfaces may play a central role in promoting interfacial redox chemistry and enabling reaction pathways that are otherwise inaccessible in bulk phases.[2]

In this work, we investigate the potential of these interfacial processes to contribute to the oxidative removal of methane (CH_4) and nitrous oxide (N_2O),[3] two long-lived greenhouse gases with significant atmospheric warming potential. By combining electronic structure calculations and molecular dynamics simulations with kinetic modeling, we aim to identify the key factors governing interfacial water-gas reactivity and to develop strategies for controlling the kinetics of CH_4 and N_2O chemical capture and conversion.

Results and Discussion

We first investigate the formation of OH· radical from hydroxide ions as a precursor to interfacial reactivity of water nanodroplets. Using a bottom-up approach spanning gas-phase clusters to large QM/MM interfacial systems, we search for suitable descriptors to map the chemical condition for OH· generation to local environment properties, such as hydration structure, interfacial curvature, and local electric fields. These insights pave the road to the mechanistic study of ROS-mediated reactions with the greenhouse gases, where Marcus Theory and kinetic modeling are employed to estimate rate constants in electron-transfer processes occurring at heterogeneous interfaces. Future work will explore synergies between reactive nanodroplet interfaces and heterogeneous catalytic surfaces to promote greenhouse gas activation and the selective synthesis of valuable compounds.



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2D material-supported rhodium catalysts for efficient and selective styrene hydroformylation

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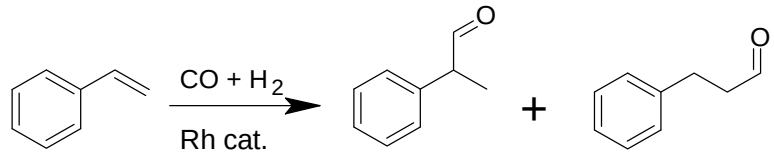
Introduction

Hydroformylation is an important industrial process converting alkenes and syngas into aldehydes.[1] Since its discovery in 1938, it has become a major homogeneous catalytic reaction, as aldehydes are key intermediates for numerous chemicals.[1,2] Rh–phosphine catalysts such as the Wilkinson complex provide high activity and regioselectivity, but homogeneous systems are difficult to separate, sensitive to impurities, and prone to deactivation. This motivates the development of heterogeneous Rh catalysts that are more stable and recyclable, though they often suffer from lower selectivity and higher hydrogenation rates.

To address these limitations, a wide range of 2D materials, including transition-metals dichalcogenides (TMDs), hexagonal boron nitride (h-BN), and emerging 2D zeolites, have been explored as supports due to their high surface area, tunable electronic properties, and ability to stabilize isolated Rh species for improved hydroformylation performance.



Scheme: 1: Hydroformylation of styrene toward desired aldehydes

Results and Discussion

Successful preparation of Rh catalysts supported on 2D supports (MoS_2, WS_2, h-BN, and selected 2D zeolites) was confirmed by XRF, XRD, SEM, TEM, FTIR, and N_2 physisorption. All catalysts were evaluated in styrene hydroformylation and compared with the Wilkinson benchmark, which achieved 98 % conversion and 85 % aldehyde selectivity under identical conditions (100 °C, 3 MPa CO/H_2 = 1/1, 6 h). Among the heterogeneous systems, Rh/h-BN showed the best performance, reaching 90 % styrene conversion with aldehyde selectivities above 90 %. Overall, 2D supports consistently provided higher aldehyde selectivity than their bulk 3D counterparts due to the strong suppression of side hydrogenation to ethylbenzene.

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NO_2 adsorption on oxygen-modified Ag(111) at ambient conditions

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Introduction

Silver-based materials are a promising alternative for the detection and removal of environmental NO_2 by surface reactions. Adsorption of NO_2 at ambient conditions on silver surfaces has usually been reported through X-ray photoelectron spectroscopy (XPS) assignment as NO_3. However, theoretical calculations are in conflict with the N 1s XPS assignment of NO_3 adsorbed on Ag(111). Here, we use density functional theory (DFT) calculations, ab initio thermodynamics, and core-level shift calculations, in combination with XPS measurements, to investigate the adsorption of NO_2 on oxygen-covered Ag(111). [1]

Results and Discussion

Experimental measurements are performed on a silver surface supported on a gold substrate, fabricated by electrochemical deposition. Exposure of the Ag-based chemoresponsive system to 10 ppm of NO_2 (equilibrated in N_2 at 1 atm) at a temperature of 298 K produces clear XPS signatures for the N 1s BE at 405.8 eV (Figure 1a) and at 532.0 eV for the O 1s BE (Figure 1b), associated to the surface adsorbate. Similarly, an spectral peak at the O 1s BE of 530.4 eV is observed on the surface before and after NO_2 exposure, associated to surface oxygen.

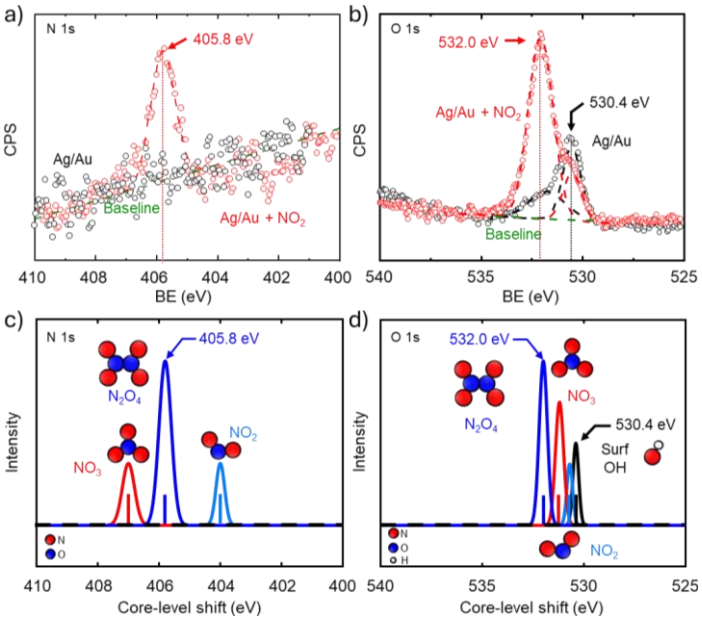

Figure 1. Photoelectron emission spectra and core-level shift peak assignments for adsorption of NO_2 on oxygen/modified Ag surface. (a) N 1s spectra. (b) O 1s spectra. (c) Simulated N 1s core-level shift position. (d) Simulated O 1s core-level shift position. Figures adapted from Ref. [1].

Thermodynamic analysis and core-level shift calculations show that the adsorption of NO_2 in dimer form (N_2O_4) on an oxygen-modified p(4×4)-Ag(111) elucidates the N 1s BE signature observed at 405.8 eV (Figure 1c). This is corroborated with the calculated O 1s BE, where N_2O_4 uniquely elucidates the spectral peak position at 532.0 eV. Additionally, the O 1s CLS of surface hydroxyls explains the surface oxygen features on Ag at O 1s BE of 530.4 eV. The findings suggests that the species assignment for N 1s BE of 405.8 eV on oxygen-modified silver surfaces upon NO_2 exposure should be reconsidered.

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Switching from Tip- to Base-Growth CNTs in Methane Decomposition over Nickel Phyllosilicates: Insights from In Situ Characterization

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Introduction

Carbon nanotubes (CNTs) are high-value materials with broad technological relevance, yet conventional synthesis routes based on hydrocarbon precursors such as acetylene or ethylene generate CO_2 as an inherent by-product. In contrast, catalytic methane decomposition (CMD) offers a more sustainable pathway, producing CNTs together with CO_2-free H_2 as the only gaseous product. For industrial deployment, it is crucial to develop catalysts that promote base-growth CNTs, which simplify harvesting and enable catalyst regeneration, overcoming the limitations of tip-growth systems where metal nanoparticles detach and become encapsulated. Nickel phyllosilicates (Ni-PS) emerge as promising precursors, as their strong metal–support interaction stabilizes small Ni nanoparticles and can switch the growth mechanism from tip- to base-mode, enabling cleaner and more scalable CNT production.[1] In the present work, we aim to investigate via several in situ techniques the reaction conditions that govern the transition between base- and tip-grown CNTs.

Results and Discussion

In situ TEM and in situ XRD measurements reveal that the strong metal–support interaction in nickel phyllosilicates stabilizes small Ni nanoparticles and keeps them anchored during methane decomposition, thereby controlling their size and enabling a transition from conventional tip-growth to a base-growth mechanism as a size-dependent phenomenon. The in situ observations further highlight the critical influence of temperature and reduction environment on particle restructuring and CNT morphology, providing key insights into the conditions that favor controlled CNT formation. In real time, we track the full CNT-growth sequence, from CH_4 cracking on Ni nanoparticles to their transformation into tubular carbon structures.

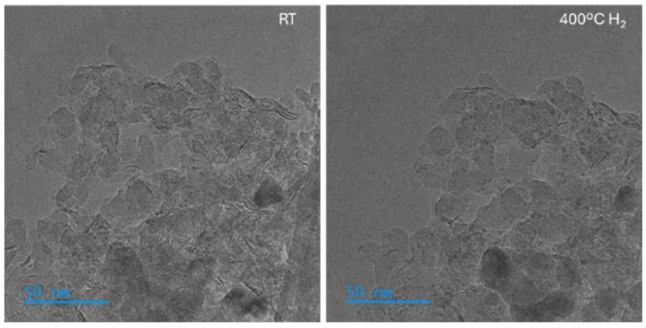

Fig.1 In situ TEM micrographs show the annealing of Ni-PS into Ni NPs with a very narrowly controlled size.

Unsupported molybdenum sulfides for slurry phase upgrading of lignocellulosic pyrolysis bio-oil

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Introduction

Liquefaction of lignocellulosic biomass into bio-oils is a promising approach for the production of sustainable biofuels. To reach fuel specifications, the bio-oils require further upgrading and deoxygenation due to challenges with stability, high acidity, viscosity and high oxygen content. However, conventional fixed-bed upgrading by hydrotreatment faces significant challenges, including rapid catalyst deactivation and even reactor blockages. To overcome these challenges, catalytic slurry-phase hydrotreatment in a CSTR reactor is a robust method to upgrade challenging feedstocks; clogging is avoided and fresh catalyst can be added and spent catalyst removed continuously to manage deactivation.[1] In our previous work, unsupported cobalt molybdenum sulfides were studied in the hydrodeoxygenation of isoeugenol as a model compound for bio-oils.[2] In this work, we establish unsupported molybdenum sulfides as efficient catalysts for the slurry-phase hydrotreatment of real bio-oils. Novel method for the catalyst synthesis is presented; parameters such as precursor concentration and additives are shown to have great impact on the catalyst structure and consequently on the deoxygenation performance.

Results and Discussion

Unsupported molybdenum sulfides were synthesised by hydrothermal precipitation with cobalt as promotor metal. The catalysts were tested in the slurry-phase hydrotreatment of lignocellulosic catalytic fast pyrolysis bio-oil in batch autoclave. Catalyst performance is evaluated by thorough analysis of the products as well as the consumption of hydrogen gas (Table 1). Detailed characterisation of the catalysts is presented, drawing a clear connection between the catalyst properties and activity. This work highlights the potential of unsupported MoS-catalysts in the slurry-phase upgrading of bio-oils, and moreover, emphasises the importance of catalyst synthesis to reach desired performance.

Table 1. The effect of catalyst precursor concentration on the surface area and catalytic activity of CoMoS-catalysts in hydrotreatment of catalytic fast pyrolysis bio-oil.

Catalyst	Precursor [Mo] (mol/l)	BET (m^2/g)	Pore volume (ml/g)	H_2 consumption ($g_{H2}/kg_{bio-oil}$)
CoMoS-1	0,18	165	0.30	16.6
CoMoS-2	0,36	54	0.19	15.5
CoMoS-3	0,54	19	0.10	13.0

Acknowledgements

Funding from Business Finland project Bio4All is gratefully acknowledged.

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Effect of biofuel-derivated impurities on NH_3-SCR catalyst activity and deactivation

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Introduction

This study examines the deactivation mechanisms of Fe-based selective catalytic reduction (Fe-SCR) catalysts exposed to inorganic impurities originating from bio-based fuels. As renewable and waste-derived fuels introduce elevated concentrations of alkali and phosphorus species into exhaust streams, understanding their impact on SCR durability is increasingly important. The work focuses on Fe-SCR catalysts supported on Beta zeolite and evaluates the individual and combined effects of hydrotreatment and S with Na, K, Ca of P under demanding, multi-poison ageing conditions (hydrothermal+S+poison).

Results and Discussion

Catalytic performance was assessed through NO_x reduction activity measurements, with simultaneous monitoring of NH_3 and N_2O conversions. Structural and surface modifications were characterised using DRIFTS, BET surface area, XRD, and SEM–EDS analysis to correlate physicochemical changes with catalytic activity. The results indicate that catalyst deactivation proceeds primarily via chemical poisoning of active Fe and zeolitic sites and a reduction in microporous surface area, leading to diminished NH_3 adsorption capacity.

The SCR activity dropped with all investigated contaminants, the NO_x, NH_3, and N_2O conversions on aged samples followed all the order: HT > KS > CaS > S > PS > NaS (Fig. 1). Na and P caused the most severe performance loss by significantly suppressing NO_x conversion and reducing zeolitic microporosity. In contrast, K- and Ca-containing samples retained comparatively higher activity, particularly after S ageing, suggesting differences in interaction mechanisms between the deposited species and the zeolite framework. SEM-EDS showed the accumulation of other poisons in the presence of SO_2 at 500 °C on the catalyst inlet zone: KS > CaS > NaS > PS and more exactly on top layer.

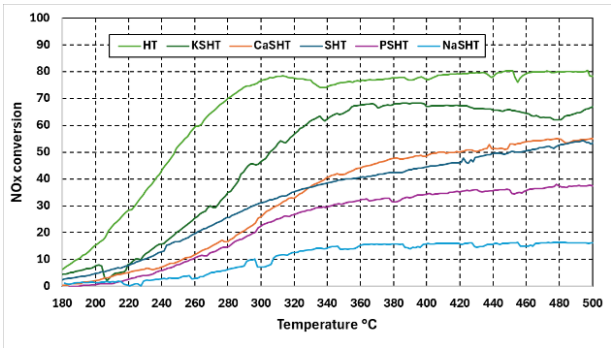

Figure 1. NO_x conversions by poison compounds (NH_3/NO_x= 0.8)

Overall, the findings demonstrated the serious deactivation of by known poisons for NH_3-SCR catalysts. The preserved microporous accessibility and sufficient catalyst and acid sites are critical factors governing Fe-SCR catalyst stability in environments containing multiple fuel-derived impurities. The results provide insight into durability challenges associated with renewable fuel applications and support the development of more poison-resistant iron-based SCR and N_2O removal catalysts.

When CO_2 meets amino acids and calcium salts: Building a supramolecular catalytic system

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Introduction

As the years go by, carbon capture, utilization and storage (CCUS) processes have increasingly focused on the development of atom-efficient chemical pathways involving the CO_2 capture and conversion.[1] To further improve the applicability of this technology, integrated CO_2 absorption and mineralization (IAM) has recently emerged as a promising route to merge capture and fixation within a single process.[2] Yet, its industrial viability remains fragile, due to the kinetic mismatch between the rapid CO_2 absorption and the much slower carbonation.

Results and Discussion

To address the critical knowledge gap governing CO_2 capture and conversion, this study aims at elucidating, at a molecular scale, the phenomena that occur when a renewable non-toxic amino acid (being lysine) is employed to capture CO_2 in the presence of alkaline industrial residues, to ultimately recover calcium carbonate. At first, the dynamic covalent and non-covalent molecular subsystem obtained from two components (aqueous lysine and CO_2) has been compositionally characterized by ^{13}C qNMR analyses. While investigating the full three component system (lysine-CO_2-CaO model entity), an unexpected and unprecedented Ca-lysine-CO_2 coordination complex could be identified and may act as a key intermediate in the accelerated mineralization process. Series of experiments have been conducted to entirely identify the key parameters leading to the formation and conversion of this non-covalent complex, which appears to play a crucial role in lowering the activation energy of total carbon fixation, thereby accelerating the CO_2 transfer under mild conditions.

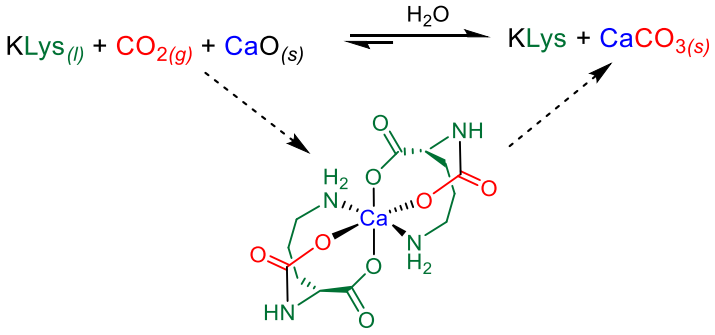

Figure 1. Schematic representation of the reactive system and proposed chemical structure of the Ca-lysine-CO_2 ternary adduct studied in this work.

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Probing catalyst surfaces with NO monitored by EPR

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Understanding catalyst surfaces are central to rational design of tailored catalysts. Morphology, accessibility, and distribution of metal sites are all parameters of crucial importance for catalytic performances. Here, we use of nitric oxide (NO) as a probe molecule for catalytically active sites and detection by electron paramagnetic resonance (EPR).

NO(g) is paramagnetic and offers different ways of interacting with the catalyst surface. It can coordinate to surface metal sites as a charge-neutral molecule forming nitrosyl complexes or it can engage in redox reactions with surface metal sites forming new metal sites.

Activated surfaces (300-500 K) of solid catalyst materials were exposed to controlled doses of paramagnetic NO(g) (0.5 – 1000 mbar) using a new setup in the Mossin Lab. Detection by quantifiable and time-resolved EPR is possible at different temperatures from 500 K down to 77 K.

This method was applied on different material types and we will show results and discuss the possibilities and limitations of the method. Below are the results of a NO dosing experiment on a Mo_xS_y cluster supported in the cages of NaY zeolite. We observe a clear evolution of the EPR signal as a function of increasing NO exposure (Figure 1, left and middle). The difference spectrum is shown (Figure 1, right). In conclusion: a) the Mo related broad signal is not changing. b) the original radical signal at $g = 2.03$ (assumed to originate in edge sulfur sites) is partially consumed and c) a new radical signal with an N hyperfine coupling pattern corresponding to adsorped NO appears at $g = 2.02$.

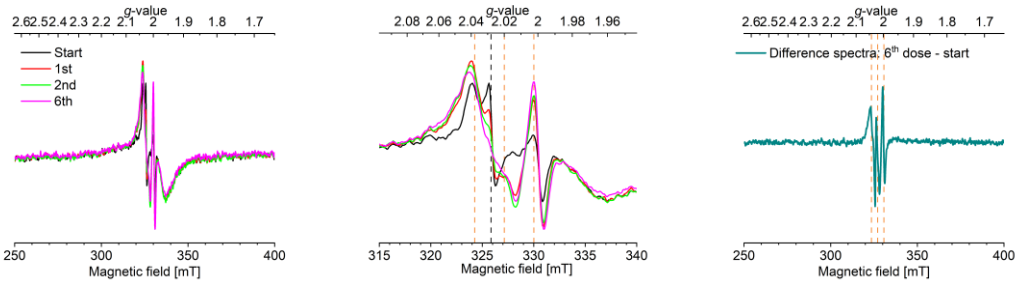

Figure 1. Left: NO dosing experiment performed on a Mo_xS_y sample encapsulated in a NaY zeolite The NO dosing experiment is performed at room temperature.The four graphs represents exposures pressures of 0, 0.6, 1.4, and 5.0 mbar, respectively. **Middle:** A magnified view of the spectra on the left **Right:** Difference spectrum of the sample before and after NO exposure (5.0 mbar).

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Effect of NO on Hydrogen Oxidation over Pd/Al_2O_3

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Introduction

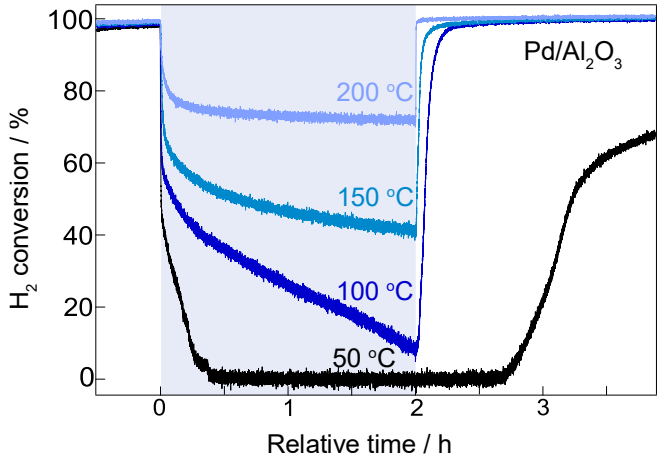
The development of hydrogen internal combustion engines (H_2-ICEs) is considered a promising pathway to decarbonizing heavy-duty transports; However, the effective control of exhaust emissions is a persisting challenge [1]. Although hydrogen combustion does not produce CO_2, it can still lead to undesirable products, such as the formation of NO_x emissions [2] and unburned hydrogen, the latter particularly under cold-start or humid operating conditions. Therefore, implementation of hydrogen oxidation catalysts (HOCs) is essential to reduce H_2 emissions in the aftertreatment systems.

This contribution is focused on understanding the effects and underlying mechanisms of the hydrogen oxidation reaction over palladium supported on alumina (Al_2O_3) across diverse operating conditions. Here, we investigate the reaction under low temperature conditions, and the presence of nitrogen oxide (NO).

Results and Discussion

A Pd/Al_2O_3 monolith catalyst was prepared and the H_2 oxidation was evaluated in a chemical flow reactor where the monolith outlet stream directly passes a heated quartz capillary connected to a mass spectrometer. In the experiments shown in the figure, the sample had been pretreated in hydrogen at 250 °C and then cooled to room temperature. The initial feed consisted of H_2 and O_2 and the temperature was ramped to the desired set-temperature to establish a stable hydrogen conversion. Then, at relative time = 0, 500 ppm NO was added and co-fed for 2 h before switched off at relative time = 2 h, while the H_2 conversion was measured continuously.

During the first cycle at 50 °C, NO is inhibiting the hydrogen oxidation reaction completely, H_2 conversion falls to zero, and the recovery time is slow. At 100 °C a significant decrease in H2 conversion is observed over time, however, the recovery is instant once NO is switched off. At higher temperatures, the presence of NO results in a similar behavior, although with less inhibition and immediate recovery each time. These results highlight the temperature-dependent effects of NO on the HOC inhibition and recovery. Underlying mechanisms for the NO inhibition will be discussed.



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X-ray Absorption Spectroscopy study of electrocatalytic Oxygen Evolution Reaction on $Ni_xFe_{1-x}O_yH_z$ - A Mechanistic Study

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Introduction

Iron-doped nickel (oxy)hydroxides $Ni_xFe_{1-x}O_yH_z$, are among the most active non-precious electrocatalysts for the oxygen evolution reaction (OER) in alkaline media. Although Fe is known to be essential for the high activity, its exact role under operating conditions remains unresolved.[1,2] Previous operando hard X-ray absorption spectroscopy (XAS) studies showed that Fe largely retains a 3+ oxidation state while its local coordination changes from distorted octahedral to square-pyramidal, suggesting the presence of a weakly coordinated or readily dissociable ligand.[1] To obtain a more complete picture of the electronic structure under bias, here we investigate these materials using operando soft XAS. In contrast to hard XAS, transition-metal L-edge XAS directly probes metal 3d-derived states and is particularly sensitive to changes in local electronic structure and ligand-field environment.[3] This makes soft XAS a complementary approach for tracking the potential-dependent evolution of both Ni and Fe sites during OER.

Results and Discussion

Operando soft XAS at the metal L-edges and O K-edge was performed on $Ni_xFe_{1-x}O_yH_z$ samples with 10% and 30% Fe in 0.1 M KOH at open-circuit potential (OCP), OER onset, and active OER conditions. In both samples, the Ni L-edge shows clear potential-dependent line-shape changes, indicating evolution of the local Ni electronic structure under anodic bias. Smaller but reproducible changes are also observed at the Fe L-edge, suggesting that the Fe sites are likewise electronically responsive during OER. At the O K-edge, the pre-edge feature near 529 eV increases with applied potential, consistent with changes in metal–oxygen hybridization. Comparison of the two compositions suggests that Fe loading influences how these changes develop: the 10% Fe sample shows more evident multi-edge changes already near OER onset, whereas the 30% Fe sample shows its strongest response more clearly at higher bias, particularly at the Ni L-edge. While these trends require further analysis and should not be overinterpreted at this stage, they indicate that Fe content affects not only catalytic performance but also the way the electronic structure evolves under reaction conditions. With further analysis and comparison to complementary hard XAS data, these operando soft XAS results may provide valuable insight into the potential-dependent evolution of Ni, Fe, and O states in NiFe OER electrocatalysts.

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Performance and stability evaluation of Fe-zeolite catalysts for NH_3-SCR of N_2O and NO_x in green shipping

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Introduction

Green ammonia (NH_3) is widely regarded as a promising alternative to fossil fuels in the shipping industry, as neither its production nor combustion results in CO_2 emissions. However, its combustion can lead to the formation of nitrous oxide (N_2O), a greenhouse gas roughly 300 times more potent than CO_2. Since NH_3-fueled marine engines are still under development, their potential N_2O emissions remain uncertain. It may therefore be necessary to implement flue gas cleaning technologies to ensure that the climate benefits of green ammonia are maintained [1].

To avoid delaying the large-scale adoption of NH_3 as a maritime fuel, NH_3-SCR catalysts capable of removing N_2O under ship-relevant operating conditions must be developed. Onboard SCR units can be installed either upstream of the turbocharger (>350 °C; 2-5 bar) or downstream (<300 °C; ~1 bar). Fe-zeolite NH_3-SCR catalysts, commonly used in the chemical industry, have shown insufficient performance under post-turbocharger conditions [2], while elevated pressure has shown promising but insufficiently explored effects [3]. In this work, we therefore systematically investigate the activity and durability of various Fe-zeolite catalysts for NH_3-SCR of N_2O and NO_x under elevated temperature, pressure, and water vapor conditions.

Results and Discussion

Fe-zeolite catalysts covering a range of zeolite frameworks (BEA, ZSM-5, SSZ-13), Si/Al ratios (10-20), and Fe/Al ratios (0.1-0.4) are synthesized using common preparation methods, including wet ion exchange, solid-state ion exchange, and impregnation. The physicochemical properties and catalytic performance of both fresh and spent samples are characterized using techniques such as FTIR, XPS, XRD, and UV-vis spectroscopy. Catalyst performance and durability tests are performed using a continuous-flow test rig operating at elevated pressures, exploiting the influence of varying N_2O/NO_x ratios, long-term stability (>200 h on stream), and assess the impact of SO_2 exposure - originating from the pilot fuel - on the most promising catalyst formulations.

The presentation compares the NH_3-SCR performance of the synthesized Fe-zeolite catalysts with that of a benchmark catalyst at different pressures, temperatures, gas compositions, and operation durations. This comprehensive evaluation enabales a realistic assessment of the suitability of placing the SCR unit upstream of the turbocharger.

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Robust Anodes for PEM Electrolyzers Based on Carbon Nanofibers and Low Iridium Loading

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Introduction

Climate change represents a critical global challenge, with near-surface temperatures rising by 1.42 °C in 2025. To meet the Paris Agreement targets and manage a global electricity demand expected to rise by 3.6% annually through 2030, expanding power grid flexibility via low-temperature electrolysis is essential. Proton exchange membrane water electrolysis (PEMWE) is a leading solution due to its high purity and efficiency. However, the scarcity of Iridium,the primary catalyst for the oxygen evolution reaction (OER) at the anode, remains a bottleneck.

Current research focuses on reducing Iridium loading to meet long-term targets of 0.125 mg/cm^2. Porous transport electrodes (PTEs) can improve catalyst utilization via direct electronic contact, but traditional designs often suffer from non-uniform catalyst layers or degradation under harsh assembly and operational conditions. We propose an engineered anode designed to optimize mass transport and durability in the near-membrane region.

Results and Discussion

We present a novel PTE anode utilizing carbon nanofibers to create a rigid, high-surface-area environment. To protect against carbon corrosion, the nanofibers feature a 0.5 mg/cm^2 anti-corrosion layer of platinum. The OER catalyst consists of of electrodeposited Iridium.

Characterization using identical location SEM (IL-SEM) and Raman spectroscopy confirms the robustness of this structure. The design creates a rigid nano-structure capable of remaining intact through assembly/disassembly cycles and operando single-cell performance testing over a 1000 h interval.

Key findings include:

- **Structural Integrity**: IL-SEM shows that the fibers survive the mechanical stresses of MEA assembly/disassembly and long-term operation.
- **Membrane Interaction**: The rigid fibers leave distinct imprints in the membrane. Raman spectroscopy reveals localized losses of -SO_3 groups in imprinted regions.
- **Performance**: Single-cell operando tests show the evolution of polarization curves and overpotentials.

By engineering the near-membrane electrode to account for interfacial contact resistance and local transport, this carbon fiber-based PTE provides a path toward sustainable, low-loading Iridium anodes for large-scale PEMWE implementation.

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O_2 Chemisorption and CO Oxidation Study on a Curved Ir(111) Crystal

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Introduction

The study of O_2 chemisorption and carbon monoxide (CO) oxidation is crucial for a basic understanding surface catalytic reactions. Detailed studies after introducing a gas in ultrahigh vacuum (UHV) conditions provide atomic-scale insights on the surface, and serve as reference for ambient pressure X-ray photoelectron spectroscopy (AP-XPS). The high data quality and the controlled conditions enable the investigation of catalytic process in atomic scale.

In this poster, we investigated the role of steps in the chemisorption of oxygen, using a curved Ir(111) crystal. This crystal exposes A-and B-type (111) vicinal surfaces, with the vicinal angle α refering to the tilt between the stepped surface and the high symmetry (111) facet. This curved samples enable a systematic comparison of different facets and step densities under the reaction conditions, allowing the investigation of structure-reactivity across the surface.[1]

Results and Discussion

In this study, we conducted the O_2 chemisorption and the titration of these O-covered Ir surfaces with CO. The O *1s* spectra across the curved Ir(111) crystal (O 1s α-scan) was acquired after dosing 10 L O_2 at 25 ℃ (L = Langmuir, 1L = 10^{-6} Torr·s). Oxygen chemisorption experiments show that this process strongly depends on the surface structure. The O_{terr} is dominant on (111) surface, on the othe hand, both stepped surfaces exhibit chemisorbed oxygen on terraces (O_{terr}, 530 eV) and steps (O_{step}, approximately 529.5 eV)[2].

The surface reactivity of O_{terr} and O_{step} was further examined via CO titration. The measurement was conducted by exposing the O_2-saturated curved Ir crystal to 10^{-9} mbar CO and subsequently increasing temperature. On both stepped surfaces, the oxygen was depleted and CO adsorption peaked (CO_{ads}) after approximately 35 mins. In contrast, some O atoms remain at the center after 55 mins of the experiment. These results indicate that step sites, specifically the B-steps, are more active than terraces for CO oxidation.

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Performance of dendritic MFI zeolites as a versatile catalytic platform for production of fine chemicals and sustainable fuels

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Introduction

Dendritic nanomaterials possess radially oriented meso-macropores with a high degree of connectivity, which provides them with very accessible 3D disordered superstructures. These materials have been explored recently as supports of a number of guest molecules and functionalities, leading to an increasing number of studies in a variety of fields.[1]

In contrast, the preparation of zeolitic materials with dendritic nano-architectures has been revealed rather elusive. However, as reported in recent works,[2,3] our research group has been successful in the synthesis of dendritic MFI zeolites through the crystallization of protozeolitic nanounits that were previously functionalized with amphiphlic organosilanes.

Results and Discussion

ZSM-5 zeolites with a well-defined and fully crystalline dendritic nano-architecture have been developed, showing outstanding accessibility, enhanced textural properties (with a multi-modal porosity, external surface areas over 300 m^2/g and total pore volumes up to 1 cm^3/g) and a balanced Brønsted/Lewis acidity. Important variations in the morphology of the dendritic nanoarchitecture in ZSM-5 can be obtained by changing the synthesis conditions (Figure 1).

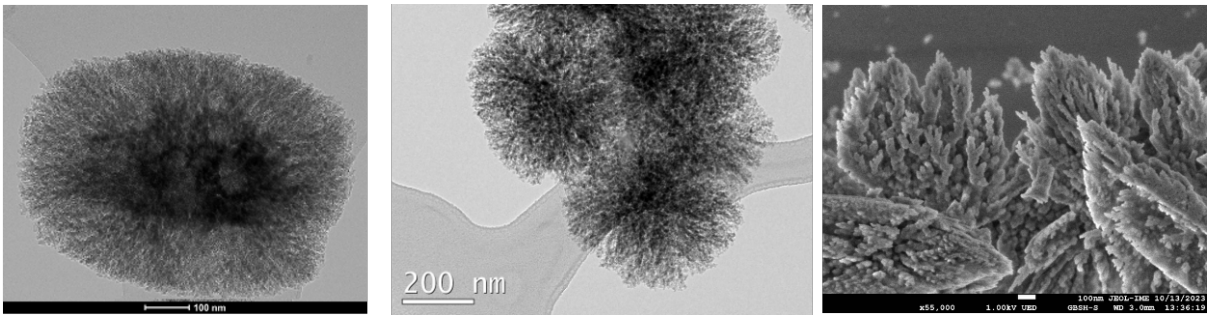

Figure 1. TEM/SEM images of ZSM-5 zeolites showing different dendritic motifs: core-shell (left), stars (centre) and tree-like (right).

These materials have shown remarkable properties as catalysts in a variety of reactions. In particular, outstanding performance has been achieved in fine chemicals synthesis through limonene and terpenes epoxides isomerization.[4] Likewise, dendritic ZSM-5 materials, modified with TiO_2 and ZrO_2, have demonstrated excellent behaviour in the production of sustainable fuels precursors by aldol condensation of furfural and cyclopentanone and through the isopropanol-assisted conversion of furfural into γ–valerolactone, respectively.[5]

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The Impact of Fe on Surface Structure Dynamics in Ni Electrolysis

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Introduction

Green hydrogen is key in transforming various industrial sectors towards decarbonization. Non-noble metal electrode materials like Ni, Co and Fe are preferred in alkaline water electrolysis due to their low cost and availability. A major challenge in achieving efficiencies close to the thermodynamic optimum is to overcome the slow kinetics of the oxygen evolution reaction (OER). Moreover, the impact of Fe incorporation on the catalytic properties is not fully understood.[1] Unraveling the correlation between the surface structural dynamics on NiFe electrode systems with the catalytic activity during OER will help the rational design of more efficient electrocatalysts. High-energy surface X-ray diffraction (HESXRD) and surface optical reflectance (SOR) allow us to monitor the Ni (oxy)hydroxide surface structures in model single crystal Ni(111) electrodes on an atomic scale under *operando* conditions.[2,3,4]

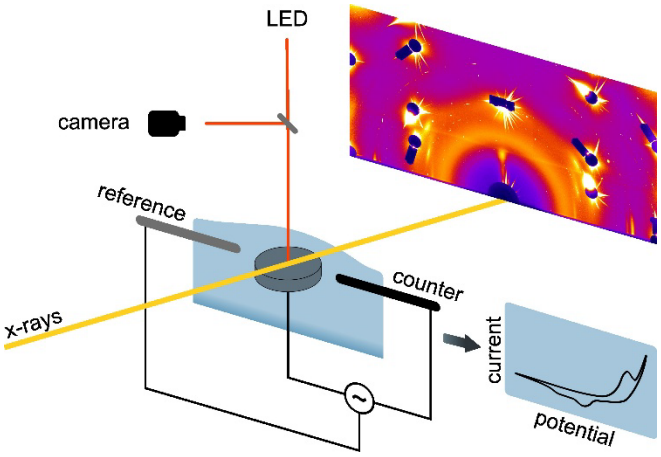

Figure: Illustration of experimental approach combining HESXRD and SOR in an electrochemical cell setup.

Results and Discussion

We were able to correlate HESXRD, SOR and electrochemical data to identify potential-dependent surface structure transformation processes between Ni (oxy)hydroxides in the transition to OER. Fe doping of the Ni(111) electrode lowered the overpotential required for OER and could be linked to changes in the surface structure. We found that SOR is surprisingly sensitive to chemical and structural changes in the Ni(111) surface.

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Dissolution mechanism and activity tuning of oxide perovskites for O_2 evolution via surface doping

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Introduction

The oxygen evolution reaction (OER) is the major bottleneck in electrochemical water splitting. Developing stable and efficient catalysts from earth-abundant materials is therefore crucial.[1,2] Perovskite oxides are promising OER catalysts due to their tunable electronic structure and multiple oxidation states. In this study, we investigate $SrMnO_3$, $SrFeO_3$, $SrCoO_3$, and $SrNiO_3$ and explore B-site surface doping with transition metals (Mn, Fe, Co, and Ni) to tune catalytic activity and stability.[3]

Results and Discussion

Density functional theory calculations show that surface doping reduces the thermodynamic overpotential (η_{tD}) by altering the active sites on the perovskite surface. Such trends are consistent with recent advances in thermodynamic and kinetic modeling of electrocatalytic reactions using first-principles approaches.[4] Dissolution free-energy calculations across different pH and potentials are performed to evaluate stability and possible dissolution pathways. The results indicate that $SrCoO_3$ and $SrNiO_3$ exhibit improved stability upon transition-metal doping while maintaining enhanced OER activity.

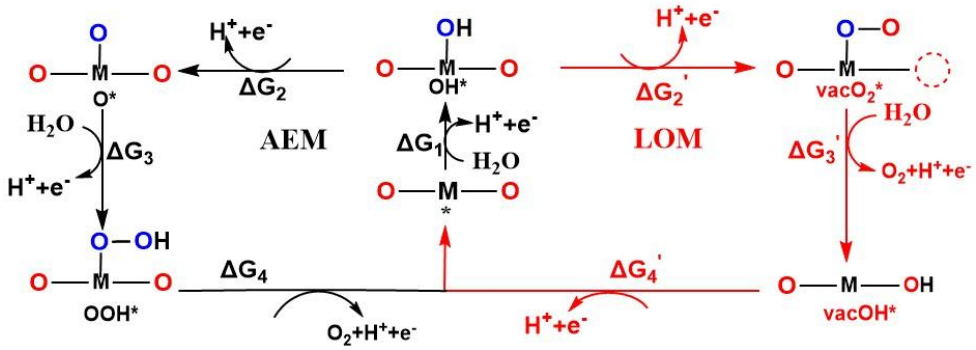

Figure 1. Illustration of the adsorbate evolution mechanism (AEM) and lattice oxygen mechanism (LOM) with corresponding free-energy changes (ΔG_i).

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Integration of Pd/Al2O3 monolith catalyst inside a MW plasma for complete oxidation of methane.

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Introduction

Methane (CH_4) is a potent greenhouse gas, and converting methane to carbon dioxide is a promising strategy. Nevertheless, the catalytic oxidation of methane to CO_2 requires elevated temperature (above 400 °C) to activate the strong carbon-hydrogen (C-H) bonds, making it energy intensive[1]. MW plasma generates highly reactive species that can activate methane at room temperature and atmospheric pressure, providing alternative reaction pathways[2]. However, due to the extreme gas temperatures of plasma core exceeding 1000 K, the catalyst cannot be placed directly in the plasma zone, and the reactives species generated in MW plasma are short lived, making the placement and integration of catalyst challenging[2].

Results and Discussion

In this study, we successfully integrated a Pd/Al_2O_3-based monolith catalyst inside a MW plasma reactor. The effect of different downstream flow rates on methane oxidation and CO_2 selectivity was studied. Methane conversion was primarily driven by the MW plasma, while the catalyst played a key role in promoting the oxidation of CO into CO_2, resulting in the complete oxidation of methane.

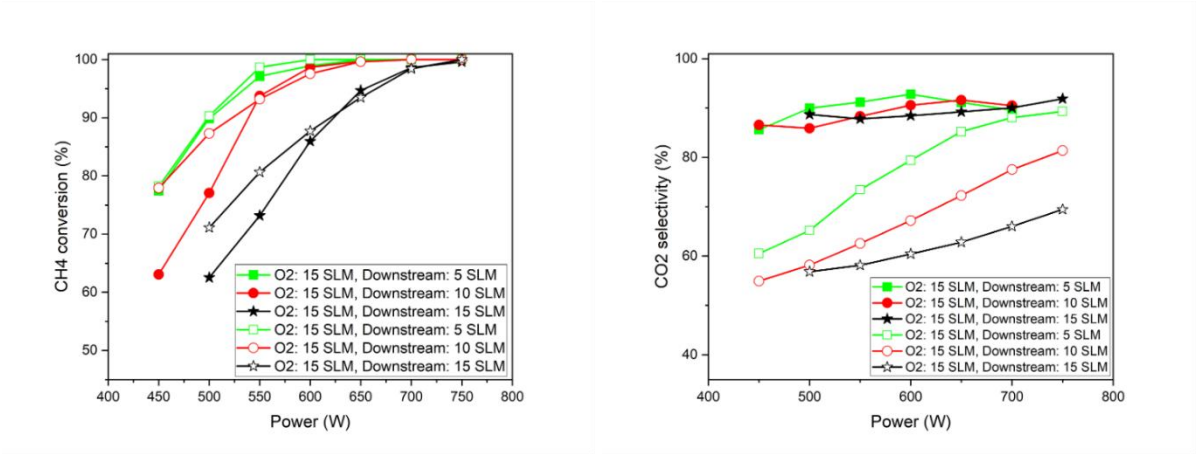

Figure 1. Effect of downstream flow and plasma power on Methane conversion and CO2 selectviity in empty MW reactor (open symbol) and in presence of catalyst (filled symbol).

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Tomographic surface X-ray diffraction: A new method for spatially resolved measurements of polycrystalline surfaces

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Introduction

In many catalytic applications the performance of the system is governed by processes at the catalyst surface [1,2], making understanding surface behaviour crucial. These surfaces undergo dynamic changes, which makes *in situ* characterisation essential. Surface studies providing atomic structural information are often performed on low-index single-crystal model catalysts. Polycrystalline surfaces are interesting as more realistic model catalysts and they allow us to measure more than one facet simultaneously. However, tools for studying polycrystalline surfaces are typically limited to low-pressure environments. Surface X-ray diffraction (SXRD) can probe long-range atomic structures, even in high pressures, but is limited to simple samples such as single crystals. We are developing tomographic SXRD (TSXRD) to add spatial resolution while retaining the advantages of SXRD [3].

Results and Discussion

The first part of this project is grain mapping of polycrystalline surfaces using grazing incidence X-ray diffraction. Using tools from 3D-XRD [4] adapted to an SXRD setup and the near-surface Bragg reflections, spatially resolved maps can be achieved as shown in Fig. 1a. In the second part of the project, the grain map is used in our TSXRD analysis, where the surface diffraction signals for different grains are sorted. The ability to extract surface signals for single grains from measurements of a polycrystalline surface (see Fig. 1b-c) allows us to study surface structures of more industry-relevant model systems at different conditions and even *in situ/operando*, as commonly done for single crystals using SXRD. Here, we will show how TSXRD works with examples of the applications that have been tested so far.

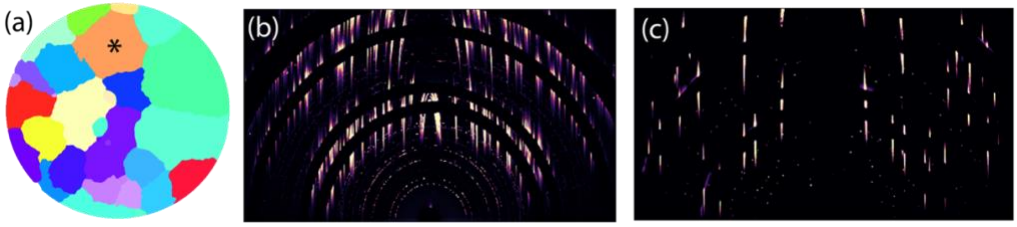

Figure 1: a) Grain map created using X-ray diffraction. b) Diffraction from polycrystalline Pd. c) Extracted diffraction from the grain marked with * in a.

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Steering Photocatalytic Nitrate Reduction Selectivity via Proton Suppression on Au–Hg/TiO_2 Nanotube Arrays

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Introduction

Engineering photocatalytic materials with controlled reaction selectivity remains a major challenge in heterogeneous catalysis. In aqueous TiO_2-based systems, the reduction half-reaction is typically dominated by proton reduction, competing with alternative substrate-driven pathways and limiting the efficiency of targeted photocatalytic transformations. In this work, anodically grown TiO_2 nanotube arrays modified with Au–Hg alloy nanoparticles were designed to address this issue. Hg-enriched catalytic sites are expected to suppress hydrogen evolution due to its high overpotential, thereby redirecting photogenerated electrons toward other reduction processes. Nitrate (NO_3^-) was selected as a model electron acceptor given the global environmental interest and the complexity of its reduction mechanism, which involves multiple competing pathways: a deoxygenation route leading to N_2 (through N_2O intermediate) and a hydrogenation route leading to NH_4^+ [1]. Therefore, limiting proton availability at the catalyst surface is expected to disfavor deep hydrogenation, promoting gaseous nitrogen products (N_2, N_2O) while limiting NH_4^+ accumulation, environmentally undesired since it causes eutrophication. Thus, controlling product selectivity in NO_3^- reduction represents an environmental priority and a benchmark for tuning photocatalytic performance.

Results and Discussion

Three photocatalytic materials were tested under UV irradiation (365 nm) using a 50 mg/L NO_3^- solution: bare TiO_2, Au–TiO_2, and Au–Hg–TiO_2. Au–Hg nanoparticles were obtained by Hg photodeposition onto sputtered Au nanoparticles [2], potentially exploiting Hg-contaminated waters as Hg source. Leaching tests confirmed no Hg release during photocatalytic operation, supporting the material's stability and safety. All reaction products and intermediates were monitored: residual NO_3^- and NO_2^- by ion chromatography (IC), NH_4^+ by UV-Vis spectroscopy, and gaseous products (N_2, N_2O) by mass spectrometry. Bare TiO_2 achieved 72% NO_3^- conversion after 3 hours, with a NH_4^+ selectivity of 35%, indicating significant deep hydrogenation of NO_3^- reduction intermediates. Au–TiO_2 showed a dramatic drop in NO_3^- conversion (30% after 3 hours), accompanied by significant hydrogen evolution even in the presence of NO_3^-, indicating that Au nanoparticles act as preferential proton reduction sites that compete with NO_3^- reduction. Upon introduction of Hg into Au nanoparticles, hydrogen evolution was completely suppressed, consistent with the high overpotential for H_2 on Hg-enriched surfaces, and NO_3^- conversion was restored to 69%, comparable to bare TiO_2. However, a key difference emerged in product selectivity. Au–Hg–TiO_2 reduced NH_4^+ selectivity to 13%, compared to 35% for bare TiO_2, demonstrating that limiting proton availability at the catalyst surface effectively disfavors the hydrogenation pathway, promoting the formation of gaseous nitrogen products, with N_2O as the dominating product. Although N_2O is a greenhouse gas, if captured it can be useful for many industrial applications while simultaneously removing nitrogen compounds from water.

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From Atomic Active Sites to Jet-Engine Performance: Multiscale Design of High-Temperature NOx Catalysts

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Introduction

Nitrogen oxide (NOx) emissions from aviation engines remain a major challenge for reducing the environmental impact of air transport.[1] However, the extreme temperatures (>1000 K), high exhaust velocities, and chemical environment characteristic of jet engines impose stringent requirements on catalyst activity and durability. In particular, the link between atomic-scale catalyst properties and macroscopic NOx conversion under realistic engine conditions remains poorly understood. Here we investigate Ni-based ternary alloys as potential high-temperature NOx catalysts using a multiscale modeling framework that combines first-principles calculations, thermodynamic phase stability analysis, microkinetic modeling, and reactive computational fluid dynamics simulations of catalytic coatings on turbine components. This framework bridges atomic-scale catalyst design and engine-scale performance, enabling the rational development of catalytic NOx mitigation strategies for next-generation aircraft.

Results and Discussion

First-principles analysis reveals robust scaling relationships between adsorption energies of key intermediates (N, O, C, NO, and CO) on transition-metal surfaces, enabling descriptor-based analysis of catalytic activity consistent with previous work.[1] Combined with transition-state scaling relations and microkinetic modeling, these relationships yield volcano-type activity maps identifying Pt-, Pd-, and Rh-containing surfaces near the optimal activity region for NO decomposition under representative turbine conditions with CO and unburnt hydrocarbons as main reductants of NOx. High-throughput screening of Ni-based ternary alloys shows that alloying Ni with catalytically active elements preserves adsorption energetics close to the optimal descriptor while retaining the thermal robustness characteristic of Ni-based superalloys. DFT-informed thermodynamic modeling predicts that the leading candidates maintain a stable fcc phase across the relevant temperature and composition range. Among the investigated systems, alloys such as NiCoPt and NiCoPd emerge as particularly promising, combining favorable catalytic descriptors, resistance to coking, and stable active-site ensembles. Reactive CFD simulations of catalytic coatings on turbine components further indicate that, when applied to the full rotor and stator surface area of the low-pressure turbine, these catalysts could enable substantial reductions in NOx emissions under realistic engine operating conditions.

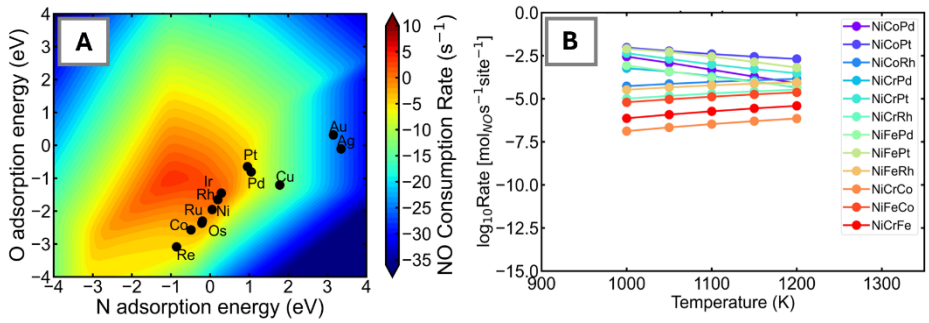

Figure. In A, rate plot for NO conversion over elemental fcc (211) transition metal surfaces at low pressure turbine conditions. In B, predicted rates for Ni-based ternary alloys over fcc (211) surfaces.

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Size-Dependent Reactivity and X-ray-Induced Effects in Cu_2O Nanocubes Model Catalysts: A NAP-XPS Study

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Introduction

Cuprous oxide (Cu_2O) nanocubes are promising catalysts for oxidation reactions and photocalytic reactions, but their instability under oxidative conditions limits practical applications.[1] While single-crystal studies reveal facet-dependent oxidation,[2] the role of particle on oxidation mechanisms remain unclear. This work investigates the oxidation behavior of ligand-free Cu_2O nanocubes (15–400 nm) under O_2 using near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) and morphological analysis (by SEM). It also addresses photon energy-dependent effects observed during synchrotron and laboratory experiments.

Results and Discussion

NAP-XPS and SEM analyses reveal distinct size-dependent surface chemistry: larger Cu_2O nanocubes (>90 nm) retain significantly more organic and hydroxyl contamination compared to smaller particles. Under 1 mbar O_2, nanocubes smaller than 90 nm undergo complete oxidation to CuO at 480–530 K, driven by surface-reaction-controlled kinetics. In contrast, larger nanocubes (>90 nm) exhibit a plateau in oxidation temperature at ~560 K, indicating a shift to diffusion-limited kinetics. Morphological analysis via SEM further demonstrates that the cubic morphology remains intact until oxidation progresses, beyond which edge rounding and structural reorganization occur.

These findings establish a critical 90 nm threshold: below this size, complete oxidation to CuO occurs, while above it, hydroxyl-passivated CuO shells form a stable core-shell structure, enabling tunable stability for catalytic applications.

Additionally, this project highlights dramatic photon energy-dependent effects. Systematic investigations of beam damage under O_2 and water reveal that the oxidation of Cu_2O nanocubes is highly sensitive to photon energy and flux. Comparisons between synchrotron ($h\nu$ = 750 eV) and laboratory X-ray sources ($h\nu$ = 1486 eV) confirm significant X-ray-induced radiolysis effects, underscoring the critical role of photon energy in oxidation studies.

This study demonstrates that size-controlled Cu_2O nanocubes bridge the gap between model systems and real catalysts, revealing a kinetic transition at ~90 nm and emphasizing the impact of photon energy on oxidation behavior. These insights inform catalyst design for optimized stability and performance under oxidative conditions.

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Probing adsorption sites on doped-MoS_2 for hydrodeoxygenation of lignin

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Introduction

Lignin, an abundant aromatic biopolymer representing 15–30 wt% of dry biomass, remains largely underutilized and is mainly incinerated for energy recovery during the kraft process.[1] Its catalytic valorization is hindered by the difficulty of C–C bonds cleavage while avoiding catalyst deactivation, particularly due to sulfur. Ni-promoted MoS_2 catalysts have recently demonstrated promising activity for lignin depolymerization.[2] However, the role of promoters in hydrogen activation remains poorly understood.

Results and Discussion

We present a Density Functional Theory (DFT) investigation of hydrogen activation and lignin dimer adsorption on pristine and doped MoS_2 surfaces. The promoting effects of Ni and alternative dopants (Co, Cu, Fe, Zn) were analyzed in terms of hydrogen activation, stability, and mobility, as presented on Fig. 1(a). Calculations were performed using GPAW with ASE, including D4 dispersion and dipolar corrections. Preliminary lignin dimer adsorption structures were explored via MACE-based minimum hopping.[3] MACE is a machine learning interatomic potential that can act as a surrogate for DFT in order to reduce computational cost for large systems. We find that hydrogen adsorption is strongly influenced by surface doping. For all dopants, hydrogen preferably adsorbs on neighboring sulfur atoms, as shown in Fig. 1(b), leading to thermodynamically favorable configurations and enhanced hydrogen availability for transfer reactions. The reaction pathway, including the effect of Ni promotion as an example, is presented in Fig. 1(c). Hydrogen desorption is primarily limited by a kinetic barrier. While SH_2 desorption is kinetically more accessible, H_2 desorption is thermodynamically more favorable. Co and Fe exhibit similar behavior, whereas dopants Cu and Zn display higher kinetic and thermodynamic barriers for hydrogen desorption. These findings provide atomistic insights into promoter effects and highlight promising directions for catalyst design. Ongoing work investigates the adsorption and reaction pathways of representative lignin model units on hydrogen-covered surfaces.

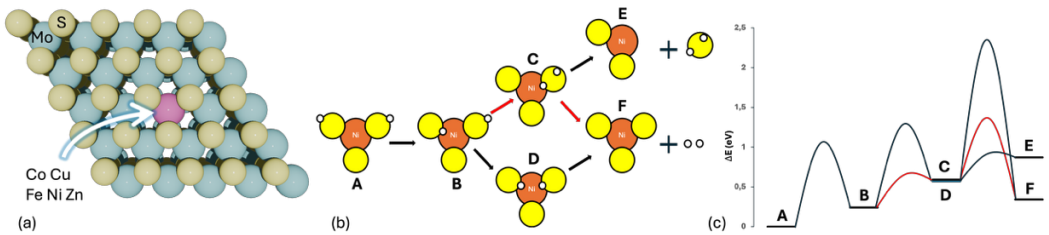

Figure 1 – (a) (001) MoS_2 basal surface; (b) Simplified visualization of hydrogen adsorption and diffusion intermediates on Ni-doped MoS_2 (S: yellow, H: white); (c) Corresponding reaction energy profile.

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Co-oligomerization of ethylene and propylene

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Introduction

Promising renewable route for sustainable aviation fuel (SAF) production is Methanol-to-Jet which includes sustainable methanol production and conversion to C_2-C_4 olefins (MTO) and a subsequent oligomerization step of short-chain hydrocarbons to the jet fuel range of C_8-C_{16}. While oligomerization of C_{3+} olefins occurs on solid acid catalysts like zeolites, ethylene possesses a significant challenge for the overall pathway due to its limited reactivity with acidic catalysts. Typically ethylene oligomerization takes place on homogenous Ziegler-Natta catalysts or heterogenous nickel-based systems supported on low-acidity materials [1]. Therefore an approach to convert olefin mixtures including ethylene by co-oligomerization over an optimized catalyst system is needed to enhance the efficiency and selectivity of the overall process integration. Catalysts with both metal and acid sites capable of simultaneous co-oligomerization of ethylene and propylene are studied to address the challenges with ethylene. Ethylene oligomerization requires transition metal as a catalyst and nickel-based materials have shown high activity for ethylene oligomerization. [2] As a catalyst support, mesoporous silica-aluminas or zeolites are interesting due to their high activity and stability. The catalytic materials studied in this work are ion-exchanged Ni on ZSM-5 zeolite and impregnated Ni on amorphous silica-alumina catalysts that were prepared and tested with mixed olefin feeds of ethylene and propylene. The production of jet fuel range hydrocarbons by oligomerization of ethylene and propylene was studied with tubular fixed-bed reactor at temperatures of around 200-300°C and pressure of 7-14 bar. During the experiments the products were analyzed with online GC-FID and TCD, and the liquid products were analyzed with offline GC-FID.

Results and Discussion

In Table 1, the reaction conditions and ethylene and propylene conversions are shown for ion-exchanged Ni-ZSM-5 and impregnated Ni/SiO_2-Al_2O_3 catalysts at around 20 h time-on-stream.

Table 1. Converison of ethylene and propylene with two different Ni-based catalysts.

Catalyst	Temperature (°C)	Pressure (bar)	WHSV (h^{-1})	Ethylene conversion (%)	Propylene conversion (%)
1 wt.% Ni-ZSM-5	275	6	0.8	13	96
1 wt.% Ni/ASA	275	7	2.6	62	36

The amount of nickel loading and the acidity stregth of the catalyst support affect the activity on converting ethylene and propylene. By optimizing the catalyst properties and reaction conditions, catalyst system can be found to maximize the total olefin conversion and yield on jet range hydrocarbon production.

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Discrete Denoising Diffusion Probabilistic models in inverse design of metal alloy catalysts

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Introduction

Climate change motivates the development of efficient methods for converting CO_2 into other useful chemical compounds, which requires catalysts capable of activating CO_2 at low temperatures. Conventional computational screening methods for discovering new catalysts involve creating a candidate material by assembling certain spatial configurations of elements, followed by evaluation of its catalytic properties. However, recent advancements in generative artificial intelligence have paved the way for inverse materials design. Here, desirable catalytic properties, e.g., activity or selectivity for a given reaction, are specified first, and new candidate materials are then generated to match these targets [1,2].

In this work we investigate how a Discrete Denoising Diffusion Probabilistic Model (D3PM [3]) can be used to guide the search towards highly active metallic alloy surfaces. Specifically, we aim to optimize the reaction rate of the reverse-water-gas-shift (RWGS) reaction by varying the composition of alloy surfaces across a broad range of metallic elements.

Results and Discussion

We define a catalytic surface as a grid of fixed atomic positions, allowing the atomic species to vary among different metallic elements. The catalytic performance is assessed by evaluating the reaction rate for the RWGS reaction from a microkinetic model based on rate equations. The input to this model, adsorption and transition state energies in the reaction mechanism, is predicted using a graph-based Gaussian Process Regression model (WWL-GPR [4]), trained on density functional theory data [5]. A conditional D3PM is then trained to recover structures from noise by only corrupting the elements, analogous to discrete token corruption in text generation. This is done using a Graph Neural Network (GNN), which produces probabilities for each element at each site. This enables efficient sampling by learning chemically meaningful correlations that distinguish high- and low-performing surfaces.

Overall, the results show that the developed approach preferentially samples regions of composition space associated with high reaction rates, significantly outperforming random search. These findings illustrate how diffusion-based generative models can be used as a tool for guiding the discovery of new catalytic materials.

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Confinement-Controlled Methane Activation over Zeolites with Distinct Framework Topologies

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Introduction

The high C-H bond strength and the rapid overoxidation of intermediates fundamentally limit the selective oxidation of methane to methanol[1]. Beyond active site composition, spatial confinement within microporous zeolite frameworks can significantly influence reaction pathways by stabilizing key intermediates and restricting secondary oxidation[2]. To experimentally validate the confinement effect, we compare zeolites with distinct framework topologies; FER: 2D channels[3]; CHA: cage-based[4], MOR: large 1D channels[5], and MFI: 3D medium pores[6] under identical reaction conditions.

Results and Discussion

Using in situ DRIFT spectroscopy, methane oxidation was evaluated over H-FER, H-CHA, H-MOR, and H-ZSM-5, with γ-Al_2O_3 as a non-microporous reference. Over γ-Al_2O_3, methane activation predominantly yields formate species ($HCOO^-$) and CO_2, indicating rapid deep oxidation (Fig. 1). Similar behavior, though less pronounced, is observed for MOR and MFI, whose relatively open channel systems allow further oxidation beyond methoxy formation. In contrast, FER exhibits dominantly surface methoxy (CH_3O^-) signals with significantly suppressed COx formation. The constrained pore systems in FER stabilize methoxy intermediates and limit diffusion-driven overoxidation.

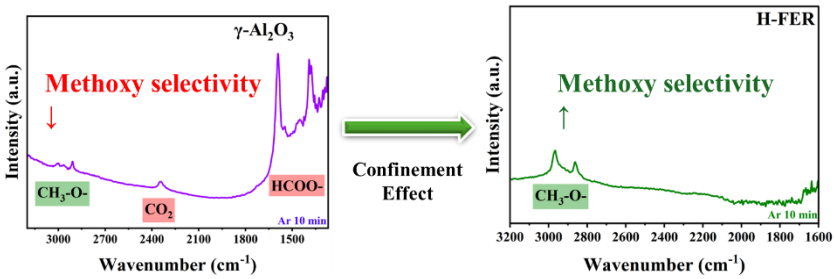

Figure 1 Confinement-Enhanced Methoxy Selectivity Revealed by in situ DRIFTS

The selectivity correlates with the framework topology demonstrating that geometric confinement governs intermediate lifetimes and reaction pathways. These results provide direct experimental evidence that zeolite confinement modulates methane activation by stabilizing transition states and suppressing deep oxidation. Overall, rational control of micropore architecture offers an effective strategy to enhance methoxy selectivity in dry methane oxidation.

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Pd/CeO_x Inverse Opals for Alkaline Hydrogen Oxidation

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Anion exchange membrane fuel cells (AEMFCs) have emerged as a promising alternative to proton exchange membrane fuel cells due to their less corrosive cell environment permitting a wider choice of catalysts beyond platinum. However, the switch to alkaline conditions in turn leads to sluggish kinetics in the hydrogen oxidation reaction (HOR) at the anode. It has been suggested that an ideal HOR catalyst balances active sites for both H_{ads} and OH_{ad} which has been scarcely realized with non-Pt catalysts.[1] In this work, porous Pd/CeO_x inverse opal networks were synthesized, which maximize active site accessibility, mass transport and key Pd-Ce interfacial area. The CeO_x support functions as an oxyphilic OH^- donor to Pd, while metal–support interactions modulate the hydrogen binding energy of palladium.[2]

The inverse opal structure was fabricated by self-assembling monodisperse polymer microspheres onto a glassy carbon electrode (Fig 1a). The template was then infiltrated with Ce and Pd precursors before calcination at 500°C yielding highly ordered IOs (Fig 1b). Polymer microspheres of size 100, 330 and 500 nm were employed with 100 nm spheres yielding the highest current density at 0.1 V_{RHE} with 10 wt% Pd loading, likely due to higher surface area and better dispersion of Pd throughout the framework (Fig. 1c). A peak current density of 0.27 mA/cm^2_{Pd} at 0.1 V_{RHE} was achieved with a 100 nm IO with 10 wt% Pd, 11-fold that of a planar Pd film. The electrochemically active surface area (ECSA) was found to decrease with increasing pore size, with an estimated value of 0.04 cm^2 for the 100 nm sample. The reduction in ECSA observed for larger pore sizes highlights the need to balance mass transport within the support material and its conductivity, particularly when using semiconducting supports such as CeO_x. The results demonstrate that scaling pore size down to the mesoporous regime preserves sufficient conductivity while enhancing kinetics and mass transport.

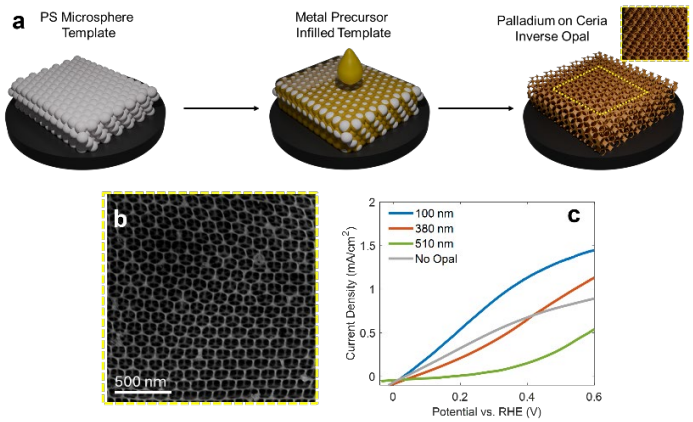

Figure 1: (a) Schematic showing fabrication of Pd/CeO_x inverse opal electrocatalysts. (b) SEM micrograph of Pd/CeO_x inverse opal film. (c) HOR performed in H_2-saturated 0.1 M KOH at 5 mV s^{-1} and 1600 rpm.

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SERIAL CHEMICAL CRYSTALLOGRAPHY FOR AUTONOMOUS STRUCTURE AND PHASE ANALYSIS FOR POROUS MATERIALS

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Introduction

Recent advancements in robotics and artificial intelligence have significantly propelled the development of autonomous synthesis and characterization workflows. Powder X-ray diffraction (PXRD) is the dominant method for characterization in these workflows. Nevertheless, challenges arise when a polycrystalline product contains multiple phases, phases with low contents (<5%), phases with similar unit cell parameters and structures with peak overlaps in PXRD patterns. As autonomous synthesis usually produces many samples within a short timeframe, there is a pressing demand for innovative techniques that can match the speed and obtain the compositions and atomic structures for complex mixtures simultaneously.

Here we present SerialED with tilt (t-SerialED), a multi-shots-per-crystal method that enables autonomous quantitative analysis for complex mixtures. Our method addresses the challenges in small molecule SFX (smSFX) and SerialED by combining robust indexing using three-dimensional reciprocal space information with still shot integration methods from serial crystallography. The structure determination can be achieved by integrating and merging indexed still frames using existing serial crystallography programs. We conducted autonomous data collection and analysis of the compositions and crystal structures across a range of beam-sensitive and polycrystalline mixtures, spanning from nanoporous materials to pharmaceutical compounds. We expect t-SerialED to become a general method for chemical crystallography and phase analysis of submicron or nano-sized mixtures, complementing PXRD for routine sample checking and phase analysis.

Results and Discussion

Ab initio structure determination of metal-organic frameworks

We chose MOF-235 as our test sample for structure determination from t-SerialED datasets. As shown in Figure 2a, some of the crystals are well-isolated and some of them tend to stick together. The crystal finding algorithm will identify both as targets and collect t-SerialED datasets. The ED pattern from aggregated crystals shows a typical multi-crystal ED pattern, which is successfully indexed and all three lattices with different orientations are resolved. As aggregated particles are unavoidable for most of TEM samples, inclusion for these areas will not only increase the data collection efficiency but also reduce the bias and systematic error in quantitative phase analysis. We reached a complete dataset with high multiplicity by merging 160 datasets collected within around 1h, containing 159 indexed datasets. The 3D reciprocal space was visualized from an individual t-SerialED dataset and space groups were determined from the systematic absence conditions. The unit cell distribution analysis is performed after using DIALS to index all the datasets. The analysis shows very small standard deviations (below 0.5%) for both lengths and angles. As shown in Figure 1b, the crystal structure can be determined ab initio using direct methods in SHELXT in the space group of $P\bar{6}$ 2c and the structure can be refined anisotropically. The final R1 reached below 14%, which is as good as those for 3DED/MicroED datasets. The framework atoms are correctly resolved and all

Hydrogen catalytic oxidation at sub-zero temperature

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Introduction

Hydrogen is emerging as one important alternative as a fuel for sustainable heavy transport applications. It could be produced, via electrolysis, from renewable sources such wind or solar power yielding a fuel with out any CO_2 emissions. In trucks the hydrogen could be used in fuel cells, transforming it into electricity, or in conventional internal combustion engines. The latter offeres a good alternative for a faster application as they are built on proven technology.

The availability of hydrogen on-board the truck opens up new possibilities for using hydrogen as a heat source for heating of the engine and other components at cold start conditions. Earlier studies connected to NASA's space program have shown that catalytic oxidation of hydrogen could be initiated at as low temperatures as -112 °C. However, more in-depth studies of the kinetics of the reaction at sub-zero temperatures are mostly lacking in the literature. The present study aims to study the catalytic combustion of hydrogen at sub-zero temperatures.

Results and Discussion

Initial test using a flow reactor set-up with a platinum based monolith catalyst have proven that total hydrogen oxidation could be achieved at temperatures lower than -20 °C. Further, work is ongoing to gain deeper understanding of the kinetics of the reaction. Moreover, additional development of the designated test rig will make it possible to gain better time resolved and kinetic data. These data will be used to set up a model for the reaction.

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Dilute Alloy Electrocatalysts for CO_2 Electroreduction

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Introduction

Electrochemical conversion of CO_2 into fuels and value-added chemicals offers a compelling alternative to address the challenges associated with fossil fuel dependence and renewable energy intermittency. Copper (Cu) is one of the most promising electrocatalysts for the electrochemical reduction of CO_2 to value-added multicarbon (C_2^+) chemicals and fuels. However, the development of practical CO_2 electroreduction technologies remains limited by the difficulty of achieving high selectivity toward C_2^+ products on Cu-based catalysts, and the lack of systematic studies conducted at high current densities. While dilute alloys have emerged as a promising materials[1], the influence of their preparation method for CO_2 electroreduction remains crucial as it dictates their surface composition which can directly influence their electrocatalytic performance. The goal of this work is to provide in-depth understanding of the influence of preparation methods on dilute alloys for CO_2 electroreduction.

Results and Discussion

In this work, PdCu dilute alloys were prepared via two different wet-chemical methods, namely co-reduction and sequential reduction. In the co-reduction method, Cu and Pd precursors are introduced and reduced simultaneously to obtain PdCu dilute alloy nanoparticles. In the sequential reduction method, Cu nanoparticles are prepared first, and Pd is added via galvanic replacement. A narrow size distribution of ca 4 nm was obtained and the Pd composition was varied and controlled at 2, 4, and 6 at.% in both cases. Importantly, electrocatalytic tests were carried in zero-gap electrolyzers at high current density (>100 mA cm^2). An important finding is that the selectivity for C_{2+} products and notably ethylene is highest for PdCu with 4 at.% Pd. Investigation of the effect of the size and preparation method on the catalytic activity and selectivity of CuPd dilute alloys will be discussed in details.

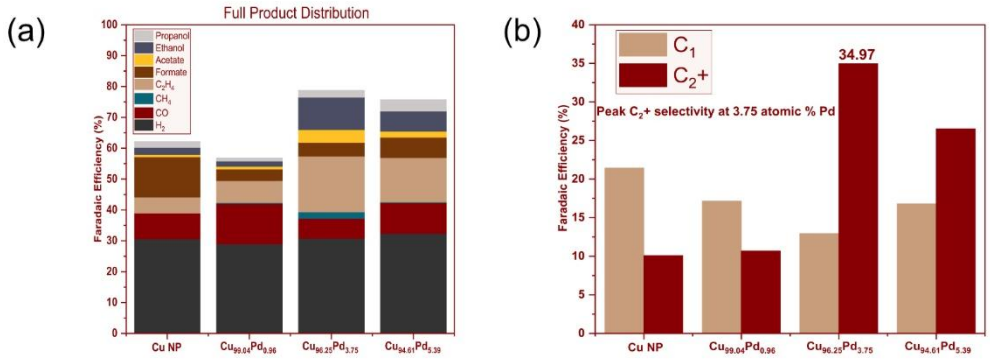

Figure 2. (a) Full distribution of products obtained from CO_2 electroreduction in a zero-gap electrolyzer at 100 mA cm^{-2} for Cu and Cu–Pd dilute alloy nanoparticles. (b) Comparison of C_1 and C_{2+} selectivity

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Effects of sulfur on dehydrogenation activity of Pt

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Introduction

Liquid organic hydrogen carriers (LOHCs) are a promising solution for hydrogen storage and transport. In LOHCs, hydrogen is covalently bound to an organic molecule and later extracted through catalytic reactions, resulting in a system compatible with existing fuel infastructure. One example is the methylcyclohexane/toluene (C_7H_{14}/C_7H_8) system, which has already been commercialized [2]. However, catalyst performance must still be improved to ensure economic viability. Pt catalyzes the dehydrogenation of C_7H_{14} but also promotes unwanted C-C bond cleavage reactions [3], such as the demethylation of C_7H_8, which destroys the carrier. These reactions are known to preferentially occur at under-coordinated sites [4]. One proposed strategy to suppress them is sulfur decoration of the Pt surface, which may block these sites and thereby reduce unwanted side reactions [5]. Here, we use density functional theory (DFT) to study sulfur-modification of Pt(111) and Pt(553), and its effects on dehydrogenation of MCH.

Results and Discussion

We find that the surface geometry determines the distribution of sulfur: adsorption is strongest on Pt(111), followed by the step edge of Pt(553), and finally the terrace of Pt(553). We also find that sulfur partially oxidizes its nearest neighbor Pt atoms upon adsorption and lowers their d-band centers. Consequently, sulfur weakens the adsorption strength of co-adsorbates in its immediate vicinity. The weaker adsorption bonds yield increased selectivity for toluene desorption over demethylation at the end of the dehydrogenation cycle over Pt(111) (see Figure 1). Promotion of toluene desorption also results in improved catalyst activity, as it frees up reaction sites, allowing for higher turnover frequency. These results agree with experimental observations on Pt nanoparticles [5]. We conclude that sulfur may restrict access to under-coordinated sites, but that its more significant contribution is its electronic modification of the catalyst surface. By destabilizing chemisorbed reaction intermediates, moderate sulfur poisoning of a Pt catalyst can enhance the selectivity and activity of C_7H_{14} dehydrogenation to C_7H_8.

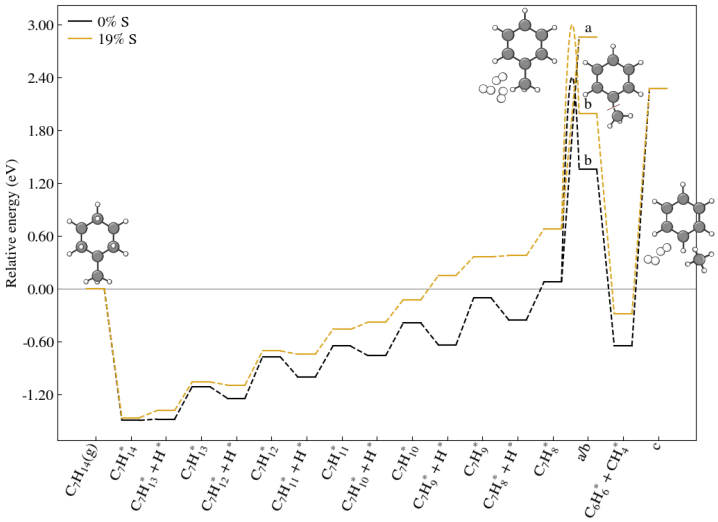

Figure 1. Energy diagram of C_7H_{14} dehydrogenation over pristine and sulfur-modified Pt(111). Labels a, b and c indicate $C_7H_8(g) + 3H_2(g)$, $C_6H_5^* + CH_3^*$, and $C_6H_6(g) + CH_4(g) + 2H_2(g)$, respectively.

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Designing High-Surface Area Ordered Mesoporous In_2O_3 for CO_2 hydrogenation

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Introduction

To mitigate global warming and advance the circular carbon economy, technologies for CO_2 capture, storage and utilization have become essential for modern society [1]. Specifically, the development of efficient and highly selective catalysts for reverse water-gas shift (RWGS) and CO_2 hydrogenation is of interest. However, achieving high selectivity remains challenging as competing reaction pathways and thermodynamic limitations restrict the formation of desired products (CO, CH_4 or CH_4OH) [2,3]. Indium oxide (In_2O_3) is a catalyst known for its high selectivity in hydrogenating CO_2 to methanol, as well as its high activity at RWGS below 400 °C [4]. Studies have demonstrated that CO_2 adsorption and activation is highly sensitive to structural parameters such as surface area and morphology [5]. In this work, we show that synthesizing In_2O_3 using KIT-6 as a hard template allows well-defined and high-surface-area In_2O_3 catalysts with tunable structural features, resulting to enhanced catalytic activity.

Results and Discussion

The N_2-physisorption isotherms in figure 1a demonstrate that In_2O_3 synthesized via hard templating KIT-6 (m-In_2O_3) exhibit characteristic type IV isotherms for mesoporous materials confirming well-defined mesoporosity. In contrast to bulk In_2O_3, m-In_2O_3 display significantly higher surface area of 62 m^2/g compared to 5 m^2/g. The increase in surface area is relevant when the catalysts are tested in the RWGS reaction. Results from the catalytic tests are shown in figure 1b. At 400 °C m-In_2O_3 achieves a CO_2 conversion of 25% compared to 10% in bulk In_2O_3. By using complementary techniques such as CO_2-TPD, XPS and TEM the difference in activity is attributed to the surface chemistry and active site availability. Ongoing work aims to extend this correlation to CO_2 hydrogenation to methanol where the interplay between structural features and activity is equally critical.

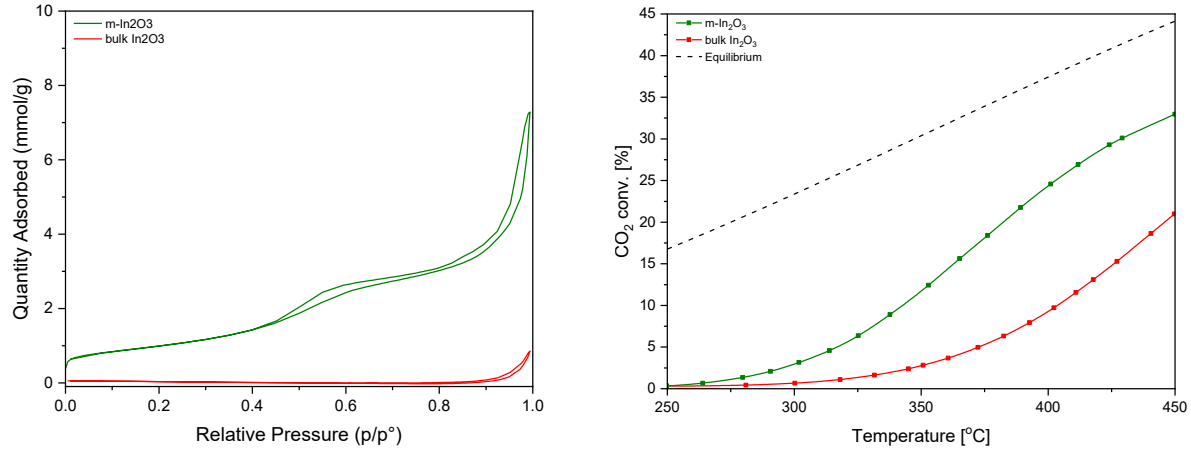

Figure 1. *Left a) N2 physisorption of the mesoporous catalyst Right b) catalytic activity of the materials (CO2 conversion%)*

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Effect of water and hydrogen on the NH_3-SCR performance over vanadia-based catalysts for H_2-ICE exhaust aftertreatment

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Introduction

Hydrogen internal combustion engines (H_2-ICE) offer a compelling pathway toward carbon-free transportation, eliminating fuel-borne carbon emissions and hydrocarbon by-products entirely. However, the high-temperature combustion of hydrogen still drives thermal nitrogen oxidation, producing NOx emissions that contribute to acid rain, photochemical smog, and adverse respiratory health effects. Furthermore, hydrogen combustion yields substantial water vapor (up to approximately 25 vol%) as its primary combustion product, which distinguishes H_2-ICE exhaust from conventional diesel exhaust streams. Ammonia-selective catalytic reduction (NH_3-SCR) is a well-established aftertreatment technology for NO_x abatement. Vanadia is a highly active SCR catalyst, where the nature of surface vanadyl species - monomeric, polymeric or crystalline V_2O_5 - is strongly governed by vanadium surface density and a crucial determinant for both activity and selectivity[1][2]. However, the characteristically high concentrations of water vapor and potential unburnt hydrogen in H_2-ICE exhausts introduce unique challenges and opportunities for the SCR performance. This work examines vanadia-based (V-Sb/TiO_2) catalysts under H_2-ICE exhaust conditions, with particular focus on the influence of water vapor and hydrogen on the NOx conversion, N_2O selectivity, and NH_3 oxidation behavior.

Results and Discussion

For all V-Sb/TiO_2 formulations tested in the present study (1.5V/4Sb, 2V/4Sb, 2V/0Sb, and 3.5V/4Sb), addition of water resulted in a moderately positive effect on the NO_x conversion at higher temperatures (>375–400°C), while a slight inhibition was observed below 200°C. This low-temperature inhibition could be attributed to competitive adsorption of H_2O on active Brønsted acid sites, limiting the availability of surface-bound ammonium species for the SCR cycle[3]. Antimony doping reduced the formation of N_2O (i.e. lower N_2O selectivity) without compromising the NO_x conversion, and its suppression effect combined additively with that of water. Increased vanadium loading enhanced low- to mid-temperature activity but simultaneously promoted non-selective NH_3 oxidation at high temperatures, yielding significant NO_x/N_2O production and ultimately negative NO conversion, which is consistent with the dominance of oxidative polymeric vanadyl species at high surface coverage[1]. The addition of 1000 ppm H_2 had no significant effect on the NOx conversion or N_2O formation, showing that V–Sb/TiO_2 is largely insensitive to hydrogen under lean H_2-ICE exhaust conditions[4]. The results obtained in this study indicate that for vanadia-based SCR catalysts for H_2-ICE applications, the selectivity is governed primarily by water content, acid-site chemistry, and V-Sb loading and interactions.

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Comparative study on the influence of dewatering of pyrolysis oil: properties and hydrodeoxygenation upgrading

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Abstract: Pyrolysis oil from residual biomass, such as sawdust, requires pretreatment before hydroprocessing due to high oxygen and water content. This study investigates azeotropic distillation with mesityl oxide as a cost-effective dewatering method. The treated oil showed improved thermal stability, with removal of water and oxygenated compounds, including sugars and acids. Subsequent hydrodeoxygenation (HDO) using a $NiMoS/Al_2O_3$ catalyst yielded more deoxygenated products and greater water-phase separation, despite some char formation. Reintroduction of water reversed these benefits, indicating water—not organic composition—primarily inhibits HDO. Dewatering enhances pyrolysis oil quality and HDO performance, offering a practical route for biofuel upgrading.

Keywords: Pyrolysis oil, Upgrading, Dewatering.

Harnessing biomass resources is essential to reduce environmental impact and promote sustainability. Pyrolysis oil, derived from waste biomass such as sawdust, holds strong potential as a biofuel feedstock [1]. However, its inherent properties, particularly high oxygen and water content, make it unsuitable for direct processing in conventional refinery hydrotreating reactors, necessitating pretreatment [2]. The main objective of pyrolysis oil upgrading via hydrotreatment is to lower oxygen content, which generates water as a by-product.

In this study, pyrolysis oil was subjected to nearly complete dewatering via azeotropic distillation using mesityl oxide as the solvent. This process altered the oil's composition by removing volatile compounds and specific oxygenates soluble in water and/or mesityl oxide, including sugars and acidic compounds. It also reduced the carbonyl compound content and concentrated more complex oxygenates. These compositional changes significantly impacted the efficiency of the subsequent hydrodeoxygenation (HDO) performance. The yields and composition of products obtained from upgrading both untreated pyrolysis oil (PO) and dewatered oil (DPO) through hydrodeoxygenation (HDO) using a $NiMoS/Al_2O_3$ catalyst were analyzed (results shown in Figure 1). The upgrading of the dewatered oil demonstrated that reduced acidity and carbonyl compound concentrations mitigated the potential inhibitory effects of these compounds. This resulted in a higher yield of hydrocarbons (41.4% vs. 33.0%) and a lower proportion of oxygenates (19.3% vs. 26.3%) according to the GC/MS detectable compounds (note that larger oligomers cannot be detected with this technique). In addition, an increased water formation in a separate phase was observed. However, a moderate increase in char formation was observed, likely due to the higher overall reaction rates and HDO activity. These findings highlight the importance of water removal before upgrading and hydrodeoxygenation, as it enhances the overall efficiency of the HDO upgrading process.

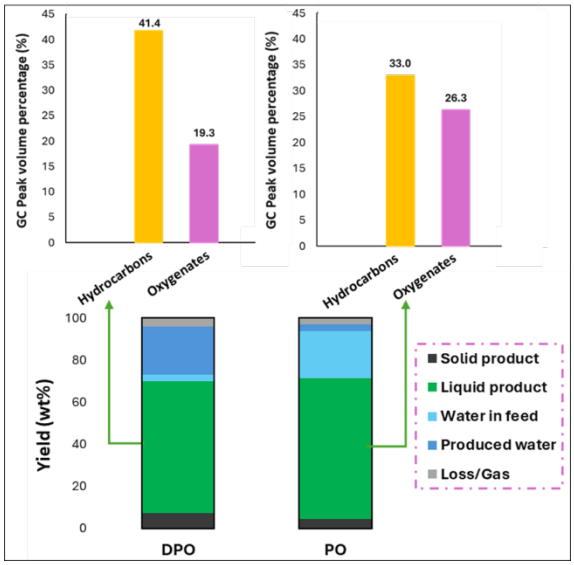

Figure.1 Product yields and GC-detectable compositions from catalytic hydrotreatment of PO and DPO over $NiMoS/Al_2O_3$ (400 °C, 73 bar H_2).

Acknowledgements
This work was conducted at the Competence Centre for Catalysis (KCK) and the Chemical Engineering division at Chalmers University of Technology, in collaboration with Preem.

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Hydrocracking of polyolefin waste model compounds in the presence of amide impurities

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Introduction

Approximately 370 million tonnes of plastics are produced yearly, but only 10% of all plastic produced has been recycled [1]. The recycling of mixed plastic waste or waste containing impurities is especially challenging[2]. Due to this, chemical recycling methods, such as catalytic cracking or hydrocracking, have attracted considerable attention[1]. However, real plastic waste contains many impurities, including nitrogen-containing polyamides[3]. The presence of such impurities is concerning, since nitrogen compounds deactivate the zeolite catalysts that are applied for catalytic cracking of plastic waste[4]. Thus, there is a need to study the effect of amide impurities on the plastic cracking process, and to develop catalysts more resistant to such impurities. In this work, we studied the effect of caprolactam, an amide which is the monomer of the polyamide Nylon 6, on dodecane hydrocracking. Experiments were performed in a flow reactor, with HZSM-5 zeolite and NiMo/HZSM-5 sulfide catalysts.

Results and Discussion

The results show that caprolactam deactivates the zeolite cracking catalyst. NiMo/HZSM-5 efficiently removes nitrogen from the liquid phase by hydrotreating. With such a catalyst, simultaneous hydrocracking and hydrotreating is possible at elevated temperatures (Fig. 1), although at a greatly reduced activity for hydrocracking, likely due to poisoning by ammonia. Removal of nitrogen from the feed allowed the deactivated catalysts to regain activity (Fig. 2); poisoning by caprolactam is thus reversible. These results imply that a bifunctional hydrocracking-hydrotreating catalyst combined with a system allowing for removal of ammonia (e.g. a semi-batch reactor) could allow for one-step processing of plastic waste containing polyamide impurities, which deactivate conventional zeolite cracking catalysts.

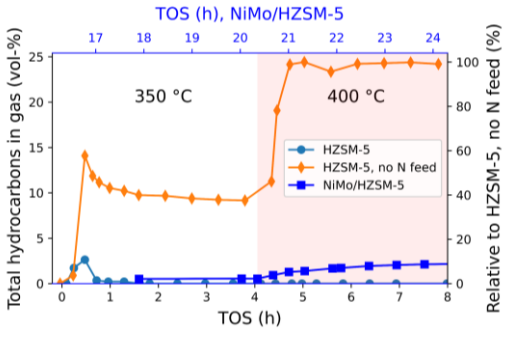

Figure 1 Light cracking products in the gas phase for different catalysts in the presence of caprolacam.

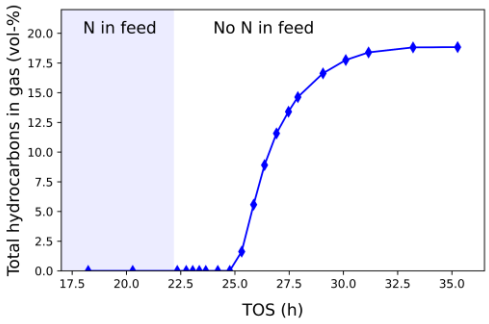

Figure 2 Recovery of activity as N is removed. 400 C, 50 bar H_2, HZSM-5 catalyst.

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AMAZE: Technologies for Sustainable Ammonia Production and Catalytic Cracking Toward Zero-Carbon Hydrogen Delivery

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Introduction

Ammonia has emerged as a leading option for zero-emission energy storage thanks to its high energy density and well-established global distribution network. However, conventional Haber–Bosch ammonia production relies heavily on fossil fuels and lacks the flexibility required to operate alongside variable renewable power. The AMAZE project (AmMoniA as a ZEro-carbon fuel and H_2 carrier) aims to overcome these limitations by creating a modular, decentralized production system paired with on-site catalytic cracking for hydrogen release. The project targets three main catalytic pathways, all based on non-critical raw materials (nCRM): 1) Green Ammonia Synthesis: Development of improved catalysts that enable low-temperature NH_3 formation using electrolytic hydrogen, with a goal of achieving 90% single-pass efficiency. 2) Thermocatalytic Cracking: Creation of durable nCRM catalysts capable of reaching equilibrium at temperatures 50–100 °C below those required by current benchmark materials. 3) Electrocatalytic Cracking: Exploration of a new approach using zero-gap electrochemical cells designed to exceed 70% energy efficiency under near-ambient operating conditions.

Results and Discussion

The integrated validation of the AMAZE technology at pilot scale will demonstrat the feasibility of modular green ammonia production coupled with on-site hydrogen recovery. The TRL 6 pilot unit, designed for a minimum output of of 4 tons/y of green ammonia, successfully operated as a closed loop from renewable electricity input to hydrogen release via catalytic cracking, confirming the robustness and compatibility of the newly developed synthesis and decomposition catalysts. Coupling the system with a Digital Twin enabled real-time performance optimization, improved predictive control, and highlighted key operational levers for enhancing efficiency and resilience under fluctuating energy conditions. These results will underscore the potential of decentralized ammonia processing as a practical and economically attractive route for carbon-free hydrogen distribution. By overcoming the conventional bottlenecks of small-scale ammonia synthesis and selective cracking, the AMAZE concept aims to demonstrate significant advantages for energy systems as well as for reliable power supply in remote or underserved areas

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