From Wind and Solar Energy to Chemical Energy Storage: Understanding and Engineering Catalysis under Dynamic Conditions

758. WE-Heraeus-Seminar

10 – 13 January 2022

ONLINE

WILHELM UND ELSE
HERAEUS-STIFTUNG

Introduction

The Wilhelm und Else Heraeus-Stiftung is a private foundation that supports research and education in science with an emphasis on physics. It is recognized as Germany's most important private institution funding physics. Some of the activities of the foundation are carried out in close cooperation with the German Physical Society (Deutsche Physikalische Gesellschaft). For detailed information see https://www.we-heraeus-stiftung.de

Aims and scope of the 758. WE-Heraeus-Seminar:

The German Energy Transition ("Energiewende") aims at decreasing net emissions of CO_2 by 95 % and increase the renewable energy fraction to 60 % by 2050. Similar targets are aimed at in other European countries and around the globe. An important aspect in the future is storage in chemicals and the production of fuels and chemicals based on renewable sources, particular based on wind turbines and photovoltaic solar power. The idea is to transform low-energy molecules such as water and CO_2 into high-energy reactive molecules: hydrogen, hydrocarbons, oxygenates and fuels. In contrast to conventional resources, wind and solar power fluctuates on time scales of minutes to days – depending on season, time of day and weather. Processes in focus are water electrolysis into hydrogen and oxygen, as well as conversion of CO_2 into hydrocarbons and oxygenates including methane, methanol and CO. Primarily, these processes were developed and well-studied for steady-state applications. In order to understand and optimize them under fluctuating conditions, new catalyst concepts must be developed – a very challenging topic in catalysis.

Orchestrating the complex interplay between imposed dynamic operation conditions and a concomitant or intrinsic structural evolution of the working catalysts will require an unprecedented mechanistic understanding at the atomic scale. Besides traditional catalyst preparation and testing, novel hierarchical catalyst design, advanced characterization tools as well as detailed modeling and simulation approaches will become ever more important to this end. Research in this area thus embraces predictive - quality first - principles calculations, multiscale modeling, data science and analytics, operando spectroscopies and in situ microscopies, as well as kinetic measurements, materials and reactor design. This requires a strong interaction of scientists from physics, theory, chemistry and engineering.

Bringing scientists from these various disciplines together, this WE-Heraeus Seminar aims at presenting the current state of research and advances towards such dynamic operation of catalytic energy storage systems, with significant focus on the fundamental methods that drive this research.

Introduction

Scientific Organizers:

Prof. Dr. Jan-Dierk Grunwaldt	Karlsruhe Institute of Technology, Germany E-mail: grunwaldt@kit.edu
Prof. Dr. Roger Gläser	University of Leipzig, Germany E-mail: roger.glaeser@uni-leipzig.de
Prof. Dr. Karsten Reuter	Fritz Haber Institute of the Max Planck Society, Berlin, Germany E-mail: reuter@fhi.mpg.de

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Program

Program *(CET)*

Monday, 10 January 2022

Chair: Jan-Dierk Grunwaldt

08:30 – 08:40	Jan-Dierk Grunwaldt Roger Gläser Karsten Reuter	**Welcome**
08:40 – 09:35	Ulrike Diebold	**Fundamental Studies Using Surface Science Technique**
09:35 – 10:20	Petra de Jongh	**Design of Heterogeneous Catalysts**
10:20 – 10:45	*COFFEE BREAK / NETWORKING*	
10:45 – 11:30	Beatriz Roldan Cuenya	**From Clusters to Catalysts in Energy Storage**
11:30 – 12:15	Ib Chorkendorff	**Experimental Aspect of Electrochemical Ammonia Synthesis**
12 :15 – 12:30	Stefan Jorda	**About the Wilhelm and Else Heraeus Foundation**
12:30 – 14:00	*LUNCH BREAK / NETWORKING*	
14:00 – 14:45	Karl J. J. Mayrhofer	**Electrocatalysis**
14:45 – 15:30	Eranda Nikolla	**Electrocatalytic Reduction of CO_2**
15:30 – 16:00	*COFFEE BREAK / NETWORKING*	
16:00 – 16:45	Ulrike Krewer	**Modelling of Electrocatalytic Systems**
16:45 – 18:15	**Posterflash (1 min) and Poster Session I** (MeetAnyway)	

Program *(CET)*

Tuesday, 11 January 2022

Chair: Karsten Reuter

08:30 – 09:30	Robert Schlögl	**Future of Energy Storage in Chemicals**
09:30 – 10:15	Regina Palkovits	**CO_2-Hydrogenation and Oxymethylene Ethers**
10:15 – 10:45	*COFFEE BREAK / NETWORKING*	
10:40 – 11:30	Martin Muhler	**New Insights into Methanol Synthesis**
11:30 – 12:15	Nico Fischer	**Advanced Characterization and Understanding of Fischer-Tropsch Catalysts**
12:15 – 13:30	*LUNCH BREAK / NETWORKING*	
13:30 – 15:00	**Posterflash (1 min) and Poster Session II** (MeetAnyway)	
15:00 – 15:30	*COFFEE BREAK / NETWORKING*	
15:30 – 16:30	Ferdi Schüth	**Future Energy Scenarios**
16:30 – 18:15	Angelika Heinzel Andreas Förster Maximilian Fleischer Bert M. Weckhuysen	**Panel Discussion** **"Our Energy System in 2050"**

Program *(CET)*

Wednesday, 12 January 2022

Chair: Roger Gläser

08:30 – 09:30	Bert M. Weckhuysen	**Operando Spectroscopy and Microscopy in Catalysis**
09:30 – 10:15	Marc Willinger	**Advances in Electron Microscopy**
10:15 – 10:45	*COFFEE BREAK / NETWORKING*	
10:45 – 11:30	Mirijam Zobel	**In Situ/Operando Characterization Using Synchrotron Scattering Techniques**
11:30 – 12:30	Jens K. Nørskov	**Electrochemical Nitrogen Activation, Insights from Theory**
12:30 – 14:00	*LUNCH BREAK / NETWORKING*	
14:00 – 14:45	Jan Rossmeisl	**Predicting Electrocatalysis at the Atomic Scale**
14:45 – 15:30	Zachary W. Ulissi	**Continued Progress towards Generalizable Machine Learning Models in Computational Catalysis**
15:30 – 16:00	*COFFEE BREAK / NETWORKING*	
16:00 – 16:45	Olaf Deutschmann	**Novel Tools for Digitalization and Archiving of Experimental and Modelling Data in Reaction Kinetics**
16:45 – 17:45	Julia Schmoeckel (TBC)	**Weather Forecast and Renewable Energies**

Program *(CET)*

Thursday, 13 January 2022

Chairs: Karsten Reuter / Roger Gläser

08:30 – 09:15	Stephan Schunk	**Catalyst Design by Digitalization Approaches**
09:15 – 10:00	Anke Hagen	**Solid Oxide Electrolyzer under Dynamic Load for Hydrogen and Syngas Production**
10:00 – 10:30	*COFFEE BREAK / NETWORKING*	
10:30– 11:15	Roland Dittmeyer	**Decentralized Processes: Energy-Related Catalysis Using Modular Reactor Design**
11:15– 12:15	Gabriele Centi	**Outlook for CO_2-Reduction and Future Scenarios on a European Level**
12:15 – 12:30	Organizers	**Closing Remarks and Poster Prize**
12:30	*END OF THE SEMINAR*	

Posters

Poster Session 1 – Monday, 10 January 2022

1	Timo Engl *	**Model Reactor for Investigations on CO2 Methanation under Dynamic Reaction Conditions**
2	Sebastian Weber *	**X-ray Ptychography as a Tool to Understand Catalyst Synthesis and Deactivation in 3D**
3	David Kellermann	**Integrated Modelling of Dynamic Surface Changes and Kinetics of a Novel Nickel-Based Catalyst for CO2 Methanation**
4	Moritz Langer	**Holistic Kinetic Modeling of the CO2 Methanation Reaction**
5	Nils Prinz	**The Pair Distribution Function (PDF) – a Powerful Method to Study Energy Materials**
6	Leif Schwensow	**Stabilized MOF-Derived Ni/C Catalysts for the Methanation of CO2 under Dynamic Operating Conditions**
7	Sven Wendholt	**Ni-Based Catalysts for CO2 Methanation Probed by X-ray Spectroscopy under In-Situ Conditions**
8	Alexander Hopf *	**Hollow carbon spheres as model catalyst supports for polymer exchange membrane fuel cells**
9	Tao Jiang *	**Diatomic Fe-Co Sites for Efficient OER**
10	Daniel Escalera López *	**Strategies to uncover activity-stability relationships in Ir-based catalysts for water splitting**
11	Karin Kleiner *	**Charge Transfer Multiplet Calculations - Solving the Electronic Structure (the d-Band) of Perowskite for the OER in Alkaline Media**

Poster Session 1 – Monday, 10 January 2022

12	Katrine Svane *	**High Entropy Oxides for the Oxygen Evolution Reaction**
13	Yuechao Yao *	**Metal-Organic Frameworks Derived High Entropy Sulfides Encapsulated by Porous Carbon for the Oxygen Reduction Reaction and Oxygen Evolution Reaction**
14	Francesco Mattarozzi *	**Ligand-Free Silver Nanoparticles for CO2 Electrocatalytic Reduction to CO**
15	Julian Borowec *	**Structure-Activity Correlations in Electrocatalysis Investigated by Means of Combined Atomic Force and Scanning Electrochemical Microscopy**
16	Joel Britschgi *	**Novel Electrochemical Method to Functionalize Methane on a BDD-anode**
17	Inga Dorner *	**Differences between Dynamic and Stationary Analysis of the Electrochemical CO2 Reduction**
18	Antonia Herzog *	**Operando Insights into Bimetallic Cu-Ag Nanocubes during CO2 Electroreduction toward Liquid Products**
19	Hendrik Heenen *	**Mechanism for Acetate Formation in CO(2) Reduction on Cu: Selectivity Trends with pH and Nanostructuring Derive from Mass Transport**
20	Fabio Dionigi	**Operando X-Ray Scattering to Track Atomic Level Structural Transformation in NiFe LDH**
21	Juliane Titus	**Control of Textural Properties and Ni Species of Ni-Catalysts Supported on Si-Stabilized ZrO2**

Poster Session 1 – Monday, 10 January 2022

22	Mariam Schulte	**Spatially-Resolved Insights into Local Activity and Structure of Ni Based CO2 Methanation Catalysts in Fixed-Bed Reactors**
23	Amanda Petersen	**pH and Anion Effects on Cu-Phosphate Interfaces for CO Electroreduction**
24	Steffen Czioska	**Mechanistic and Structural Investigation of OER Catalysts by Oxygen Evolution Reaction at High Potentials Probed by Operando Spectroscopy**
25	Javier Villalobos	**Requirements for the Activation of Co-Based Catalysts during Electrochemical Restructure for Oxygen Evolution**

*** incl. Flash Talk**

Poster Session II – Tuesday, 11 January 2022

1	Gereon Behrendt *	**Malachite- and Mcguinnessite-Based Catalyst Precursors for Methanol Synthesis from CO_2-Rich Synthesis Gas**
2	Alexey Boubnov *	**X-Ray Spectroscopy on Zinc in Methanol Catalysts: Using Theory to Understand Experimental Data**
3	Arik Beck *	**Following the structure of copper-zinc-alumina across the pressure gap in carbon dioxide hydrogenation**
4	Laura Barberis *	**Particle size effects for copper-catalyzed CO2 hydrogenation to methanol**
5	Jakub Pazdera	**Impact of the Local Environment of Amines on the Activity for CO2 Hydrogenation over Bifunctional Basic – Metallic Catalysts**
6	Nienke Visser *	**Particle Size Effects of Ni/C Catalysts for High Pressure CO2 Hydrogenation**
7	Tugce Beyazay *	**Hydrothermal CO2 Fixation with Metal Nanoparticles**
8	Arne Nisters *	**Immobilisation of Molecular Catalysts on Phosphine-Based Hyper-Crosslinked Polymers for the Activation of CO2**
9	Jonas Wentrup	**Dynamic Operation of Fischer-Tropsch Synthesis for Power-to-Liquid Concepts**
10	Özgül Agbaba *	**Oligomerization of Acetylene to 1,3-Butadiene**
11	Lorena Baumgarten *	**5-(hydroxymethyl) furfural (HMF) as platform molecule from bio-based feedstocks for noble metal based selective oxidations**

Poster Session II – Tuesday, 11 January 2022

12	Alexander Bodach *	**Hydrogen Activation by Al-N Lewis Pairs and Mechanochemical Syntheses of Organometallic Compounds**
13	Charlotte Fritsch *	**Development of a Ceramic Membrane Reactor for Coupled Propane Dehydration and Hydrogen Production**
14	Florian Hausen *	**Revealing Surface Transformations by operando Friction Force Microscopy**
15	Klara Sophia Kley *	**Selective Hydrogenation of High Concentrated Acetylene with Mechanochemical Prepared Pd-Ag/α-Al2O3 as a Catalyst**
16	Kevin Kuhlmann *	**Reactive CFD and NMR: Bringing Research Areas Together for Detailed, Full-Field Validation**
17	Xiaoran Liu *	**Al-N Compounds for Hydrogen Activation and as Energetic Materials**
18	Fei Wang *	**24/7 Dispatchable Solar Power System Powered by High Temperature Hydrogen Storage Materials**
19	Yonghyuk Lee	**Data-Efficient Iterative Training of Machine-Learning Gaussian Approximation Potentials for Surface Structure Determination of Living Heterogeneous Catalysts**
20	Felix Studt	**Theoretical Studies on the Conversion of Methanol to Olefins Using Acidic Zeolites**
21	Daliborka Nikolić	**Analysis of Possible Improvement of Forced Periodically Operated Chemical Reactor with Methanol Synthesis Based on Nonlinear Frequency Response Method**

Poster Session II – Tuesday, 11 January 2022

22	Andrej Uhrich	**Structure-Activity Correlations of CeO2-Promoted Cu-Co-Based Catalysts Applied in the CO Hydrogenation to Higher Alcohols**
23	Qingxin Yang	**In situ reaction-induced and externally forced dynamics of Fe-based catalysts in CO2 hydrogenation**
24	Shilong Chen	**Synergistic Effect of Co and Fe Catalysts for Ammonia Decomposition**
25	Marina Armengol Profitós	**Effect of Ruthenium Addition to CeO2-Supported Cobalt Catalyst for Dry Reforming of Methane**
26	Andrea Braga	**Bimetallic NiFe/CeO2 Catalysts for Methane Steam Reforming: In-Situ XPS and XRD Characterisation**
27	Henrik Kristoffersen	**Local Order in AgAuCuPdPt High Entropy Alloy Surfaces**

* incl. Flash Talk

Abstracts of Lectures

(in alphabetical order)

Outlook for CO_2-reduction and future scenarios on a European level

Siglinda Perathoner[1] **and** **Gabriele Centi**[1,2]

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[2] *European Research Institute of Catalysis (ERIC aisbl), Bruxelles, Belgium*

The EU aims to be climate-neutral by 2050, e.g. to realize an economy with net-zero greenhouse gas emissions (NZE_{GG}). This objective is at the heart of the European Green Deal and Next Generation EU plans. However, the challenge is that to realize the NZE_{GG} target a radical change in the energy (and associated chemical production) system is required, what indicated as deep transition [1]. This concept, however, is often not properly understood, being the assessments of the different solutions and their feasibility not accounting the differences between an evolution of the current system and a deep transition [2].

An example is given in cost estimation to produce methanol from CO_2 and the related implications in terms of large-scale impact and role of methanol as a key element for a scenario based on deep transition to a renewable energy-based economy [3].

This introduces the discussion on i) the role of electrification of production, with a short analysis of the different options and technologies, and their impact on NZE_{GG} scenario, ii) the options for the closure of the carbon cycle, particularly in energy-intensive industries, and iii) the role of solar fuels (SF) and artificial-leaf type devices in future scenario [1,4]. SF represent the step forwards to e-fuels, where the latter term indicates those produced by power-to-X technologies. There are contrasting indications on the role of SF and e-fuels to meet NZE_{GG} target, and even large agencies such as the International Energy Agency (IEA) indicate that their contribution will be less than 1% of global energy consumption. However, it will be argued how NZE_{GG} target requires instead a larger role of SFs, above 10%. A proper scientific development and to create a community is necessary, but based on the identification of the crucial factors to implement on an industrial scale. Some aspects will be discussed in relation to the development of artificial-leaf type devices [5].

References

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Experimental Aspect of Electrochemical Ammonia Synthesis

Ib Chorkendorff, SurfCat, Department of Physics, Technical University of Denmark.

Abstract

In our current transition to rely on sustainable energy we have identified some of the most significant obstacles for making fuels and chemicals [1]. One of the most challenging processes is the activation of molecular nitrogen, which is essential for life where it constitute a part of all amino acids and nucleic acid. It would not be possible to sustain earths current population without having access to nitrogen making fertilizers. After brief review of the history of activating nitrogen I shall concentrate on the ammonia synthesis and motivate why an alternative route to the current commercial Haber-Bosch could be attractive both for the thermal and electrochemical route [2]. We have for more than 15 years tried to activate molecular nitrogen electrochemically at ambient conditions and have made ammonia many times, however, when we performed the appropriate control experiments, we found that it was only impurities that were converting into ammonia. This also applies for many of the studies also published in the literature we tried to reproduce. Recently we found that a method published by Tsuneto et al. 25 years ago worked and proved that by simultaneous depositing Li in an N_2 atmosphere it was indeed possible to synthesize ammonia [3]. We shall discuss these results and the methods making us confident that we actually did activate N_2. A very simple model for the synthesis has been proposed and based on this insight devised experiments that significantly improved the Faradaic and energy efficiency [4] by oscillating the potential. Further improvements have been gained by controlling the oxygen content [5] and by synthesizing of high area electrodes [6] leading to Faradaic efficiency of ~80% and current densities above 100 mA/cm^2. Despite this excellent recent progress there are still substantial outstanding questions concerning the energy efficiency which will also be discussed.

References

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2. H. Iriawa, S. Z. Andersen, X. Zhang, B.M. Comer, J. Barrio, P. Chen, A.J. Medford, I.E.L. Stephens, I. Chorkendorff, Y. Shao-Horn, “Activation of Molecular Nitrogen by reduction and oxidation” Nature Reviews Methods Primers (2021) 1:56 DOI: 10.1038/s43586-021-00053-y.
3. S. Z. Andersen, V. Čolić, S. Yang, J. A. Schwalbe, A. C. Nielander, J. M. McEnaney, J. G. Baker, A. R. Singh, B. A. Rohr, M. J. Statt, S. J. Blair, S. Mezzavilla, K. Enemark-Rasmussen, J. Kibsgaard, P. C. K. Vesborg, M. Cargnello, S. F. Bent, T. F. Jaramillo, I. E. L. Stephens, J. K. Nørskov and I. Chorkendorff, “Benchmarking the Electrochemical Nitrogen Reduction Reaction” NATURE, 570 (2019) 504-508
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Supported Catalyst Preparation – Combining Fundamentals with Relevance

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Heterogeneous catalysis, whereby a gas or liquid phase reaction is performed over a solid catalyst, is at the heart of the modern energy and chemical industries. The catalytic activity for these materials often resides with metal(oxide, sulfide) surface sites, and efficient use of the metals and space available requires small particles, located on a mostly inert support to enhance the thermal stability of the catalyst. The field of catalyst preparation, aims at establishing the desired composition and structure of these materials.[1]

Controlling the structural parameters that are essential for the catalyst performance, such as metal particle size and metal spatial distribution, while using techniques that are compatible with large scale application, such as impregnation and drying, requires a thorough understanding of the different steps that occur during catalyst preparation.[2] Practical strategies will be discussed for controlling the metal particle size, and spatial distribution, and examples of how this greatly influences catalyst performance.[3,4]

Finally we will extend the methodology to the preparation of 3D model catalysts; catalyst which for instance due to the specific nature of the support allow fundamental studies on stability, promoter and particle size effects, while at the same time being robust enough to be tested at industrially relevant pressure and temperature conditions. Most notably we will highlight examples involving the conversion of syngas or CO_2 with hydrogen to renewable fuels and chemicals.

References

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Digitalization in catalysis and reaction kinetics: Novel tools for archiving and re-use of experimental and modeling data

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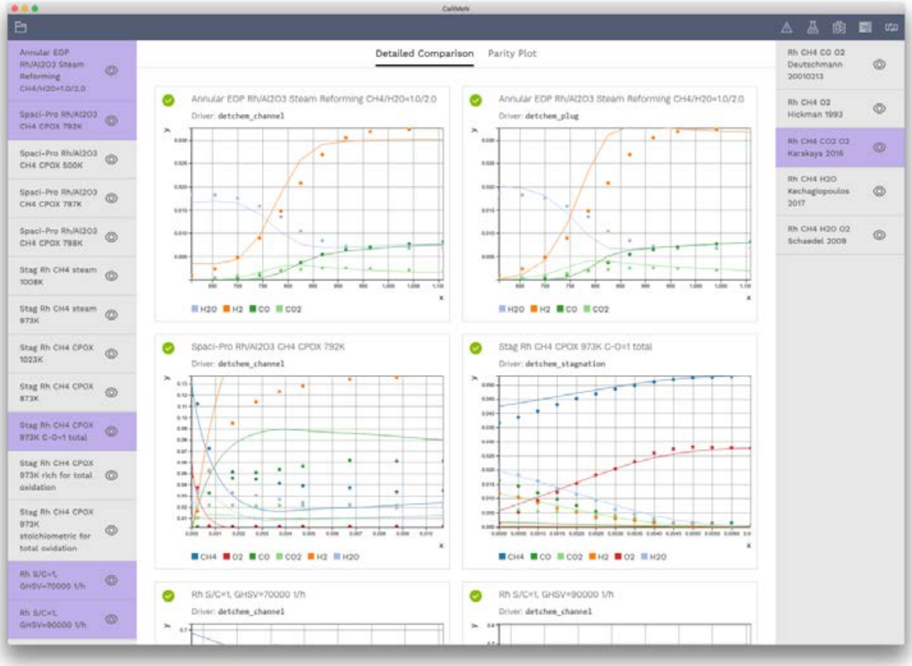
The progress in experimental and modeling methods and computational tools in catalysis and reaction leads to enormous amount of research data, which calls for novel tools for managing the data. Aside from efficient structuring and archiving the data, central challenges are data re-use and the associated rapid transfer of the knowledge represented by the data from the laboratory to real world scale. A vision for integrating all research data along the catalysis value chain, from molecule to chemical process, needs to be developed. Respective core development topics include ontologies, metadata, automatized workflows, infrastructure, IP, and the acceptance by the community [1]. This contribution will exemplarily present the potential of newly developed tools such as CaRMeN [2] and Adacata and their application in the field of catalysis and reaction kinetics such as methanation [3].



Screenshot of CaRMeN comparing experimentally measured and numerically predicted axial profiles of catalytic syngas production in flow reactor using an automatized work flow meta data trasnfer from experiment to modeling and simulation.

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Fundamental studies using surface science techniques

U. Diebold[1]

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The arrangement of the top layer of atoms on a solid -- and the resulting electronic and chemical properties – affect and sometimes even dominate its functionality. In the talk, I will showcase how we can use surface science techniques to measure surface properties in an atom-by-atom fashion. By investigating well-defined samples in a controlled environment, such experiments can be tightly interlinked with theoretical computations. Examples include assessing the reactivity of individual surface atoms [1]; pushing the size of catalytically-active nanoclusters to their physical limit [2]; and extending ultrahigh-vacuum experiments to the liquid phase [3].

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[2] J. Hulva; M. Meier; R. Bliem; Z. Jakub; F. Kraushofer; M. Schmid; U. Diebold; C. Franchini; G. S. Parkinson, Unraveling CO adsorption on model single-atom catalysts. *Science* **371,** 375 (2021)

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Decentralized processes: energy-related catalysis using modular reactor design

R. Dittmeyer[1]

[1]*Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany*

In response to climate change carbon dioxide emissions need to be reduced worldwide as far as possible and in all sectors. Renewable power generation from wind energy and by photovoltaics has seen dramatic cost reductions over the past decades and is now among the cheapest options for power generation. Yet due to its intermittent nature and to the mismatch between its availability and the power demand, both in time and regarding locations, conversion of renewable electrical energy into chemical energy, also called Power-to-X, has emerged as a new field of technology which will be required at large scale in future energy systems. This is generally accepted now, and industry is preparing for implementation, but there is an ongoing debate about where Power-to-X plants should be located, which products and technologies should be in the focus, and whether such plants could be operated load-flexible, be it in isolated networks or grid-integrated to reduce the demand for grid expansion.

Against this background the presentation will assess the current status of the development of modular plants for Power-to-X conversion from the author's perspective and highlight ongoing research in a number of related projects where the Institute for Micro Process Engineering is involved. This concerns work on the Fischer-Tropsch route as well as on methanation, methanol synthesis and ammonia synthesis. The rationale for decentralised Power-to-X plants, their potential and their feasibility will be discussed.

Advanced characterization and understanding of Fischer-Tropsch catalysts

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The Fischer-Tropsch (FT) synthesis, originally developed in the 1920s [1], is an industrially applied process which converts synthesis gas into hydrocarbons which can act as replacement for crude oil derivatives. As such, the process has historical application in regions which lack access to crude oil reserves but have other fossil reserves such as coal. First plants in Germany and in South Africa in the 50s were based on this coal liquification process [2]. Cheap methane extracted as by-product of the crude oil production or in from of shale gas, resulted in a shift of feedstock and the installation of large production capacities by SASOL and Shell in Qatar. Fluctuating low oil prices and a growing environmental consciousness, caused the FT synthesis to fall into some disrepute in the early 21st century and new plants were only developed in China, where coal remains the main feedstock. However, the advent of the Power-to-X (PtX) concept, has identified the FT synthesis, next to the methanol synthesis, as viable option to generate synthetic hydrocarbons from CO_2 [3], especially when captured from the atmosphere [4] or from biogas [5].

The key difference between PtX and industrial FT plants is the scale. The PtX concept is generally envisaged to encompass many decentralized production units instead of world scale plants. As a result, the well-established economy of scale of industrial FT plants must be overcome through innovative process, reactor, and catalyst design. One key aspect is intensification. While large plants can afford to operate at synthesis gas conversion levels of 65 to 75 % with a recycle, this is challenging, if not cost prohibitive in small scale units. Required high single pass conversions result in harsher reaction conditions. Current catalyst formulations struggle with these conditions and deactivate through sintering and oxidation. The design of more robust catalyst formulations without compromising on performance, requires a clear understanding of the deactivation mechanisms at play. In this paper we share our recent advances in *in situ* and *operando* characterization of cobalt FT catalysts with a special focus on steam induced deactivation.

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Solid oxide electrolyser under dynamic load for hydrogen and syngas production

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Wind farms, both on shore and off shore, harvest electricity at the scale of gigawatt; solar cells cover roofs and streaks of land. Renewable energy sources are high on the political agenda while fossil fuels are retreating in the transition towards clean energy systems. It is not a secret that electricity production from those sources is fluctuating in nature and is not matching the need of the societies. Furthermore, de-fossilization of the transport sector, particularly the share that cannot be electrified, asks for renewable fuels. This calls for efficient technologies to convert fluctuating electricity into storage media and into green fuels as well. Among such technologies, solid oxide electrolysis (SOE) is an attractive option, specifically due to extremely high efficiencies. The electrolysis can reach 100%. Furthermore, SOE allow for combined electrolysis of steam and CO_2 yielding a synthesis gas H_2 + CO, which is the feed for known catalytic processes towards high density fuels – so called e-fuels.

The SOE cell is a composite of two electrodes sandwiching an oxide ion conducting solid oxide electrolyte. Materials compositions and structures determine performance and durability. Typical materials of state-of-the-art cells are Ni/YSZ (yttria stabilized zirconia) or Ni/CGO (ceria gadolinium oxide) for the fuel electrode, LSCF / LSC (lanthanum strontium cobaltite ferrites) perovskite single phases or composites with CGO for the air electrode, and YSZ for the electrolyte. The electrodes possess catalytic and electro-catalytic activity and are often the main sources for degradation. Recent research efforts have contributed to improving both performance and lifetime of SOE towards a matureness allowing for medium to large-scale demonstration units. The presentation attempts an overview of the status of SOE in relation to dynamic operating regimes, both from the scientific and commercial point of view.

Insight into electrocatalytic systems and their dynamics via kinetic modeling

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Our future sustainable energy systems rely on electrochemical cells, such as fuel cells, batteries and electrolysers, to buffer intermittent renewable energies vs. demand and provide CO_2-free energy for mobility. Furthermore, the power-to-chemicals concept promises to generate also base chemicals, supporting defossilation of the chemical industry. A bewildering range of cell chemistries exists, with many of these showing high thermodynamic efficiencies. Still, only few technologies succeed to enter mass market. This can be attributed to high cost materials, but also to performance losses due to reaction kinetic issues at electrodes. Dynamic operation of these technologies increases complexity and requires additional efforts to avoid performance or life-time losses.

Already analysis of electrodes under steady state operation is challenging as the surface, reaction and transport processes at electrodes are complex, highly interconnected and only very few variables can be measured directly. Reaction kinetic modeling can provide not only the missing pieces, i.e. variables and electrode states, but it also gives a comprehensive insight into the interaction of surface, reaction and transport processes during steady state and dynamic operation.

This talk gives an insight into the state and processes in electrodes via model-supported microkinetic and macrokinetic analysis. Special emphasis is given on dynamic methods, which are shown to facilitate analysis of processes and their interaction.

Besides complex multistep reactions, the role of adsorbates, local operating conditions, side reactions and surface changes of and at electrodes will be elucidated. Further, the effect of transport phenomena and reactions in the electrolyte is illustrated. Examples cover a wide range of established technologies like PEM electrolysis, and electrodes of next generation cells, like alkaline fuel cells. The combination of kinetic modelling and dynamic electrochemical measurements is shown to yield a better quantitative and qualitative understanding of electrode performance. It is also the base for a knowledge-driven, model-based electrode and cell development.

Evaluation of Electrocatalyst Activity, Stability and Selectivity during dynamic operation – Online Coupling of Analytical Techniques to Electrochemical Flow Cells

Presenter: Mayrhofer, Karl; Cherevko, Serhiy; Katsounaros, Ioannis; Berkes, Balazs
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The investigation of novel catalyst materials for applications in fuel cells and electrolyzers, as well as the assessment of operation regimes, demands fast and highly informative characterization methods. Standard electrochemical approaches are often insufficient in information depth particularly when it comes to studying dynamic processes with high time resolution, so in-situ or online coupled analytics are necessary to enhance knowledge on catalytic materials. In this presentation I will demonstrate the portfolio of coupled analytical techniques that have been developed over the last decade in our team, and which help obtaining complementary data on particularly stability versus dissolution and selectivity towards gases and liquid chemical products. Starting out from an advanced high-throughput screening approach as the electrochemical platform, namely the Scanning Flow Cell (SFC), various coupled mass spectrometry tchniques with second time resolution provide novel insights into electrocatalytic processes. Hopefully these insights aid in the further technical developments of novel catalysts and improved reaction conditions for fuel cells and electrolyzers, which are so desperately required for the successful implementation of the Energiewende.

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New insights into methanol synthesis

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The heterogeneously catalysed reaction of hydrogen with carbon monoxide and carbon dioxide (syngas) to methanol is nearly 100 years old, and the standard methanol catalyst $Cu/ZnO/Al_2O_3$ has been applied for more than 50 years. Still, the nature of the Zn species on the metallic Cu^0 particles (interface sites) is heavily debated. Here, we show that these Zn species are not metallic, but have a positively charged nature under industrial methanol synthesis conditions. Our kinetic results are based on a self-built high-pressure pulse unit, which allows us to inject selective reversible poisons into the syngas feed passing through a fixed-bed reactor containing an industrial $Cu/ZnO/Al_2O_3$ catalyst under high-pressure conditions. This method allows us to perform surface-sensitive operando investigations as a function of the reaction conditions demonstrating that the rate of methanol formation is only decreased in CO_2-containing syngas mixtures when pulsing NH_3 or methylamines as basic probe molecules.

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Embracing the Complexity of Catalytic Structures: Engineering Nonstoichiometric Mixed Metal Oxides for Electrocatalysis

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Dwindling fuel resources and high levels of CO_2 emissions have accelerated the need for renewable energy resources and more efficient energy conversion and storage systems. The goal of our research group is to design active, selective and stable electrocatalysts for electrochemical transformations related to energy and chemical conversion. We focus on engineering complex, non-stoichiometric mixed metal oxides as a potential avenue for addressing limitations with the current state-of-the-art metal based electrocatalysts. The compositional versatility of non-stoichiometric metal oxides belonging to the perovskite family, of the general form $A_{n+1}B_nO_{3n+1}$ (n = 1, 2, 3… ∞; A = rare earth/alkaline earth metal; B = transition metal), presents numerous opportunities to tune the catalytic performance of these oxides for targeted reactions. However, identification of nonstoichiometric metal oxides for these reactions is often limited by their complexity and lack of effective descriptors of their activity and stability. We have combined theory, advanced characterization, controlled synthesis and electrochemical studies to shed light on the factors that govern electrochemical reduction and evolution of oxygen along with electrochemical reduction of CO_2 to CO on these oxides and have identified ways to tune their activity and stability.[1-6] These studies have paved the way for engineering active and stable cationic centers in nonstoichiometric mixed metal oxide electrocatalysts for targeted reaction chemistries.

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Electrochemical nitrogen activation, insights from theory

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The current industrial ammonia synthesis based on the Haber-Bosch process has a substantial carbon footprint, and an alternative process based on the energy input from sustainable sources, solar or wind, would be highly desirable. Such a process could even open the possibility of using ammonia for chemical energy storage. I will introduce a model to describe electrochemical dinitrogen reduction. In particular, I will discuss a Li mediated process. I will also discuss the possibility of new catalysts for a thermal process ammonia synthesis process to be combined with electrolysis.

Heterogeneous Catalysis and Material Design across Disciplines and Value Chains

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The energy transition and the aim of a comprehensive circular economy pose numerous challenges for the transformation of chemical value chains. Material design and catalysis present key elements for valorizing renewable carbon resources such as biomass, CO_2 and even plastic waste potentially together with renewable energy. An additional challenge is imposed by both fluctuating energy and resource availability. In particular, the interfaces of material design and heterogeneous catalysis with biotechnology, electrochemistry and process engineering offer opportunities for the design of efficient technologies.

Herein, the development of tailored solid catalysts for the selective transformation of renewable carbon feedstock will be discussed. Major emphasis is on CO_2 as future feedstock, e.g. for the catalytic synthesis of formic acid and synthetic natural gas as well as the opportunities and challenges associated along the design of value chains for a future circular carbon economy. Therein, examples are in focus where redesign of the chemical value chain and the dynamic evolution of the catalytically active species are of major importance comprehending Ir single site catalysts for formic acid decomposition and CO_2 activation, Ni catalysts for coupling co-electrolysis and methanation as well as hydrogen efficient dimethoxymethane production.

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From Clusters to Catalysts in Energy Storage

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Climate change concerns have spurred a growing interest in developing environmentally friendly technologies for energy generation (i.e. green H_2 from water splitting) and to re-utilize CO_2 in thermal catalysis applications where it is reacted with green H_2 to produce methanol and high-order hydrocarbons. Moreover, the electrochemical reduction of CO_2 (CO_2RR) into value-added chemicals and fuels offers an additional possibility to store renewable energy into chemical bonds. It is therefore of particular interest to develop efficient, selective and durable (electro)-catalysts that can operate under mild reaction conditions (lower pressures and temperatures, lower overpotentials). Nonetheless, in order to tailor the chemical reactivity of nanocatalysts, fundamental understanding of their structure and surface composition under reaction conditions must be obtained. It should be kept in mind that even morphologically and chemically well-defined pre-catalysts will be susceptible to drastic modifications under *operando* conditions, especially when the reaction conditions themselves change dynamically. To fulfill this challenging aim, a synergistic experimental approach taking advantage of a variety of cutting-edge microscopy (EC-AFM, EC-TEM) and spectroscopy (XPS, XAS, Raman Spect. MS/GC) methods must be undertaken.

This talk will provide new insights into the thermal and electrocatalytic reduction of CO_2 as well as the oxygen evolution reaction (OER) using model pre-catalysts ranging from single atoms to small clusters and large nanoparticles. Some of the aspects that will be discussed include: (i) the design of size- and shape-controlled catalytically active nanoparticle pre-catalysts (Cu, Cu-Zn, Cu_2O cubes, octahedra, Ag-Cu_2O cube NPs, CoO_x NPs), (ii) the role of the support (SiO_2, ZnO, Al_2O_3, ZnOAl) on the catalytic performance, (iii) the understanding of the active state formation, and (iv) the correlation between the dynamically evolving structure and composition of the (electro-)catalysts under operando reaction conditions, including pulse electrolysis treatments, and their activity and selectivity. These results are expected to open up new routes for the reutilization of CO_2 through its direct conversion into industrially valuable chemicals and fuels such as ethylene, methanol and ethanol and the generation of H_2 through water splitting.

Predicting Electrocatalysis at the Atomic Scale

Jan Rossmeisl

Center for High Entropy Alloy Catalysis, Department of Chemistry, University of Copenhagen.

Catalysis is key in the future development of green chemistry and in the renewable production of chemicals and fuels. However, this transition requires a new approach to catalysis, as central chemical reactions cannot be catalyzed with existing materials. The grand challenge is to discover new catalyst materials, which are both stable and active. We identify three energy conversion reactions, which are corner stones for the green transition and in urgent need of new catalysts.

High Entropy Alloys are solid solutions where five or more elements are mixed randomly together. The realization of HEAs has opened for a vast composition space with a practically infinite number of new not yet explored catalyst materials. We can tune their properties by smoothly change their composition. This has led to the statement that: HEA is a shift of paradigm “from using the materials we have, to engineer the materials we need”. The hypothesis is that among the HEAs there are catalysts with superior stability and activity for the important green reactions.

I will present the challenges regarding simulations and prediction of the relation between surface structure and catalytic activity on HEA surfaces. Further, I will show studies where the flexibility of the vast chemical space of HEAs is utilized to predict new catalysts.

Future of Energy Storage in Chemicals

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Mankind has underestimated the lever it has in changing the biogeochemical state of the planet earth by emitting greenhouse gasses. We are in a position where the state of the planet is about to change into a condition that may be for mankind. It is thus extremely urgent to minimize the emission of greenhouse gasses in a global dimension. This can only be achieved if the existing world market of fossil energy is replaced by a world market of renewable energies using as many infrastructures as possible. Even so it is a challenging task and requires rebuilding the largest industry on earth within one generation.

The primary source of renewable energy is electricity that can locally be used with better efficiency as fossil molecular energy carriers. But it cannot be stored and transported (traded) in grid dimensions. Future energy systems need a dual approach using green electrons and green molecules as energy carriers. Hydrogen is the primary molecular source. It needs transformation into transportable derivatives that may also be used as fuels.

Catalysis as electrocatalysis and as interfaces for gas phase transformations are a strategic ingredient enabling large scale-processes that are operated at the scale of the global energy system. Although all essential process for chemical energy conversion (CEC) do exist as mature technologies they still show substantial deficiencies. One is the sector-coupled systemic interconnection (dynamical operation, feed gas purification), others are production processes for the infrastructure (electrolysers) and it is unclear what the fundamental limitations are driving the processes at thermodynamic limits under optimized conditions. Catalyst design educated by functional understanding and modernized digital tools based upon clean experimental data is a critical scientific contribution to energy science. Likewise, cutting-edge chemical engineering bridged to catalyst material science through computational catalysis science is another critical element.

The presentation links a systemic view on the dimension of energy transformation to examples of where we stand in the functional understanding of important catalytic systems namely dehydrogenation and ammonia synthesis/ reforming. Research should clearly discriminate between novel approaches that are needed for future generations of CEC processes and contributions to establish the first generation of CEC that is highly time-critical and thus needs focussed efforts translating verified fundamental knowledge into technology relevant transfers.

Weather and Renewables

J. Schmoeckel

UBIMET GmbH, Karlsruhe, Germany

The talk will give an overview about the relevance of weather itself and of weather data – especially forecasts based on meteorological information – for the energy market. Main focus will be the perspective of a meteorological data provider. Examples of specific forecasts for the energy market (and expected quality) will be given. In this context the role for storage processes will be discussed.

Abstract for Poster “From Wind and Solar Energy to Chemical Energy Storage: Understanding and Engineering Catalysis under Dynamic Conditions” – 758. WE Heraeus Seminar

“Catalyst Design by Digitalization Approaches”

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Digital transformation efforts in catalysis and materials science have become an important topic within the last years. Generally, the topic is discussed as “Digitalization” and associated to the high-tech agendas and discussed to have game-changing potential. The four guiding principles which are the core elements that are addressed within the context of digitalization are interoperability, information transparency, technical assistance, and decentralized decisions. It is not self-evident how “industry 4.0” and the underlying principles can have an impact on research and development for catalysis and materials sciences. Traditionally natural sciences, and especially chemistry, have been science disciplines based on knowledge about chemicals and materials, physical chemistry as solid foundation and following the canon of experimentation aiming at experimental evidence and interpretation of the obtained results. In the era of digital transformation with an increased availability of data, the potential to predict behavior of complex chemical systems and the opportunity to do experimental work augmented by fully automated and integrated devices question traditional workflows that have been followed in R&D for decades – do these models still fit with the means that digital transformation is offering? Can or should R&D be decoupled from digitalization – and what will the appropriate digital R&D agenda?

Approaches for catalyst and process development fostered by the coupling of high throughput modelling and high throughput experimentation will be discussed in the context of the talk. In the chemical catalysis arena, high throughput experimentation efforts have led to an early assimilation of digitalization from the cradle on within the context of big data and harmonized data formats, including approaches in the field of AI. Therefore, the lessons learned here can serve in many aspects as a role model for a holistic digital transformation within research and development in the domains discussed. The main values that have been captured in the direction of digitalization build on the fully standardized workflows that generate data of high quality, which allow the assessment of chemical properties through an integrated data view and enhanced data analysis methods with high efficiency based on artificial intelligence. Nevertheless, one of the major challenges that still must be worked on is the closure of the information cycle to the disciplines dealing with theoretical approaches in catalysis. In the lecture we will discuss which demands digital approaches in technical catalysis have, not only on the way we perform experiments, but also which approaches can be taken in the materials science arena to arrive at a state where theory and practice can work synergistically through digitalization.

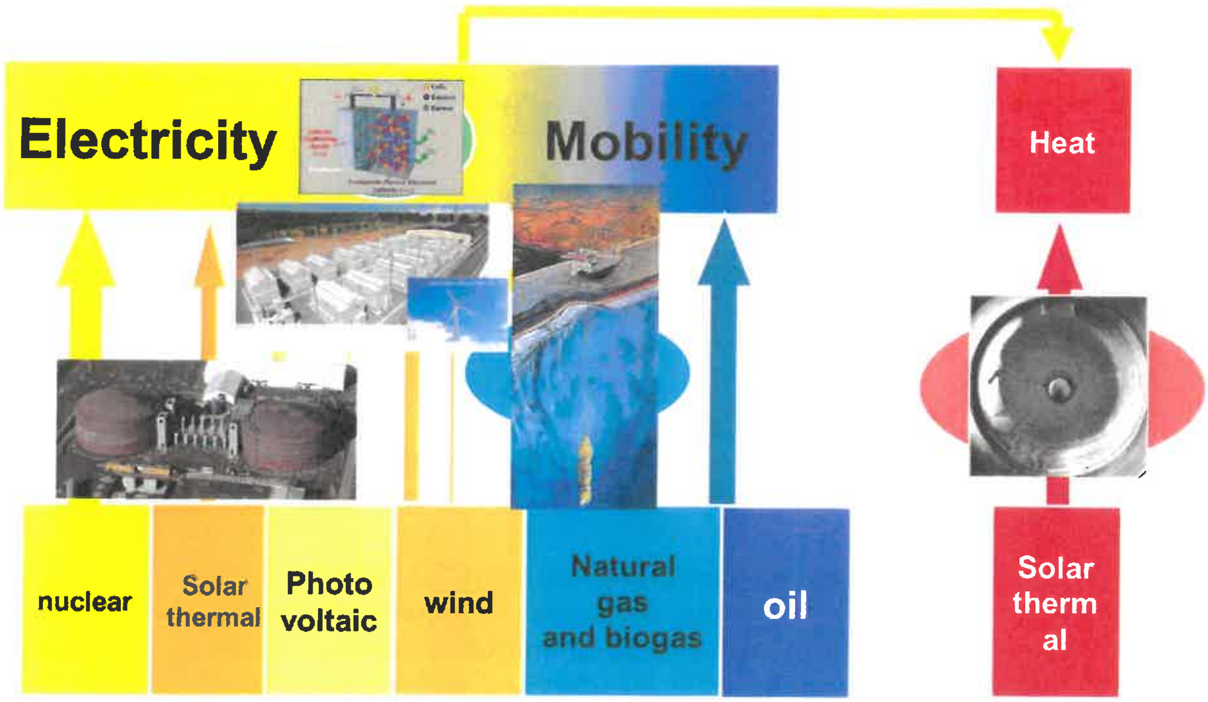
Future Energy Scenarios

Ferdi Schüth

Max-Planck-Institut für Kohlenforschung

Our energy systems are facing fundamental changes due to energy-related CO_2 emissions and resulting climate change. This requires increased use of renewable energy, which is typcially intermittent, such as solar radiation and wind energy. Harvesting, storing, and distributing renewable energy is a challenge for many disciplines, but it is clear that science and engineering are often at the heart of it.

This concerns, for instance, materials and solutions for wind turbines, photovoltaics, and a potential hydrogen economy. Moreover, intermittent electricity needs to be leveled, for which storage in batteries or in chemical compounds seem to be most suitable, in addition to grid extension and demand side management. Biomass in its various forms is another energy vector which is more easily dispatchable than electricity. The presentation will address the challenges and possible solutions for future energy scenarios, which are currently being developed.



Continued progress towards generalizable machine learning models in computational catalysis

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Machine learning accelerated catalyst discovery efforts have seen much progress in the last few years. Datasets of computational calculations have improved, models to connect surface structure with electronic structure or adsorption energies have gotten more sophisticated, and active learning exploration strategies are becoming routine in discovery efforts. However, there are several large challenges that remain: to date, models have had trouble generalizing to new materials or reaction intermediates and applying these methods requires significant training.

To address these challenges, I will briefly introduce the Open Catalyst Project [1] and the Open Catalyst 2020 dataset [2], a collaborative project with Facebook AI Research to span surface composition, structure, and chemistry and enable a new generation of deep machine learning models for catalysis. I will then discuss initial results for state-of-the-art deep graph convolutional models and significant recent progress from others in the community [3,4,5], including academic and industrial AI labs. Innovation in these models is likely to improve models in related materials science areas. Finally, I will discuss current efforts and open challenges for deep graph networks and beyond in computational catalysis, and how to use the models/datasets or contribute new methods to the open leaderboard.

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Operando Spectroscopy & Microscopy of Small-Molecule Catalysis

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As we enter the era of catalytic activation of small molecules, such as CO_2, CO, N_2 and H_2O, to realize the refinery of the future one of the main questions to answer for scientists involve the coupling of carbon fragments, originating from (mixtures of) CO and CO_2, either produced at point sources, or harvested from direct air capture units. The goal is to manufacture increasingly complex (and thus value-added) carbon-containing molecules from CO_2 or via its intermediates CO and CH_3OH instead of making them from e.g., crude oil fractions. This requires knowledge of the processes taking place at the catalytic surface of both thermo- and electrocatalytic activation processes of CO_2, was well as of the subsequent conversion processes in which CO (Fischer-Tropsch synthesis, FTS), biomethane (selective C-H activation) and methanol (methanol-to-hydrocarbons process, MTH) are used. This is the topic of this lecture, in which we discuss the latest progress made in our group in understanding CO_2 activation over Ni (thermocatalytic conversion) and Cu (electrocatalytic conversion), as well as CO conversion over Fe and Co (FTS), the selective conversion of CH_4 over lanthanides and CH_3OH over zeolites (MTH). Furthermore, combination of zeolites with e.g., Fe will be exploited to evaluate the potential of tandem catalysis.

Emphasis is on the use of in-situ and operando spectroscopy and microscopy methods to elucidate reaction and deactivation mechanisms. For example, by using operando infrared and X-ray spectroscopy, we have studied the C-C coupling and formation of higher hydrocarbons, such as propane and butane, relative to the main product, methane, formed during CO_2 hydrogenation over Ni. It was found that electronic and geometric effects can be tuned by two main ways; structure sensitivity, and the proper choice of the support oxide. Reaction intermediates could be identified, while active sites on different Ni metal facets could be discerned. Theoretical calculations further supported the experimental observations. Another conceptually important conclusion from our work is that suppressing the hydrogenation activity of Ni leads to C-C coupled products. Selective suppression of hydrogenation activity over Ni is one of the biggest challenge, which can also be achieved by using promotor elements and enhancing the strong metal support effect by creating an increased Ni-support perimeter, thereby stabilizing specific reaction intermediates needed for C-C coupling. In a more recent study, we have used in-situ spectroscopy to monitor the electrocatalytic reduction of CO_2 over Cu surfaces with sub-second time resolution. Anodic treatment and subsequent reduction result in a highly active surface for ethylene production. A dynamic CO intermediate is found to correlate with the CO-CO coupling and ethylene formation, whereas a static CO intermediate with a distinct vibration is related to selective CO production. These dynamic and static CO intermediates could be pinpointed to structural heterogeneities of the Cu electrode. With respect to the use of iron, we have developed double-shelled hollow spheres, consisting of Fe-carbides and zeolite ZSM-5, which allows to produce gasoline-range hydrocarbons from synthesis gas, while for Co we will discuss the role of the metal and metal oxide phase for CO and CO_2 activation by using Co/TiO_2 as solid catalysts.

Correlative electron microcopy of dynamics at reactive interfaces

Marc Willinger

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Our aim is to understand processes that lead to the emergence of catalytic function though direct observation using a combination of operando scanning and transmission electron microscopy. Starting with simple model catalysts, such as polycrystalline metal foils, we observe the propagation of chemical waves and reveal how catalytic activity depends on grain orientation, coupling mechanisms and reaction conditions (Figure 1) [1]. In the case of redox-reactions on non-noble metals, we find that the active catalyst is operating near a phase-boundary where metallic and oxidized phases co-exist [2]. Real-time imaging reveals fascinating oscillatory redox dynamics that increase in complexity with increasing chemical potential of the gas-phase. When moving from simple model catalysts to industrially relevant metal nanoparticles supported on reducible oxide carriers, we apply in-situ transmission electron microscopy to study processes taking place at the metal-support interface. The aim of the presentation is to highlight the ability of in-situ electron microcopy and to demonstrate the importance of studying catalysts under relevant conditions [3]. It will be shown that active catalysts are dynamically adapting to the reaction environment and that catalytic function is related to the catalysts ability to participate in the reaction through reversible changes in its structure and/or (local) composition.

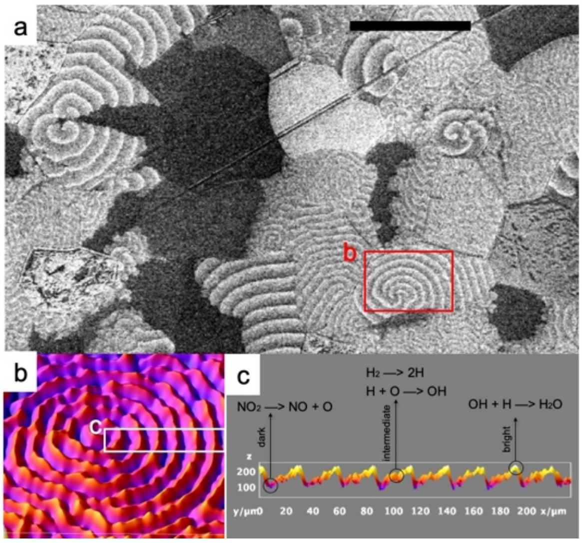

Figure 1: (a-c) Contrast variations related to the propagation of chemical waves observed during NO_2 hydrogenation on a polycrystalline Pt foil as observed by *in situ* SEM [1].

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In situ/operando characterization using synchrotron scattering techniques

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X-ray absorption spectroscopy is an established technique in catalysis to investigate the element-specific short-range order of catalyst particles. Its limitation to structural insight over the first few coordination shells can be overcome by employing the pair distribution function (PDF) technique. [1] The PDF is gained from high energy X-ray scattering data, both on laboratory diffractometers [2] and at synchrotron sources. It allows us to gain structural insight across the full length scale from molecular clusters via medium-range order in nanoparticles to bulk amorphous or crystalline support materials. While being in general a bulk technique, we can tackle the structure of a specific component of interest by calculating the difference-PDF (d-PDF), for instance, from scattering data of a heterogeneous catalyst and an unloaded support. The sensitivity of the difference-PDF approach will be highlighted in the field of heterogeneous catalysts. [3]

Within dedicated flow cells, we can follow the preparation of heterogeneous catalysts from precursor materials, their activation to active catalysts as well catalytic cycling, which can further be tracked by mass spectrometry coupled to the flow cell. Here, we will showcase *in-situ* PDF experiments of active Ni-based methanation catalysts derived from the Ni-based metal-organic framework Ni(BDC)(PNO). Multi-phase PDF refinements reveal the structural evolution of Ni fcc particles, stabilized within graphitic shells, during both the catalyst activation and the methanation catalysis, supported by catalytic studies. We found a correlation between the employed dropout scenarios during catalytic cycling and the evolution of the catalyst structure over several cycles. [4]

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Abstracts of Posters

(in alphabetical order)

Acetylene oligomerization to 1,3-Butadiene

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Acetylene was the main feedstock of the chemical industry in the first half of the last century, due to its high reactivity that resulted in a rich chemistry with many applications, including production of acetaldehyde, vinyl chloride, and acrylonitrile. By making use of increasing amounts of fluctuating power in the electricity grid from wind and solar energy, an increase in oil prices acetylene might become competitive again with naphtha-derived ethylene and other olefins [1, 2]. Here, acetylene oligomerization to produce selectively unsaturated C_4 products is the reaction of interest. Previous studies from our group revealed Cu/Zeo-Y as a promising catalyst for this reaction. The goal of this study was to understand the effect of initial oxidation state of copper on the conversion and selectivity and an increase of the catalyst lifetime. For this reason, ionic liquids (IL) were used to prepare Cu/Zeo-Y coated with a thin IL layer in order to avoid, or slow down, catalyst deactivation, which occur due to production of higher oligomers in the catalyst bed [3].

The results showed that, the initial oxidation state of copper has an effect on the conversion of acetylene, but more significantly on the selectivities towards C_2 (mainly ethylene) and C_4 products (mainly butylene). Initially having only Cu(I), showed the highest selectivity towards C_4 , which included about 30% 1,3-butadiene. The addition of certain amounts of IL did not only improve the selectivity, but also prolonged the lifetime of the catalysts. Thus, the previously encountered deactivation problem was solved by the modified Cu/NaY catalyst. As a result, an improvement in acetylene conversion and selectivity towards C_4 product was successfully achieved, while the stability of the catalyst was significantly improved. Overall, these findings provide a new catalytic systems for the hydrogenative oligomerization of acetylene under pressure into more valuable products, such as butadiene and other unsaturated C_4 products, with a control on the selectivities [3].

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Effect of Ruthenium Addition to CeO_2-Supported Cobalt Catalyst for Dry Reforming of Methane

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Dry reforming of methane (DRM) is an important way for hydrogen production and an advantageous initial step for Fischer-Tropsch synthesis. Even though being widely studied, there are still limitations to solve: deactivation due to carbon deposition, low CO_2 activation and adaptation to a green feedstock as biomethane [1]. The activation of the reactants, CH_4 and CO_2, is a vital factor in designing an active and stable catalyst and the key point for DRM. In this work, the incorporation of ruthenium in the ceria-supported cobalt catalyst is explored to enhance the activity and stability of the traditional monometallic catalyst. As can be seen in the fig. 1, between 600 and 850 ºC there is an increase of the conversion of the reactants in the bimetallic formulation in comparison with the monometallic catalysts, attributing this to a synergic effect between Ru-Co bimetallic formation. Similar effect has been seen in stability test; the deactivation of the bimetallic formulation is radically lower than in the monometallic catalysts.

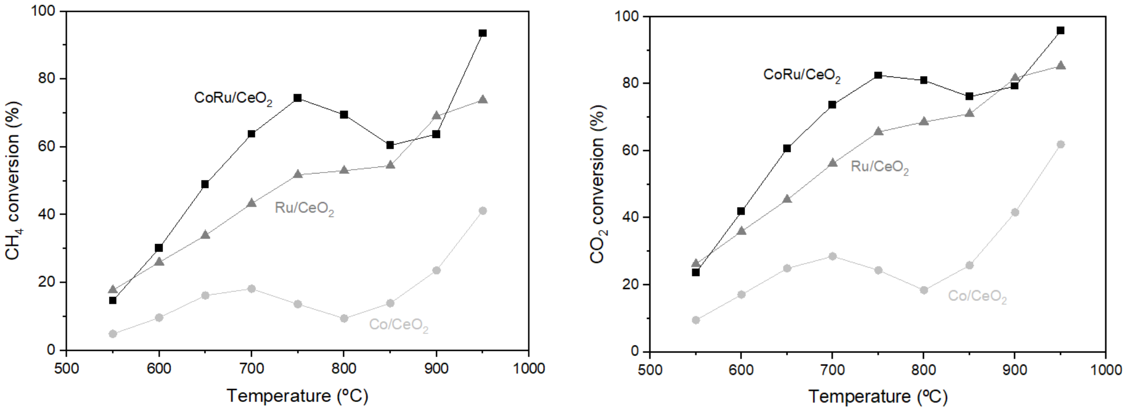

Fig. 1. Conversion of CH_4 and CO_2 as a function of temperature over $CoRu/CeO_2$, Ru/CeO_2 and Co/CeO_2 catalysts.

To understand the metal-metal and metal-support interaction, *operando* methods have been used: X-ray diffraction (XRD) and Near-Ambient Pressure X-ray Photoelectron Spectroscopy (NAP-XPS). These studies showed a dynamic behaviour in the chemical composition of the catalyst's surface and bulk. Metallic cobalt species remains on the surface thanks to the addition of the noble metal while the bulk of the monometallic catalyst contains mostly CoO.

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Particle size effects for copper-catalyzed CO_2 hydrogenation to methanol

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Methanol is an important base chemical and can be used as alternative fuel.[1] A promising environmentally-friendly route to produce methanol is via CO_2 hydrogenation.[2] Methanol synthesis from pure CO_2 is more challenging than the conventional synthesis route due to less favorable thermodynamics and undesired CO production via the competitive rWGS reaction. An in-depth understanding of the active sites and reaction mechanism is required to design catalysts that overcome these issues.

We examined the particle size effect for copper-based catalysts for the hydrogenation of CO_2 to methanol. Size-controlled Cu nanoparticles (from 4 to 20 nm) were prepared by incipient wetness impregnation of a graphitic carbon support. The catalyst performance was evaluated at temperatures of 200-260 °C and 40 bar(g) pressure in a $H_2/CO_2 = 3$ gas mixture. The Cu-catalyzed CO_2 hydrogenation reaction exhibits clear particle size effects. Small nanoparticles gave lower CO_2 conversions but higher MeOH selectivities. Theoretical models and DFT calculation were employed to explain the observed trends by considering the abundance of active sites and coverage of reaction intermediates as a function of particle size.

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The work is part of the Consortium on Metal Nanocatalysis founded by TotalEnergies.

5-(hydroxymethyl) furfural (HMF) as platform molecule from bio-based feedstocks for noble metal based selective oxidations

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Switching to renewable resources is important for a sustainable future. Apart from wind and solar, biomass can be transformed into a number of platform molecules, which can be used to produce renewable fuels and chemicals. Among these, the synthesis of furan-2,5-dicarboxylic acid (FDCA) from 5-(hydroxymethyl) furfural (HMF) represents a promising way for the sustainable production of bio-based building blocks for polymer applications. Noble metal catalysts are reported in literature to selectively oxidize HMF, which can be obtained by hydrolysis and subsequent dehydration of e.g. cellulose or inulin.[1] Biomass-derived feedstock solutions naturally contain a variety of byproducts, like sugars and amino acids. Since noble metals are prone for adsorption of e.g. amine or sulfur containing compounds, it is important to investigate their influence on catalysts used for FDCA synthesis. For this, we prepared carbon supported catalysts of Au, Pd, Pt and Ru by incipient-wetness impregnation and colloid immobilization. They were tested in the oxidation of HMF with synthetic air as oxidant and Na_2CO_3 as base. Screening in pure HMF solution the reaction rate rank was Au (Y_{FDCA}=98%) > Pt > Pd > Ru. The impact of the amino acids glutamic acid, arginine, cysteine and the dimer cystine was systematically studied. Increasing the concentration of the impurities led to decreasing FDCA yields for all tested catalysts. While the Au- and the Ru based catalysts suffered drastically from deactivation in the presence of amino acids, the catalysts based on Pt or Pd showed a comparably stable activity in the HMF oxidation at increasing impurity concentrations. The deactivation was especially pronounced for the sulfur containing compounds cysteine and cystine and particularly, the irreversible adsorption of the impurities on the noble metals seemed to be one main cause for the deactivation. Concentration threshold values for different amino acids in the solution could be derived. These results are an important step towards rational catalyst design for the production of chemicals, in particular monomers, from bio-based feedstock.

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Following the structure of copper-zinc-alumina across the pressure gap in carbon dioxide hydrogenation

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Rational catalyst design requires understanding of the structure of the catalyst in its working state. Such understanding is made possible by in situ and operando characterization. Such tools are now central to the majority of current scientific catalysis literature and research. The wealth of new insights that these methods provide into catalysis has, at the same time, created numerous strong controversies and often studies on the same catalytic system have reported contradictory results.

Copper-zinc-alumina (CZA) catalysts are the industrially-used formulation for methanol synthesis from carbon monoxide and carbon dioxide. The superior performance develops from synergies between its components. This important catalytic system has been intensively investigated, however, no comprehensive agreement has emerged as to the fundamental source of its high activity. One potential source of the disagreements is the considerable variation in pressure used in studies to understand a process that is industrially performed at pressures above 20 bar. Here, a systematic X-ray absorption spectroscopy study of the catalyst state during temperature-programmed reduction and under carbon dioxide hydrogenation is presented. The evolution of the catalyst over four orders of magnitude in pressure (1 mbar – 10 bar) shows how the state is defined by its environment [1]. In the light of the new systematic findings, existing controversies on the copper-zinc-alumina catalysts can be explained by considering the pressure regimes under which many previous studies have been conducted. As pressure gaps are a general problem in catalysis, these observations have wide-ranging ramifications.

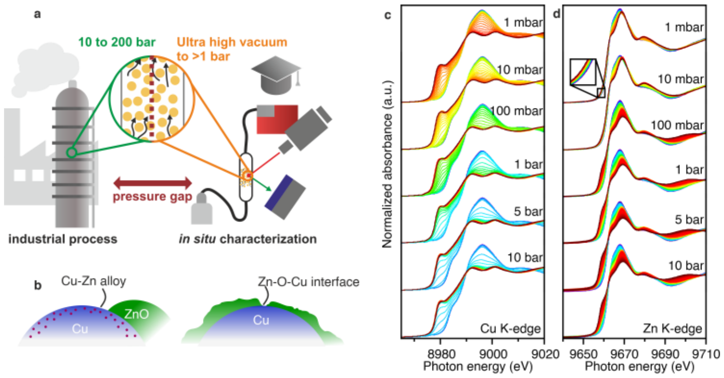

Figure 1: (a) The pressure gap existing between in situ characterization methods and conditions applied in industrial processes. (b) Proposals for the active site of copper-zinc catalysts. Cu (c) and Zn (d) K-edge XANES obtained during reduction under pressures of H_2 from 1 mbar to 10 bar.

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Malachite- and mcguinnessite-based catalyst precursors for methanol synthesis from CO_2-rich synthesis gas

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Methanol synthesis over Cu-based catalysts is promoted by zinc, which in industrial catalysts is provided by strong metal – support interactions (SMSI) between Cu and ZnO. Changing the support to the irreducible MgO offers a path to investigate the role of the support oxide and the Zn promoter under reaction conditions. For this purpose, we partially substitute copper in the malachite structure ($Cu_2(CO_3)(OH)_2$) by Mg or Zn and use these hydroxycarbonate precursors for the preparation of structurally promoted Cu / MgO and Cu / ZnO / Al_2O_3 catalysts through thermal decomposition and subsequent reduction. The effect of different synthesis parameters was systematically investigated.

Additional promoter species can be added for example by impregnation, e.g. in order to study their effect by element-specific *in situ* and *operando* X-ray absorption spectroscopy under dynamic reaction conditions.

Focusing on the precursor chemistry of the hydroxycarbonates, we have interesting findings, when gradually substituting Cu by Mg in a series of synthesis experiments: For low Mg contents (<15 at-%), crystalline green products of the malachite structure could be obtained from the pH-controlled co-precipitation and ageing in an automated lab reactor system (65 °C, pH 9.0). For larger Mg ratios (e.g. 18 or 30 at-%), ageing under hydrothermal conditions (103 °C, pH 8.0, 20 hrs.) was required for the retrieval of crystalline turquoise-colored products with the structure of mcguinnessite ($MgCu(CO_3)(OH)_2$). Since both crystal structures are similar, but not identical, we expect a distinct transition between the formation of Mg-substituted malachite and Cu-substituted mcguinnessite at a composition between 30 and 40 at-% Mg. Additionally, calcination of the Cu/Mg precursors to 700 °C revealed the formation of a poorly crystalline mixed oxide with similarities to $MgCu_2O_3$, which is in contrast to the behaviour of Cu/Zn hydroxycarbonates, where CuO and ZnO segregate upon decomposition of the precursor.

Hydrothermal CO_2 Fixation over Metal Nanoparticles

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Hydrothermal vents have received great attention in the concept of origins of life since their discovery. Their chemistry is driven by a geochemical process which is called as Serpentinization. This geochemical process occurs between ocean water and ultramafic rocks. Essential products of serpentinization process are H_2 and Fe_3O_4 [1]. In H_2- rich hydrothermal vents, metal ions Fe^{2+} and Ni^{2+} directly convert to their native metal forms or variable compositions of Fe-Ni alloys[2]. H_2 plays a crucial role for early metabolic evolution because ancient biochemical pathway of CO_2 fixation, Acetyl-coA, utilizes H_2 as an electron donor. The central enzymes that catalyze the reduction of CO_2 in acetyl-coA pathway are replete with transition metal centers (e.g. Ni^0, Fe^0) as active sites[3]. We studied the ability of Ni-Fe nanoparticles to catalyze CO_2 fixation with the addition or absence of molecular H_2 in H_2O. We investigated the effect of catalyst composition on product distribution after 24h at 100 ˚C. Formate acetate and pyruvate were obtained with all metal catalysts under mild hydrothermal conditions. Highest concentration of formate was obtained with Ni_3Fe, which shows the synergistic effect between Ni and Fe provides superior activity for CO_2 reduction.

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Hydrogen Activation by Al-N Lewis Pairs and Mechanochemical Syntheses of Organometallic Compounds

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With increasing availability and usage of green hydrogen, an increased demand of scarce elements, such as noble metals, for catalytic applications is expected. Hence, alternative catalysts based on abundant main-group elements, such as Frustrated Lewis Pairs (FLPs), may be required. Since the report of the first FLP by Stephan and co-workers,[1] the majority of FLPs still uses highly-fluorinated boron Lewis acids, phosphorus Lewis bases or both. Phosphines and boranes are generally air-sensitive, hazardous materials, while the entire synthesis of fluorinated boranes may also be rated bad for the environment. Therefore, this work presents Al-N based Lewis Pairs for hydrogen activation.[2] Amines are readily available. Alanes, as stronger Lewis acids, do not need fluorinated ligands decreasing their ecological impact and simplifying their synthesis. These alanes were also synthesized by more sustainable and fast mechanochemical reactions (<1 h compared to 4-6 h reflux). This also highlights the efficient syntheses of reactive organometallic compounds by green mechanochemical procedures.[3]

The synthesized inter- and intramolecular Al-N Lewis Pairs were tested for hydrogen activation by means of HD isotope scrambling reaction towards H_2 and D_2 monitored by NMR spectroscopy. Under benign conditions (ambient to 60°C) reasonable specific rates in the range of conventional FLPs were observed indicating a cheap and more sustainable alternative to B-P based FLPs. Furthermore, isotope labelling experiments showed that the hydrogen activation happens at the Al-site, most likely involving a higher coordinated species. X-ray crystallographic and ^{27}Al NMR spectroscopic studies indicate the Al-N distance as the crucial parameter to achieve hydrogen activation.

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Structure-Activity Correlations in Electrocatalysis Investigated by Means of Combined Atomic Force and Scanning Electrochemical Microscopy

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To increase the efficiency of the electrochemical CO_2 reduction reaction (CO2RR) an exact understanding of the electrocatalytical mechanisms and their dynamics is essential. Thus, high resolution advanced characterisation methods such as electrochemical scanning probe microscopies (EC-SPM) are required. As a member of the EC-SPM family, electrochemical atomic force microscopy (EC-AFM) has already been used to observe in-situ nanoscale structural change on a copper surface under CO2RR conditions [1]. These structural changes can have an impact on the selectivity and activity of the reaction [2].

In this work, EC-AFM is combined with scanning electrochemical microscopy (AFM-SECM) to directly reveal the impact of local copper structural features on the local electrocatalytic activity under mild reaction conditions. Next to a fundamental introduction of the technique, differences in catalytic activities at various features such as steps and terraces are identified by conducting in-situ AFM-SECM experiments. The obtained results indicate that in-situ AFM-SECM experiments can provide a key element for understanding and improving electrocatalytic reactions and its challenges with respect to dynamically operated processes.

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X-ray spectroscopy on zinc in methanol catalysts: using theory to understand experimental data

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X-ray spectroscopies are among the key techniques used to investigate the structure of heterogeneous catalysts under realistic working conditions. The measurements are element-specific and probe the electronic structure of the catalytic element, which is then used to describe the chemistry of the catalytic sites.

Bimetallic catalysts such as the Cu/ZnO system for methanol synthesis are especially challenging in terms of the accurate description of the chemical environment of zinc based on XAS data, which is currectly a subject of debate [1-3], and is known to be partially oxidized ZnOx supported on metallic Cu. Basic XAS analysis provides estimated oxidation state and coordination numbers but fails to describe the exact local geometry of the active site. One of the difficulties in interpreting Zn K-edge X-ray absorption near-edge structure is the filled 3*d*-shell, giving no pre-edge peak, which is otherwise a fingerprint of the local geometry of earlier transition metals [4].

For solving this issue, we have applied *ab initio* spectral calculations using the FEFF code [5] of various Zn chemical environments expected during CO_2 hydrogenation to methanol, and compared them to experimental data. We have measured XAS on a model ZnO-modified Cu catalyst under reaction conditions of CO_2 hydrogenation at 20 bar and 230°C, as well as reference conditions (H_2, CO_2, CO, formic acid etc.). The matched theoretical and experimental spectra gave clear impressions on the chemical nature of the zinc species in the catalyst during synthesis, activation and reaction, which is useful in optimizing catalyst design.

Theoretical spectroscopy as a field bridges molecular modelling and experimental operando characterization. It is an essential tool for qualitative and (semi)quantitative analysis of spectra when experimental references are missing. These methods are also predictive for characterization using soft X-ray and electron spectroscopies.

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Bimetallic NiFe/CeO2 catalysts for methane steam reforming: in-situ XPS and XRD characterisation

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Methane steam reforming (MSR) is the main process for the industrial production of hydrogen and syngas. Nickel-alumina nanomaterials are the most used catalysts because Ni is a very active metal for MSR, but it suffers deactivation from sintering, oxidation, coking and sulphur poisoning. Alloying Ni with a second metal is a strategy to enhance its stability and performances. Besides noble metals, a suitable element is Fe, an element known for the catalysis of the water-gas shift reaction and the Fischer-Tropsch process. NiFe-based catalysts showed increased stability and coke resistance in several steam reforming reactions[1] of different substrates compared to the monometallic Ni catalysts, with increased Ni dispersion and carbon oxidation thanks to FeOx redox properties.

In this work, $_{10-x}Ni_xFe$ (x = 0-2) catalysts supported on hydrothermally synthesised CeO_2 have been prepared by incipient wetness impregnation and a mechanochemistry method. These catalysts have been tested for MSR catalysis in the temperature range from 700°C to 950°C (F/W = 110000 $mL/g_{cat}h$) and at 700°C with different reactant loading (F/W = 54000 – 420000 $mL/g_{cat}h$), showing decreased catalytic performances for the bimetallic samples. In-situ XPS characterisation was performed after the reduction at 550°C (10%H_2/Ar, 30 min) revealing that the addition of Fe decreased the reducibility of NiO species while increasing the Ni dispersion. In-situ XRD characterisation was performed during the reduction treatment at 700°C (10%H_2/Ar, 30 min) and during MSR (1%CH_4/2%H_2O/N_2) between 700°C and 900°C, showing that the bulk composition of the catalysts is metallic, with no segregation of oxide nanoparticles. XRD characterisation confirmed the smaller size of NiO and NiFe nanoparticles.

The presence of Fe limited the quantity of metallic Ni, that is the active phase for MSR catalysis.

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Novel Electrochemical Method to Functionalize Methane on a BDD-anode

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An electrochemical system was developed, where methane is oxidized to methyl bisulfate (MBS) and methanesulfonic acid (MSA) without the addition of a catalyst on the anode side of an electrolyzer system instead of the oxygen, which is normally evolved anodically. Since MBS can be hydrolyzed to methanol, and MSA itself is a high value product, these are value generating anode reactions.

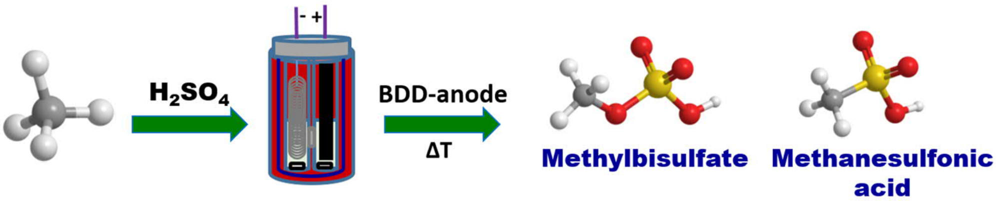

Figure 1: Graphical overview of the studied electrochemical system, equal to table of contents in reference [1].

This study shows the highly surprising finding that methane functionalization to MBS is possible without the addition of a catalyst, and to MSA without the addition of a peroxo-species as an initiator. In addition, general trends and limitations of the system were studied. While MSA is obtained at very high concentration and selectivity, MBS formation is limited. The studies reveal that the major fraction of the products is not formed anodically, but rather in a secondary process from species formed from the interaction of BDD with sulfuric acid at high potentials. To reach a high MBS concentration high temperature (140°C), pressure (70bar) and cell voltage (2.2V) are beneficial; however, the MBS concentration is limited due to product decomposition and has a maximum over time (160mM under the applied conditions). The product stability was studied in detail. As our investigations show, the decomposition, for instance to CO_2, is a general challenge for electrochemical MBS synthesis when high product concentrations are the goal. MSA on the other hand appears to be more stable. High MSA concentration (1.9M) at high selectivity (97%) was reached at moderate temperature (70°C) and cell voltage (1.4-1.7V). The results show important new aspects of reactions that were previously reported to take place only in presence of a catalyst or initiator – at similar rates, which we report. The MBS and MSA are produced by an anodically generated active species, reacting with the methane.

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Synergistic effect of Co and Fe catalysts for Ammonia Decomposition

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Ammonia, according to its high energy density, its high hydrogen content, convenient infrastructure for transportation and storage, and carbon-free conversions, is becoming as a promising energy carrier [1, 2]. Therefore, renewable hydrogen could be stored by synthesizing ammonia, and released by ammonia decomposition after transportation. However, there is still a challenge in the design of the highly efficient catalyst for ammonia decomposition at mild conditions. So far the most active catalysts for ammonia decomposition are Ru-based catalysts [3], which have an optimal nitrogen adsorption energy compared to other transition metals [4]. However, the high cost of Ru limits its application on a large scale. In contrast, the utilization of earth-abundant and cost-effective transition metals like iron is attractive. Our previous results showed active Fe-MgO catalysts are formed by the reduction of $MgFe_2O_4$ spinels obtained from co-precipitated precursors [5, 6]. Here we will introduce Co into the $MgFe_2O_4$ spinel catalyst to investigate the synergistic effect of Co and Fe for promoting the activity for ammonia decomposition reaction.

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Mechanistic and structural investigation of OER catalysts by Oxygen Evolution Reaction at High Potentials Probed by Operando Spectroscopy

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Green hydrogen produced by electrolysis is a promising solution for compensating the uneven nature of renewable energies. Moreover, it can be utilized to decarbonize steel production or in combination with CO_2 it can form fuels and industrially-relevant hydrocarbon products. Commonly used setups are PEM electrolyzers, where at low temperatures high current densities can be reached.[1] However, the acidic electrolyte used limits the number of suitable electrode materials. The 4-electron process of the oxygen evolution reaction (OER) occurring at the anode, which can only be efficiently catalyzed by the oxides of the scarce and expensive iridium and ruthenium, further complicates the process. Therefore, it is crucial to better understand the OER process, especially under dynamic conditions, with the purpose to optimize the catalysis and reduce catalyst loadings.[2]

In a comprehensive approach, with advanced operando X-ray techniques (QuickXAS, XANES, EXAFS, ME-XAS and in-situ ICP-MS) we investigated IrO_2, RuO_2 and $IrRuO_2$ catalysts under OER conditions.[3] By combined analysis (Principal component analysis and DFT calculations), we were able to extract two distinct components which could be related to different reaction modes: i) the standard absorbate electrolyte mechanism (AEM) and ii) a modified AEM which includes the formation of oxygen vacancies. For IrO_2 it could be shown that at lower OER potentials < 1.5 V the standard AEM is dominating while at higher potentials > 1.5 V, the modified AEM prevails. Under dynamic conditions at high potentials, the formed oxygen vacancies lead to the formation of increased Ir-Ir interaction, stabilizing but also deactivating the catalyst. Further experiments on RuO_2 and $IrRuO_2$ show that the differences in performance and stability of these materials can indeed be explained by the reaction modes on these catalyst materials. The combined Ir-Ru structure prevents the formation of Ir-Ir interactions, explaining the increased performance and decreased stability.

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Operando X-ray scattering to track atomic level structural transformation in NiFe LDH

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The NiFe layered double hydroxides (LDH) are among the most active electrocatalysts for the oxygen evolution reaction (OER) in alkaline electrolytes.[1] However, despite the general observation of the promoting effects of Fe in NiFe LDH, details of the catalytic active sites and mechanism are still under debate.

In this contribution, direct atomic-scale evidences will be presented, showing that NiFe LDHs are oxidized under applied anodic potentials from as-prepared α-phases to activated γ-phases.[2] The interlayer and in-plane lattice parameters of the OER-active γ-phase were obtained by performing wide angle X-ray scattering (WAXS) measurements on NiFe LDH nanoplatelets during operating electrochemical conditions and were characterized by a contraction of about 8%.

The OER activity of NiFe LDH will then be compared with that one of other transition metal LDHs. For this comparison, intrinsic activity trends were derived through a method based on electrochemical active surface area normalization.[3] Operando WAXS was also performed for other selected catalysts belonging to the transition metal LDH family of materials. Structural similarities of the catalytically active phases will be highlighted and correlated with the activity performance.

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Differences between Dynamic and Stationary Analysis of the Electrochemical CO_2 Reduction

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Electrochemical technologies, such as the carbon dioxide reduction reaction (CO_2RR) for the production of fuels and chemicals, are promising approaches for decarbonatization of energy production, conversion and storage. Improvements in (electro)chemical reactions, their dominant processes and limitations require an in-depth and, above all, quantitative understanding of the reaction mechanisms, their kinetics and their charge and mass transport processes. Dynamic kinetic modelling of heterogeneously catalysed chemical and electrochemical reactions is a key tool to understand and optimize the behaviour and performance of surfaces, electrodes and cells [1].

This contribution presents the first dynamic physico-chemical model for the CO_2RR at planar silver electrodes. It considers the dynamic description of reactions at the electrode surface, the transport processes in the electrolyte and the chemical carbonation reactions inside the electrolyte. Model-based analysis provides a detailed insight into the dynamics of the concentration profiles of species and mass fluxes in the vicinity of the electrode and its dependence on operating conditions [2].

In detail, strong discrepancies between the effect of dynamic and steady-state conditions on the concentration profiles are revealed. They originate from the slow transport and carbonation processes, which lead to a strong time dependency of the depletion of CO_2 and the buffering effect of the electrolyte. As a result, during dynamic and steady-state operation, different concentrations are present at the electrode interface and different selectivities of the reaction system follow. This results in differences in the polarization curves recorded by steady state and by voltage sweeping. This effect has been largely ignored by researchers, which makes interpretation and comparison of curves erroneous.

This study provides a detailed understanding to the dynamic processes of CO_2RR and the key role of transport and carbonatization.

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Model reactor for investigations on CO_2 methanation under dynamic reaction conditions

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The unsteady supply of renewable electricity and the spatial mismatch between generation and demand in a future energy system mainly based on renewables leads to the necessity of novel concepts of energy storage and distribution. In this context, power-to-X will play a crucial role not only to store the renewable energy in chemical carriers, but also to allow for its transportation and coupling of different energy sectors. Here, one option is the synthesis of sustainable methane from green hydrogen and CO_2 from industrial point sources or even captured from ambient air. To minimize the need of H_2 and CO_2 buffer facilities, the processes should be able to tolerate external fluctuating conditions. Therefore, it is of crucial importance to understand the behavior of the methanation catalyst involved under these circumstances. In recent literature regarding simulation and optimization of dynamic methanation, semi-empirical kinetic models based on steady-state approaches are frequently applied. However, the underlying assumptions of these models are questionable for transient operation since sorption processes, changes in the reaction mechanisms and alterations of the catalyst structure are not considered.

Therefore, in the frame of the DFG Priority Program SPP 2080, the kinetics and modulation of the dynamically operated CO_2 methanation reaction is investigated in detail. In particular, a model methanation reactor with multiple taps along the reaction path was developed and built allowing to gather spatial and temporal resolved operando data under certain process conditions. To allow ex-situ and post-mortem analysis, the catalyst is integrated by coating on changeable micro structured plates. To ensure reproducible catalyst coating, screen printing was applied, which allows similar catalyst mass and coating thickness on every plate. Additionally, the reactor is equipped with an optical window which gives the possibility for operando investigations of the species adsorbed on the catalyst via diffuse reflectance infrared fourier transform spectroscopy (DRIFTS). In the project consortium, the data obtained will be used to develop a kinetic model capable to describe transient behavior, possible changes in reaction mechanisms as well as catalyst deactivation. In this poster contribution, the model reactor and investigations on catalyst coating will be presented and discussed.

Strategies to uncover activity-stability relationships in Ir-based catalysts for water splitting

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Proton exchange membrane water electrolysers (PEMWE) are key technologies to drive the energy transition towards the hydrogen economy. For large-scale implementation, loadings of the commercial iridium (Ir) anode electrocatalyst need drastic reduction to drive down green hydrogen prices. Strategies to decrease Ir catalyst loadings generally involve the synthesis of highly-dispersed nanoparticles or the preparation of cation-substituted Ir catalysts ($Ir_xM_{1-x}O_y$). Although reports on the latter devoted to activity maximization, information is scarce regarding the activity-stability relationships.[1] This is paramount when employing cheap non-noble metals as cation substituent M, where any synergistic effects in activity could be misinterpreted if M dissolves preferentially under OER operation. We herein aim to bridge the knowledge gap by employing a scanning electrochemical flow cell coupled to inductively-coupled plasma mass spectrometry, enabling online quantification of any catalyst dissolution products under OER operation. First, we evaluate these relationships in cationic-substituted $Ir_xM_{1-x}O_2$ (100) epitaxial thin films, model systems which allow to clearly uncover any cation-dependent trends.[2] Next, we move to the industrially-promising $Ir_xRu_{1-x}O_2$ nanoparticle (NP) systems, at different relative compositions and degrees of crystallinity.[3] It was observed that the Ir stability in epitaxial films directly correlated with the OER enhancement effect of the cation substituent: higher OER activities induced by the cation yielded lower Ir stabilities and vice versa. In addition, the IrO_2 matrix does not seem to affect the thermodynamic trends of cation dissolution. For $Ir_xRu_{1-x}O_2$ NPs, the start-up/shut-down stress protocol to mimic dynamic operation showed a 1000-fold lower stability for hydrous vs. rutile-type NPs, and a non-linear activity drop in $Ir_{0.2}Ru_{0.8}O_2$ after <1 at. % Ru loss. We envision our work to provide clear guidelines for future $Ir_xM_{1-x}O_y$ electrocatalysts.

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Abstract for Poster “From Wind and Solar Energy to Chemical Energy Storage: Understanding and Engineering Catalysis under Dynamic Conditions” – 758. WE Heraeus Seminar

“Development of a ceramic membrane reactor for coupled propane dehydration and hydrogen production”

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At present, the production of olefins in a steam cracker generates a large amount of emissions with high energy consumption. At the same time, the by-product hydrogen must be separated in a complex manner for further use. In the research project "Additive Manufacturing for Zero-emission Innovative Green Chemistry", or AMAZING for short, the companies BASF, Dow and Shell, as well as WZR work together with the Institute for Energy and Climate Research at Forschungszentrum Jülich, the University of Twente and the Eindhoven University of Technology. In AMAZING, the fundamentals for a ceramic membrane-based process are to be developed, which separates the by-product hydrogen from propane dehydrogenation inside the reactor and makes it available for further use. At the same time, higher olefin yields can be reached by shifting the chemical equilibrium towards the product. If the production technology is suitable for larger-scale use, membrane modules could later be produced on a commercially relevant scale. Since two different processes are combined here, membrane reactors show great potential for industry. In this way, not only cracking can be designed to be particularly low-emission and energy-efficient, other processes beyond olefin production could also benefit from it. For example, the sustainably generated hydrogen is predestined to be used in other industrial processes or in the mobility sector.

Revealing Surface Transformations by operando Friction Force Microscopy

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A thorough understanding of surface transformations of electrocatalysts under dynamic vs. static electrochemical conditions are inevitable for a knowledge-based improvement of materials. Next to spectroscopic investigations various microscopic techniques, especially *in-situ* or *operando* scanning probe microscopy based methods, have been shown to reveal important information of the catalytic process. [1]

In this contribution operando friction force microscopy (EC-FFM), a well-known technique in tribology, [2][3] is introduced as a tool to differentiate between a bare surface and an oxy/hydroxyl-terminated adlayer in aqueous electrolytes. This becomes particularly relevant for the oxygen-evolution reaction, where subtle modifications at the beginning of the reaction might easily be overseen by pure topography mapping. The concept is verified by experiments on gold and copper single crystalline surfaces as well as on a perovskite oxide sample.

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Mechanism for acetate formation in $CO_{(2)}$ reduction on Cu: Selectivity trends with pH and nanostructuring derive from mass transport

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Nanostructured Cu catalysts have increased the yield and geometric activities for high value C-C coupled (C_2) products in the electrochemical $CO_{(2)}$ reduction reaction ($CO_{(2)}$RR).[1] Among the C_2 products the selectivity is also altered, where for instance the yield of acetate shows dependence on the catalyst morphology and increases with alkalinity.[2] The reaction mechanism behind this selectivity towards acetate vs. other C_2 products remains controversial. In this work, we elucidate the reaction mechanism towards acetate by using *ab-initio* simulations, a coupled kinetic-transport model, and loading experiments. We find that trends in acetate selectivity can be rationalized from variations in electrolyte pH and the local mass transport properties of the catalyst and not from changes of Cu's intrinsic activity. The selectivity mechanism originates in the transport of ketene, a stable (closed shell) intermediate, away from the catalyst surface into solution where it reacts to acetate. While such a mechanism has not yet been discussed in $CO_{(2)}$RR, variants of it may explain similar selectivity fluctuations observed for other stable intermediates like CO and acetaldehyde. Our proposed mechanism suggests acetate selectivity to increase with increasing pH, decreasing catalyst roughness and to significantly vary with applied potential.

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Operando Insights into Bimetallic Cu-Ag Nanocubes during CO_2 Electroreduction toward Liquid Products

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Direct conversion of carbon dioxide into multicarbon fuels and chemicals by CO_2 electroreduction (CO_2RR) can significantly contribute to reintegrate undesired CO_2 back into the carbon cycle necessary to weaken the climate change.[1] Among the variety of catalysts, Cu_2O nanocubes are able to convert CO_2 into multiple C_{2+} hydrocarbons but it remains challenging to control the selectivity toward particular products. Several approaches have been tested so far to improve the selectivity trends, such as varying catalyst structure, electrolyte composition or the potential sequence.[2]

One promising way to further improve the catalyst performance and selectivity is the introduction of a second metal. Recent studies of Cu-Ag bimetallic systems showed enhanced selectivity for ethanol and/or ethylene, which was usually accompanied by the increased production of CO.[3] However, the structural arrangement and composition of the Cu/Ag interface during CO_2RR is not understood in-depth yet but play a key role to achieve an optimal synergy between the metals.

Here, we prepared Ag-decorated Cu_2O nanocubes with 30 nm edge length, which showed a remarkable increase (30 %) in the Faradaic efficiency for C_{2+} liquid products. By means of *ex-situ*, *in-situ* and *operando* characterization techniques, we got an insight into the morphology, chemical state, and composition of the Cu-Ag catalyst under CO_2RR conditions. By the addition of Ag nanoparticles, we observed the redispersion of Ag on Cu in the STEM-EDX mappings and the formation of Cu-Ag distances in *operando* Ag K-edge EXAFS during CO_2RR. Additionally, *operando* SERS showed significant variations in the binding of CO to Cu that can be linked to the enhancement of the liquid product yields.[4] The study highlights the importance of *operando* investigations to unravel the catalyst's adaptations and intermediates during reaction and demonstrate the deconvolution of the complex interplay.

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Hollow carbon spheres as model catalyst supports for polymer exchange membrane fuel cells

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Proton exchange membrane fuel cells (PEMFCs) present a sustainable alternative to fossil fuels, especially for mobile applications. The state-of-the-art catalyst for the conversion of hydrogen and oxygen to water is platinum on carbon black. Carbon blacks are, however, heterogeneous in particle size, graphitization and porosity, which complicates the study of the highly complex 3-phase reaction in the PEMFC [1]. Therefore, we propose the use of tailored hollow carbon spheres (HCS) as uniform catalyst supports for model studies.

In our previous work, we have shown that HCS can be produced using the chemical vapour deposition of ferrocene into the pore system of a siliceous hard template [2]. The properties of the hard template determine the characteristics of the HCS. Adapting the work of Büchel et al. [3], we synthesize templates of controlled morphology and thereby produce HCS of variable diameter, shell thickness and pore geometry. Further, we show that the degree of graphitization is adjustable by annealing the HCS at different temperatures. In addition, functionalized HCS can be accessed through post-treatments with nitric acid, ozone and ammonia. Finally, the CVD process has been adapted to the use of pyridine, pyrrole, thiophene, thiazole and acetonitrile as precursors. This enables the metal free synthesis of N- and S-doped HCS.

To conclude, we develop the techniques necessary for the synthesis of HCS, which can be tailored independently in terms of dimension, pore size and morphology, graphitization, and functionalization. These materials enable us to specifically investigate the influence of one of these properties on performance, transport and stability phenomena occurring in PEMFCs and more generally in electrochemical devices.

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Diatomic Fe-Co sites for efficient OER

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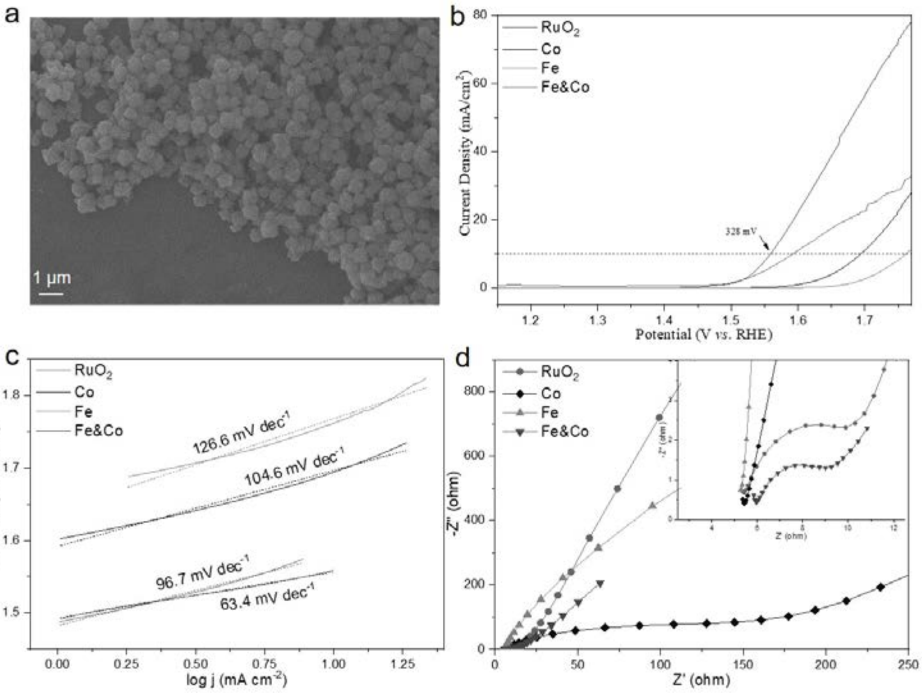
The rational design of high active catalysts for efficient oxygen evolution reactions (OERs) is desired but challenging. Transition metal hydroxides are promising electro catalysts for alkaline OER[1]. Herein, Iron-Cobalt (FeCo) oxyhydroxide nanoparticles were successfully synthesized through organic colloid synthesis method. Rich oxygen vacancies confined in the diatomic mixed-phase FeCo oxyhydroxide can result a significant enhancement in the OER activity. Notably, the optimized FeCo oxyhydroxide nanoparticles exhibited excellent OER activity with a low overpotential of 328 mV to offer 10 mA cm^{-2} and remarkable stability, revealing its potential as a high-performance OER electrocatalyst.



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Integrated modelling of dynamic surface changes and kinetics of a novel nickel-based catalyst for CO_2 methanation

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Rising global temperatures due to the anthropogenic greenhouse gas emissions led to the necessity to increase the share of renewable electricity in power generation. Since renewable energies like solar or wind are often strongly fluctuating, it is crucial to use storage technologies like CO_2-Methanation as a so-called power-to-X technology. To allow an accurate description of the reactor's behavior during transient operation, current research aims at establishing non-steady-state kinetic models. One example is the DFG Priority Program SPP 2080 "Catalysts and reactors under dynamic conditions for energy storage and conversion". In this program, the consortium of Prof. Freund, Prof. Franken and Dr. Rubin investigates reaction kinetics of catalytic systems and the influence of catalyst deactivation.

The focus of this contribution is to give an outlook on future research within the second funding period of the SPP 2080 Program. In the first funding period, a transient kinetic model was developed for a widely used methanation catalyst (IMRC), which suffers from irreversible deactivation effects. Based on the gained knowledge and understanding of the reaction system, in the second funding period, a novel dynamic responsive model (DRM) catalyst will be developed. The novel catalyst will be resistant to irreversible deactivation to a certain degree. This is achieved by triggering active site reformation during forced dynamic operation, allowing the catalyst to regain activity. After synthesizing the novel catalyst, both catalysts will be investigated with complementary in situ, operando, and ex situ measurement techniques. Kinetic models of different complexity will be established, considering catalyst deactivation during steady state as well as under dynamic operation. Eventually, optimal operation policies for dynamic methanation are derived from model-based optimization.

The role of transition metal–oxygen bonds upon OER catalysis of perovskites: NEXAFS and CTM4XAS analysis

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Near edge X-ray absorption fine structure ('NEXAFS') spectroscopy at transition metal (Me) L and oxygen (O) K edges in combination with charge transfer multiplet ('CTM') calculations are a powerful tool to study changes in the electronic structure of transition metal oxides such as perovskites (ABO3 with A = La, Sr and B = Co, Ni, Fe) and structural related materials upon electrochemical reactions [1,2,3]. NEXAFS data of epitaxial LSCO (La1−xSrxCoO3−δ), for example, shows that Co-O hybrid states, the active sites upon the OER (oxygen evolution reaction) in alkaline media, are vanishing. This is evident from the disappearance of Co-O hybrid peaks in the O K spectra and can be verified with charge transfer multiplet calculations of the Co L edge. Thereby the redox active electronic configuration of Co can be revealed which will help to modify the d-band to obtain more superior OER catalysts in future.

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Selective Hydrogenation of High Concentrated Acetylene with Mechanochemical Prepared Pd-Ag/α-Al_2O_3 as a Catalyst

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The selective hydrogenation of acetylene to ethylene is a well studied reaction to purify ethylene streams and avoid poisoning of downstream catalysts in polymerization processes. In contrast to this conventional application, we focused on the hydrogenation of high concentration acetylene streams with equimolar acetylene and ethylene amounts. These conditions would apply, when using natural gas as a carbon source for ethylene production. In a first step, natural gas would be converted in a plasma reactor to a mixture of acetylene and ethylene, followed by the hydrogenation of acetylene to ethylene.[1]

Bimetallic PdAg/α-Al_2O_3 catalysts were prepared by a classical impregnation approach as well as a novel mechanochemical synthesis. [2] Catalysts with various Pd:Ag metal ratios were synthesized and their performance compared.

The selectivity towards ethylene was found to increase with high silver contents. Further, a higher reaction temperature resulted in an enhanced selectivity. The selectivity was very similar for catalysts with same metal ratio prepared by different synthesis methods. However, a difference could be observed in the catalyst stability between the impregnated and the mechanochemical synthesized material. For example, comparing the activity of a Pd-Ag catalyst with a metal ratio of 1:5 at 150°C, the impregnated material is stable for only about 200 min, while the mechanochemical prepared catalyst no deactivation after 10 h on stream.

We show that the selective hydrogenation of acetylene to ethylene can be achieved under high acetylene concentrations. Bimetallic PdAg catalysts are well suited, and preparation by a mechanochemical approach is advantageous to achieve stable catalysts.

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Local order in AgAuCuPdPt high entropy alloy surfaces

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High entropy alloys (alloys with five or more constituent elements) are of increasing interest in catalysis. The basic idea is that the surfaces of high entropy alloys will have all kinds of local atomic combinations and therefore some surface sites with high catalytic activity. This requires that the high entropy alloy surfaces are disordered in nature.

We explored the local order of bulk equimolar fcc AgAuCuPdPt and its (111), (100) and (533) surfaces, by constructing structure ensembles for each system with random placement of the elements. The ensemble energies are used to approximate the canonical partition function and obtain values for the local order as a function of temperature (assuming thermal equilibrium). Our study finds that the ensemble energies are Gaussian distributed with a width that increases at the surfaces as (100) > (533) > (111) > bulk. Since the partition function effectively pics out the stable energy tail of the Gaussian distributions, the local order similarly increases with (100) ≥ (533) > (111) > bulk.

Two types of local order are relevant, namely the distribution of nearest neighbor elements and the composition of elements in the surface layer. The (111) surface has increased amounts of Au and Ag and less Cu, Pd and Pt, but the nearest neighbor distribution is still mostly random. The (100) surface both have an increased amount of Au and Ag and a more ordered distribution of nearest neighbors.

High entropy alloy particles can be formed by arc melting at high temperatures (≥ 1000°C) in an inert atmosphere. However, our results show that heating the equimolar AgAuCuPdPt high entropy alloy to high temperatures will likely not produce equimolar AgAuCuPdPt surfaces. Still, (111) surfaces of AgAuCuPdPt can likely be modeled by surfaces with random atomic arrangement where only the shift in overall surface composition is accounted for. This is likely not the case for (100) surfaces, because of their nearest neighbor order.

Reactive CFD and NMR: Bringing research areas together for detailed, full-field validation

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In the course of the last decade, multiscale modeling attracted considerable research interest in the chemical engineering community. Combining chemical reactions with high-resolution Computational Fluid Dynamics (CFD) can give new insights into phenomena within catalytic reactors, essential for Power-to-X technologies. These insights can be used to further optimize process parameters and reactor designs to increase the process efficiency.

Such multiscale simulations, however, are very complex. The employed models and reaction kinetics make proper validation all the more indispensable. So how do we achieve an appropriate validation? By now, integral as well as local methods are state-of-the-art. This includes measurements of gas compositions downstream of the reactor, through a capillary in the catalytic bed or temperature measurements using thermocouples. Besides most of them being invasive, these methods also do not represent the high spatial-resolution of CFD.

To fill this gap, the usage of Nuclear Magnetic Resonance (NMR) tomography is a promising approach. We already showed the feasibility of cross-validation between three-dimensional, gas-phase velocimetry measurements and CFD simulations in an Open Cell Foam (OCF) reactor. Here, we propose a new, additively manufactured reactor design for the validation of the Pt-catalyzed ethylene hydrogenation reaction at high spatial resolution. The digital reactor geometry is the basis for reactive CFD simulations implementing a microkinetic model from literature. Using NMR, spatially resolved temperature as well as full-field product concentration measurements within the reactor shall be performed, making a detailed validation of the CFD simulations possible. Thus, such a combination of CFD and NMR can provide cross-validated information about the processes within catalytic reactors, which is crucial for further developments in this area.

Holistic kinetic modeling of the CO_2 methanation reaction

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In the context of use and storage of renewable energy, an increasing scientific interest in power-to-gas processes such as the CO2 methanation has developed. Recent work focused on understanding and optimizing reactor behavior is aimed at improving load flexibility and transient operation of the methanation. To accurately describe the behavior of the reactor, the catalyst must first be sufficiently understood and depicted at the level of reaction kinetics. In the frame of the DFG Priority Program SPP 2080 "Catalysts and reactors under dynamic conditions for energy storage and conversion"; the consortium of Prof. Freund and Dr. Rubin focuses on the holistic description of the kinetics of nickel based catalysts.

This contribution gives an overview of the accomplished work regarding the kinetic model development. As basic reference, a state-of-the-art steady state kinetic model was developed for the methanation catalyst (IMRC), which is widely used within the SPP 2080. This model covers a broad operation range up to 460 °C and describes CO2 methanation as well as the reverse water gas shift reaction, which occurs at these elevated temperatures. Furthermore, at temperatures above 350°C permanent catalyst deactivation increases drastically on the freshly reduced catalyst. The deactivation is attributable to sintering of the active nickel clusters. To gain a holistic model the deactivation is investigated in an ongoing kinetic study and will be embodied in the reference kinetic model. Furthermore, to describe the dynamic behavior of methanation catalysts a semi-mechanistic kinetic model approach based on so-called rate affecting steps and the change in surface coverages will be presented. This model is able to describe the storage capacity of the catalyst surface and depicts sorption processes and changes of rate determining steps.

Data-Efficient Iterative Training of Machine-Learning Gaussian Approximation Potentials for Surface Structure Determination of Living Heterogeneous Catalysts

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Machine-learning interatomic potentials such as Gaussian Approximation Potentials (GAPs) have recently evolved as a powerful class of surrogate models to computationally demanding first-principles calculations. Along with structure exploration techniques, they enable us to examine the potential energy surface of interest with a hitherto unforeseen combination of physical accuracy and computational efficiency and to achieve global surface structure determination (SSD) for increasingly complex systems. This can be leveraged e.g. to discover novel surface motifs which are critical in understanding the “living” state of heterogeneous catalysts and their degradation under dynamic operating conditions. This versatility however may only be achieved by cautiously designed protocols for the generation of training data, which should cover the relevant structural and chemical space of the target applications. Supplementing such protocols with human chemical intuition in the form of metaheuristics facilitates further improvements.

To this end, we present a general and data-efficient iterative training protocol that allows for the on-the-fly generation of GAPs via the actual surface exploration process [1]. Demonstrating this approach for the SSD of low-index rutile IrO_2 and RuO_2, the iterative refinement of GAPs identifies plenty of unknown low energy terminations even within the restricted sub-space of (1x1) surface unit-cells [2]. By extending the protocol to larger surface unit-cells, we discovered new surface structures which provide solutions to longstanding questions in heterogeneous catalysis.

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Al-N compounds for hydrogen activation and as energetic materials

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Hydrogen is considered as a sustainable and green alternative to fossil fuel in the energy market, because it has high energy density, renewable sources and its production and consumption processes do not necessarily have CO_2 emissions.

Solid-state hydrogen storage in metal hydrides is regarded as an effective approach; especially compounds based on light group 13 elements (B, Al) have attracted particular interest. AlH_3 has great potentials in hydrogen storage applications and rocket fuel due to its high hydrogen capacity(10 wt%) and combustion energy.

However, the regeneration of AlH_3 from Al with H_2 and its metastability at ambient conditions currently limit its application. We introduced basic amines into systems to satisfy the Lewis-acidic Al center electronically and consequently generate the strong Al-N bonds, thereby forming more stable Al-N compounds. The steric effects of N-ligands coordinating AlH_3 have an impact on the activity of compounds. Ortmeyer et al. facilitated the direct hydrogenation of pure aluminum under a pressure of 100 bar H_2, with conversions up to 90%, which indicated that the presence of ternary amines allows facile hydrogenation of Al metal[1].

In our research, we found that $[H_2Al\text{-}N(CH_3)(C_6H_6)]_2$ is able to activate H_2 measured by ^1H and ^2H NMR spectroscopy to follow the isotope exchange of HD to H_2 and D_2, as well as D_2 to HD[2]. The materials, which have hydrogen activation reactivity, could potentially store hydrogen. Now we are investigating the hydrogen storage properties of $[H_2Al\text{-}N(CH_3)(C_6H_6)]_2$.

For applications as energetic materials, e.g.,fuel pellets, and rocket fuel, the combustion energy is a key parameter. Here we show increased calorimetric combustion energy of Al-N compounds with respect to pure amines or hydrazine. It indicates that Al-N compounds are promising energetic additives in solid propellants.

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Ligand-free silver nanoparticles for CO_2 electrocatalytic reduction to CO

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Ag-based electrocatalysts are selective towards CO [1], which can be utilized, together with H_2, in a Fischer-Tropsch plant to synthesize liquid fuels. Therefore, many research groups focus on the rational design of silver nanostructures supported on conductive substrates to enhance the catalytic activity [2]. Control over the nanoparticle size is essential to understand the relationship between structure and electrochemical performance. In this work, we synthesized by incipient wetness impregnation ligand-free silver nanoparticles supported on carbon. We controlled the particle size by introducing functional groups on the support and by tuning the gas composition during the heat treatment (inert or reducing atmosphere). We correlate the electrochemical performance to the morphological properties of the catalyst. In reducing atmosphere, silver nanoparticles of 21 nm were formed, while the treatment in inert environment produced 34 nm particles. We can demonstrate that the particle size inversely scaled with the density of surface groups on the carbon support. This correlation suggests that the surface groups act as nucleating sites for the silver nanoparticles during the impregnation step. Subsequently, we were able to correlate the CO partial current density with the particle size. The CO partial current density normalized by silver weight loading is inversely proportional to the particle size. Nevertheless, the CO partial current density normalized by silver surface area do not depend on the nanoparticle size, showing only a weak trend at more negative potentials. Since the electrochemical production of syngas, a mixture of hydrogen and carbon monoxide, might represent an opportunity to use 'green' hydrogen and CO to produce sustainable fuels, we evaluated the H_2 to CO ratio for the different catalysts. The H_2 to CO ratio as a function of the total current density. AgNPs_11nm generate an H_2 to CO ratio equal to 2.9 at - 5.9 mA cm while the other catalysts only produced a ratio equal to 6. This finding demonstrates that by tuning the particle size and the support surface properties, we can control the H_2 to CO ratio.

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Analysis of possible improvement of forced periodically operated chemical reactor with methanol synthesis based on Nonlinear Frequency Response Method

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Abstract

Forced periodic operations, as one way of Process Intensification, can be used in order to achieve better performances of chemical reactors, in comparison to conventional steady-state operation. In this study the Nonlinear Frequency Response (NFR) method, a powerful analytical and approximate tool which gives an answer whether and under which conditions certain periodic operation would lead to improvement of process performance was used. The analysis was done for the methanol synthesis using a standard Cu/ZnO catalyst performed in an isothermal and isobaric lab-scale CSTR. At first the single input modulations were analysed. The inputs considered for periodic modulation are: partial pressures of each reactant in the feed stream and the total volumetric inlet flow-rate. The objective was to maximize the mean molar outlet flow-rate of methanol. The specific forcing parameters were optimized. The results of the NFR analysis showed that modulations of single inputs do not provide potential for significant improvements.

The study was extended to analysis of periodic operations with simultaneous modulations of two inputs. Six possible input combinations were analysed and the optimal forcing parameters which maximizing again the time-average methanol production were determined. For all combinations an improvement is possible, but for some cases it was found to be not significant. However, significant improvements are predicted for a) simultaneous modulation of the partial pressure of CO_2 in the feed steam and the volumetric inlet flow-rate and b) simultaneous modulation of the partial pressure of hydrogen (H_2) and the volumetric inlet flow-rate [1, 2]. The highest improvement could be achieved for simultaneous modulation of the inlet partial pressure of CO and the inlet volumetric flow rate.

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Immobilisation of Molecular Catalysts on Phosphine-Based Hyper-Crosslinked Polymers for the Activation of CO_2

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Due to its promising potential in hydrogen storage applications, the hydrogenation of CO_2 to formic acid (FA) has attracted increasing attention. Because of its thermodynamic stability, the development of catalysts plays a crucial role and was addressed by various studies, leading to a large variety of active homogeneous catalyst.[1] Despite their excellent catalytic performance, difficulties occur in the catalyst separation. While classical supported catalysts exhibit considerably slower reaction rates compared to the homogeneous equivalents, the heterogenization of the latter one is a promising approach. This bridging of the gap between homogeneous and heterogeneous catalysis has evolved with great opportunities in catalyst development. In recent years, porous organic polymers, which combine a high accessibility of functional moieties with a tailorable topology, were subject of several investigations.[2] Among this class of materials, polyphosphines with permanent porosity have been reported.[3,4]

In our work, we investigated phosphine-based hyper-crosslinked polymers to immobilize ruthenium metal centres, typically used for homogeneous CO_2 hydrogenation to FA. The amorphous macroligands were synthesized via the external crosslinking of phosphine units, yielding an insoluble brown solid with a permanent porosity. The network formation and the incorporation of phosphine units were proven by ATR-IR and XRF, additionally the high thermal stability of the network was shown by TGA measurements. The ruthenium complex was impregnated on the polyphosphine by ligand exchange from solution.

Catalytic experiments for the hydrogenation of CO_2 to FA in an aqueous phase were carried out successfully in a batch autoclave. Recycling experiments suggested the ability to reuse the solid catalyst, proving the concept of a heterogenized molecular catalyst for the CO_2 activation. The future work includes investigations about the influence of varying polyphosphines on the catalytic performance as well as the transfer to the continuous gas phase reaction.

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Impact of the local environment of amines on the activity for CO_2 hydrogenation over bifunctional basic – metallic catalysts

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Bifunctional basic-metallic catalysts proved to be efficient catalysts for the selective hydrogenation of CO_2 to methanol. [1] The activity of these catalysts was found to depend on the cooperative interaction of amine groups and metallic sites, which is a function of amine group density, Pd particle perimeter length and the geometric properties of the pores. The pore width was found to have highest effect on the activity, increasing the methanol yield by about half an order of magnitude. Confining the space leads to a three – dimensional utilization of the available metal surface sites compared to a two – dimensional distribution of the bifunctional sites in larger pores, where the metal particle diameter was found to be the decisive factor for the catalytic properties.

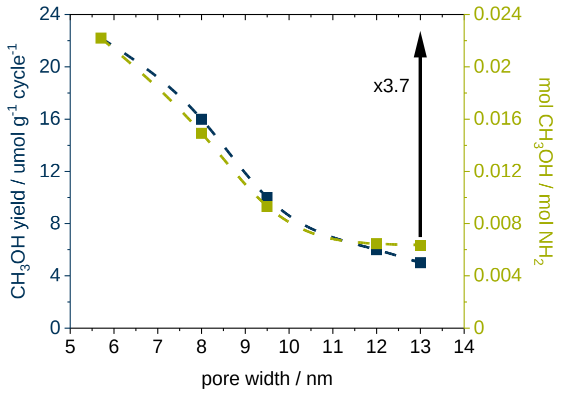

Figure 1. Methanol yield (blue) and methanol yield per amine group (green) as a function of pore width

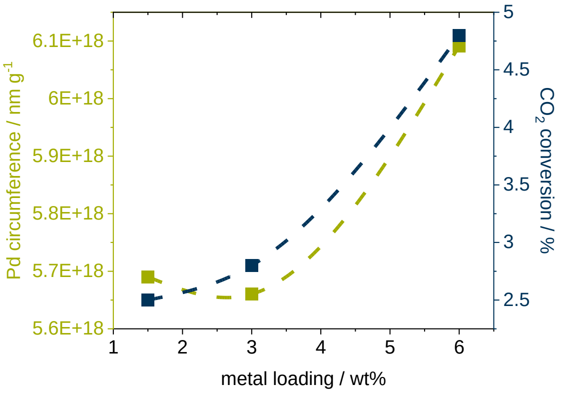

Figure 2. (blue) CO_2 conversion (based on total CO_2 adsorption capacity at $p(CO_2)$ = 100 mbar and T = 343 K determined with TGA). (green) Total available Pd circumference calculated from the metal loading and the average particle size.

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pH and Anion Effects on Cu-Phosphate Interfaces for CO Electroreduction

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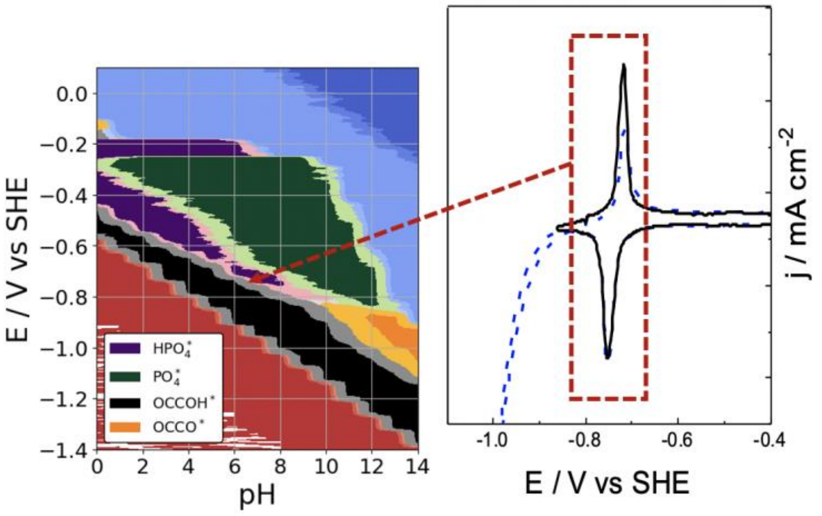
Cu electrodes are promising materials to catalyze the conversion of CO_2 and CO into renewable fuels end valuable chemicals. Nevertheless, the understanding of the CO reduction mechanism is not yet complete.

In this study, the interfacial properties of Cu(111) and Cu(100) in phosphate buffer solutions have been investigated by ab-initio molecular dynamics simulations of explicit electrolyte molecules in contact with the Cu surface and in presence of CO species.[1]

The simulations provide crucial insight into the electrochemical interface structure and allow comparison with experiments. In combination with cyclic voltammograms across the pH scale, the explicit electrolyte simulations show evidently that the onset potential, at which CO adsorbs on the surface, is controlled by the properties of the Cu-electrolyte interface and is particularly limited by the binding strength of the phosphate blocking the surface.



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The pair distribution function (PDF) – a powerful method to study energy materials

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The PDF represents all interatomic distances in a sample in real space, providing access to the short-, medium- and long-range order. This means that everything, from amorphous over disordered to crystalline materials, can be analyzed. At synchrotron facilities, in situ studies with subsecond time resolution are possible and characterization of heterogeneous catalysts are recently possible with laboratory PDF diffractometers. Various examples of PDF on energy materials are highlighted to demonstrate the potential application of the PDF.

With laboratory PDF, the tuneability of the cation site-disorder and ionic transport properties in a Li3ErCl6 superionic conductor was evaluated. For this, small box modelling was used.[1]

The crystallization of hydrothermally aged Cu/Mg hydroxycarbonates could be followed with lab PDF. They act as a precursor of Cu/Mg catalysts in methanol synthesis.[2]

The in situ formation of a Ni methanation catalyst from a MOF precursor was studied with synchrotron radiation. It could be shown that the synthesis conditions have a huge impact on the final catalyst. Further, the particle size growth and transition of different phases, like NiO, Ni and precursor MOF could be monitored via batch refinements. This established processing and refinement pipeline will now be applied on experiments under dynamic reaction conditions, for example on the methanation reaction with changing stoichiometric gas feed, to mimic the unsteady green hydrogen supply.[3]

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Promotor effect on Fe-based catalysts for CO_2-FTS: a XAS study

Erisa Saraci

Processes that store renewable H_2, from wind and solar power, in energy-dense molecules, like the Fischer-Tropsch synthesis (FTS) are in the core of a successful energy transition.[1] While the classical CO-FTS is more common[2], the CO_2-FTS that utilizes atmospheric CO_2 is highly desirable and also feasible.[3] Fe-based catalysts have the ability to catalyse this reaction and are the most industrially relevant catalysts. Iron carbides, formed *in situ*, are considered the catalytically active species in the CO-FTS.[4] These catalysts are often modified by alkali metal dopants, which act as electronic and/or structural promoters for improving product selectivity/activity.[5] In addition, these promotors are assumed to enhance catalyst basicity required for CO/CO_2 adsorption and to stabilize iron carbides against oxidants (H_2O and CO_2). However their function is still under debate and their role remains unclear.[6] Therefore, it is of eminent importance to understand effect of these dopants on the formation of Fe-carbide species during the reaction. Therefore, in this study in collaboration with Prof. Dr. E. Kondratenko (LIKAT) and Dr. D. Doronkin (KIT) we used X-ray absorption spectroscopy (XAS) to identify the structure of iron, its reducibility and carbide formation in Fe-based and alkali-doped CO_2-FTS catalysts.

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Spatially-resolved insights into local activity and structure of Ni-based CO_2 methanation catalysts in fixed-bed reactors

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On a Ni/Al_2O_3 and a $Ni\text{-}Fe/Al_2O_3$ catalyst spatial concentration and temperature profiles that occur along the axial direction of the catalyst bed during CO_2 methanation were determined in a newly established lab-scale setup.[1] This setup allows to simultaneously record quantitative integral catalytic activity (*via* gas chromatography), spatially-resolved concentration (*via* mass spectrometry) and temperature profiles (*via* thermocouple) in a single run. The concentration and temperature profiles revealed a hotspot in the first third part of the fixed-bed, which led to local CO formation (Fig.1). Complementary structural information obtained by spatially-resolved quick X-ray absorption spectroscopy (XAS) unraveled a strong impact of reaction-induced gradients in gas phase on the oxidation state of Fe. Here, a higher oxidation state of Fe was observed towards the end of the catalyst bed, while Ni was only slightly affected. Based on the concentration profiles, the oxidation of Fe could be attributed to the increasing amount of H_2O along the reactor. The spatial temperature profile was used for simulation. Therefore, the reactor was modeled by a one-dimensional flow field description with an elementary-step like microkinetic model for methanation over Ni catalysts, which incorporated both direct CO_2 dissociation and H-assisted CO_2 dissociation pathways.[2] The numerically predicted concentration profiles agreed well with the measured ones (Fig.1) and will be fine-tuned with the structural information obtained by XAS in the future.

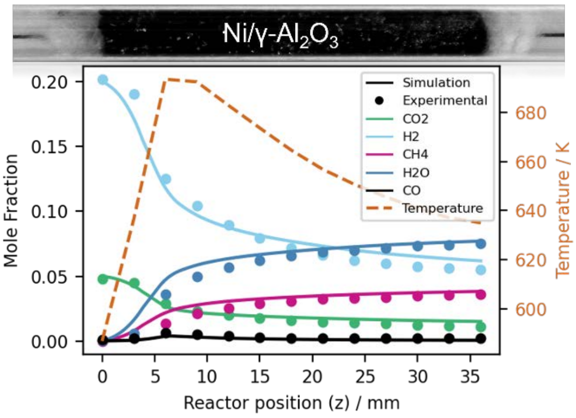

Fig. 1: Comparison of experimental obtained and simulated spatial profiles.

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Stabilized MOF-derived Ni/C catalysts for the methanation of CO_2 under dynamic operating conditions

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The methanation of carbon dioxide is a promising strategy within the "power-to-gas" (PtG) concept for the long-term storage of renewable energies. However, if fluctuating solar or wind energy is utilized to produce sustainable hydrogen, H_2 dropouts might arise, which led to a fast deactivation of commonly used Ni/Al_2O_3 catalysts in previous studies.[1] Here, we present a highly active Ni/C catalyst with enhanced stability, which was investigated under dynamic operating conditions.[2]

The catalyst was formed by the thermal decomposition of a metal-organic framework (MOF) and consisted of well-defined Ni nanoparticles with a protective carbon shell.[3] The activated catalyst was applied in different dropout scenarios at a constant temperature and the catalytic activities were tracked quantitatively. Additionally, a long-term stability test under static methanation conditions was performed to exclude effects that did not result from the dropouts. Applying full H_2 dropouts to the catalyst accelerated the gasification of the carbon support, which led to a fast sintering of the Ni nanoparticles. Since bulk Ni features a low accessible surface area and, thus, a low activity for the methanation of CO_2, the catalyst was irreversibly deactivated. In contrast, partial or stoichiometric dropout scenarios did not lead to a significant deactivation since the carbon shell remained intact, which kept the Ni nanoparticles catalytically active. However, the product yields shifted to a slightly increased carbon monoxide formation during the dropouts. Complementary operando characterization of the catalysts with advanced synchrotron-based hard X-ray techniques provided information on phase distributions, particle sizes, oxidation states, coordination spheres, and crystallinities.[2] Accordingly, the catalytic behavior could be assigned to certain material characteristics and structural changes, which were induced by the dropout scenarios, could be tracked precisely.

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Theoretical Studies on the Conversion of Methanol to Olefins Using Acidic Zeolites

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The methanol-to-olefins (MTO) process is seen as a central pillar of a renewable chemical industry as it allows the production of olefin from methanol, which itself can be based on renewable resources.[1] This inspired investigations of the underlying reaction mechanisms of these processes that occur within the pores of acidic zeotypes at high temperatures (350 – 400 °C). Computational investigations using density functional theory (DFT) have been used extensively to shed light onto how these reaction steps occur at the atomic scale. Using the zeolite H-SSZ-13 as our model catalyst, we investigated how the conversion of methanol is initiated[2] and how this is interlinked[3] with the kinetics of the olefin cycle.[4] Furthermore, DFT and ab initio calculations were also able to describe the formation of heavily methylated aromatics[5] and their reaction with methanol to short olefins.[6] These studies shed light onto the atomistic picture of the reaction mechanism and the kinetic barriers of the accompanied processes.

We further showed that while DFT calculations are prone to large errors, especially regarding barrier heights, they describe the trends from one acidic catalyst material to the next with high accuracy.[7] Likewise, the models commonly used in the calculations are simplifications of the real catalysts, and typically have high Si/Al ratios and one specific acid site. Deviations of 20 kJ/mol or higher are observed when lower Si/Al ratios[8] or different acid sites, as e.g. occurring in the zeolite H-ZSM-5, are employed.[9] We believe that the understanding will enable a move towards the knowledge-based improvement of these catalysts for the MTO reaction.

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High entropy oxides for the oxygen evolution reaction

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High-entropy oxides are oxides containing five or more metals incorporated in a single lattice. For applications within catalysis, the many different local atomic environments of the surface sites result in a range of binding energies of the catalytic intermediates. Here, the catalytic properties of the rutile (110) surface of a high-entropy oxide based on Ru, Ti, Ir, Os and Rh are investigated for the oxygen evolution reaction. Using density functional theory calculations, the adsorption energies of the catalytic intermediates are calculated for a limited number of sites and used to fit a linear model that predicts the adsorption energies for all possible local atomic environments. Two different reaction mechanisms are considered; the conventional pathway involving adsorption of *OH, *O and *OOH on the coordinatively unsaturated (cus) sites and an alternative pathway where the proton of the *OH and *OOH intermediates are transferred to a neighbouring bridging oxygen. The alternative pathway can lead to lower overpotentials than the conventional pathway, since it circumvents the scaling relations between the adsorption energies of *OH and *OOH. Our results demonstrate that the mechanism on individual sites depends on the local atomic environment. The co-existence of two reaction pathways results in an interdependency of neighbouring sites, implying that the composition cannot be optimised directly. Instead an explicit model of the surface is constructed and the catalytic activity is evaluated at regular intervals throughout the five-dimensional composition space in order to identify the optimum composition.

Control of Textural Properties and Ni Species of Ni-Catalysts Supported on Si-Stabilized ZrO_2

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Ni/ZrO_2 are attractive catalysts for the methanation of CO_2 [1]. Especially mesoporous ZrO_2 as support is desirable to mitigate mass- and heat-transfer limitations. Here, Ni supported on mesoporous Si-stabilized ZrO_2 [2] derived by surfactant assisted sol-gel synthesis are studied as catalysts. The influence of both base and method of Ni introduction on the pore system and Ni species were investigated.

Applying aqueous NH_3 solution as base leads to the formation of zirconia with mesopores of 10-20 nm. Changing the applied base from NH_3 to NaOH causes a shift and narrowing of the pore width distribution towards ~ 4 nm, which is similar if no surfactant is used during gelation. This indicates that the effect of the surfactant is hindered in NaOH. As confirmed by XRD, only tetragonal ZrO_2 is formed during the sol-gel-synthesis. NiO reflections are detected for the impregnated sample as well as for a catalyst from cogelation in NaOH solution, both of which exhibit the highest Ni loadings of 15 and 20 wt.-%, respectively. Interestingly, the cogelation in NH_3 leads to the formation of a Ni/ZrO_2 catalyst with 11 wt.-% Ni without visible NiO reflections, indicating the presence of small and highly dispersed NiO particles (Fig. 1). Besides the Ni particle size, the interaction between active phase and support is severely changed with the base or method of Ni introduction. Especially in case of an aimed Ni-loading of 5 wt.-%, NiO reduction only occurs at temperatures above 900 K. Expectedly, the fraction of Ni with weaker support interaction increases with Ni-loading, due to the formation of larger Ni particles. In case of cogelation, where NiO reflections were not visible in XRD, H_2-TPR indicates NiO species with weak ZrO_2 interaction.

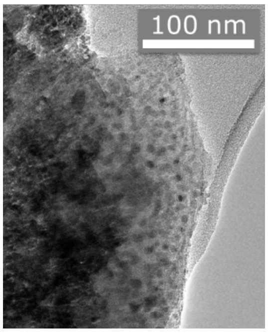

Fig. 1: TEM image of cogelated Ni/ZrO_2

The higher dispersion and lower reduction temperature (750 K) of NiO particles introduced via cogelation make those catalysts promising candidates for the methanation of CO_2.

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Structure-activity correlations of CeO_2-promoted Cu-Co-based catalysts applied in the CO hydrogenation to higher alcohols

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Motivation: The interest in the large-scale production of alternative transportation fuels and important chemical feedstock is driven by the steady depletion of fossil sources and their contemporaneously increasing global demand. Especially, the production and supply of our societies with renewable and CO_2-neutral energy sources is a key challenge. Here, the catalytic CO hydrogenation to higher alcohols (HAS) is a promising energy-efficient route. For this approach, a well-balanced interplay of dissociative CO adsorption sites forming surface alkyl species and molecular CO adsorption sites facilitating CO insertion into the surface alkyl species situated in close structural vicinity is crucial. Bimetallic Cu-Co alloy surfaces are reported to match these vital mechanistic requirements for HAS. In particular, partially reduced CeO_{2-x} as a promotor for Cu-Co-based catalyst was reported to create new CO adsorption sites by the formation of a Co–CeO_{2-x} interface, which enhances CO dissociation, and increases the formation rate of the first C–C bond. Furthermore, the hydroxyl groups of CeO_{2-x} are stated to participate in the terminating chain growth by forming alkoxy species to produce alcohols through an alternative reaction pathway.[1,2,3,4] The present contribution describes the characterization of Cu-Co-Ce-based catalysts and their application in HAS.

Results: When increasing the CeO_2 content of the reference $CuCo/SiO_2$ catalyst, X_{CO} was decreasing, while S_{MeOH} was significantly suppressed, whereas S_{EtOH} just slightly decreased. Strikingly, the $S_{n\text{-}C3+\text{-}Alc}$ was increased by the addition of CeO_2. The $CuCe/SiO_2$ catalyst exhibits unique features showing remarkably stable and high X_{CO} over 100 h TOS. Despite the uncommon reaction conditions for MeOH synthesis without CO_2 in the feed gas, the $CuCe/SiO_2$ catalyst reveals a superb S_{MeOH} combined with a moderate S_{CO2} and low S_{CH4}. Notably, the addition of CeO_2 not only boosts the MeOH synthesis performance of the monometallic $2Cu/SiO_2$ catalyst, but also promotes the Fischer-Tropsch synthesis performance of the monometallic $2Co/SiO_2$ catalyst. CO adsorption properties investigated by *in situ* DRIFTS exhibited correlations to the observed catalytic results. Furthermore, XPS revealed a structural surface reconstruction initiated by hydrothermal reaction conditions in HAS. This observation was verified through *in situ* H_2/CO TPSR DRIFTS experiments, indicating surface reconstruction by observed changes in the CO adsorption bands.

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Requirements for the activation of Co-based catalysts during electrochemical restructure for oxygen evolution

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The electrolyte's role in the activation of Co-based catalysts for the oxygen evolution reaction (OER) is still insufficiently understood, which restricts the efficiency of activation processes. Since anions usually consist of light atoms, their structural research is limited by X-ray absorption spectroscopy (XAS).[1]

We synthesized crystalline Erythrite (Ery: $Co_3(AsO_4)_2{\cdot}8H_2O$) as a Co-based catalyst model since its electrochemical restructuring to a Co oxide has been reported under OER conditions.[2] We evaluated its catalytic properties during its electrochemical restructure by cyclic voltammetry (CV) in four different electrolytes at pH and 0.1 M concentration: phosphate, borate, carbonate, and arsenate.

It was observed that Ery tends to restructure in borate, phosphate and carbonate electrolyte. The electroredox charge (ERC) was estimated by the integration of the cathodic area, and it is used as a redox activity indicator. Even though, Ery tends to restructure in three different electrolytes, only carbonate can activate the catalytic current, which was related to the slow restructuring process.

Thanks to XAS, it was observed that the average Co oxidation state increases during 800 cycles from 2+ in the pristine material up to 2.8+ (in borate and carbonate) and up to 2.4+ (in phosphate). The structural changes indicated the continuous restructure into an amorphous Co-based oxide. The restructuring rate and the final material local order depended directly on the anions in the electrolyte. Samples with higher local order (larger oxide clusters) showed higher catalytic currents. Samples owning higher average Co oxidation state and higher ERC showed higher catalytic current. Therefore, we concluded that restructure and activation are two different process, where the activation has further requirements, namely: (1) an adequate local order, a high Co oxidation state (close to 3+) and a high number of redox-active Co sites. These three requirements for a beneficial restructure provide new insight into the rational design of high-performance OER catalysts.[3]

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Particle Size Effects of Ni/C Catalysts for High Pressure CO_2 Hydrogenation

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CO_2 methanation is a valuable reaction to decrease CO_2 emissions and store renewable energy in synthetic natural gas. In this work, we present a comprehensive study of metal particle size effects on catalytic stability, activity and selectivity for nickel on graphitic carbon (Ni/C) catalysts. The performance of a set of catalysts with Ni particle sizes between 4 and 8 nm was evaluated in high pressure CO_2 hydrogenation, mimicking industrial Power-to-Gas conditions. An important factor to prevent the metal nanoparticles from severe sintering during the catalytic test is the interaction between the nanoparticles and carbon support. We found that the incorporation of acidic surface groups[1] prior to the impregnation significantly enhanced the nanoparticle stability against sintering. This method yielded a set of catalysts with reasonable stability, enabling fundamental studies under industrially relevant conditions (300 °C, 30 bar, 120 h).

The surface normalized catalytic activity (TOF) increased with increasing particle size. The apparent activation energy was the same for all catalysts (~105 kJ/mol), indicating that the particle size dependent activity is not related to a change in the nature of the active site. Rather, this dependence is ascribed to a change in the number of active sites, in particular the number of terrace sites. Lastly, we demonstrate that the CH_4 selectivity is strongly conversion and pressure dependent, where the highest selectivity is obtained at high CO_2 conversions and high pressures.

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24/7 dispatchable solar power system powered by high temperature hydrogen storage materials

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The storage of renewable energy remains a big challenge, as solar and wind power are subject to natural fluctuations limiting their dispatchability. Metal hydride-based thermal energy storage systems (MH-TES) in combination with concentrated solar power plants (CSP) have recently attracted scientific attention, as an efficient means to generate and store energy.[1] Such storage systems could enable inexpensive electricity generation by night and on cloudy days with high stability over high lifetimes.[2] Inherently, the systems stored thermal energy and hydrogen at the same time based on the reversible principle of physical chemistry property of material.

As state-of-the-art thermal solar power plants, CSPs require a storage medium for the produced energy, usually in the form of heat. In MH-TES systems, the metal absorbs hydrogen in an exothermic process and reversibly desorb hydrogen under suitable high temperature operational environment. Currently, storage system of CSPs is usually realized by high-cost molten salts, which necessitate constant heating to prevent solidification. In this case, it hinders the molten salt permanently unusable. Furthermore, operation temperatures of these systems is limited to about 450 °C with current technology, while the theoretical value of CSPs is higher than 1000 °C. Increasing operation temperatures up to 500 °C or more would be preferred, as thermal efficiency increases drastically and system expenditures decrease with increasing temperature.[3] Calcium-based metal hydrides are an alternative storage media, which allow for such high operation temperatures of 600 – 800 °C, while being inherently cheaper and of higher volumetric and gravimetric density.[2] Hence, the physical chemistry property of Ca-based metal hydrides as heat storage materials is examed. The technical barrier as hydrogen permeability will also be addressed.

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X-ray Ptychography as a Tool to Understand Catalyst Synthesis and Deactivation in 3D

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Hard X-ray imaging techniques are promising to understand the evolution of pore structures during synthesis and deactivation. Among others, X-ray ptychography is arguably one of the most powerful approaches to achieve high spatial resolution in 3D on extended sample volumes with additional quantitative information about the local electron density.[1]

In this work X-ray ptychography is shown as an enabling technique to understand the porosity evolution during calcination of hierarchically porous Ni/Al_2O_3 catalysts applied in CO_2 methanation,[2] which were obtained as dried gels after a sol-gel method. The dried gels were investigated by *in situ* 2D X-ray ptychography imaging (XRP) and *ex situ* 3D ptychographic X-ray computed tomography (PXCT). XRP studies were carried out in a nanoreactor setup with defined temperature and gas conditions, while PXCT was performed on the dried gel and calcined state of an identical Ni/Al_2O_3 particle. Textural and structural changes were followed with sub 100 nm resolution on tens of µm sized catalyst particles. Image analysis of the results allows to quantify changes of the macropore structure (e.g., pore size) during calcination. Furthermore, analysis of the electron density of the PXCT provides sub-resolution information about the mesoporosity changes of the sample.

Additionally, activated and artificially coked Ni/Al_2O_3 particles were investigated by PXCT, while the coking was confirmed by *operando* Raman spectroscopy during sample treatment. The analysis of the electron density can be applied to unravel the location of coking in the artificially coked sample, as the presence of coke increases the local electron density.[3] The results highlight the great potential of advanced spatially-resolved characterization for a fundamental understanding of the 3D structure of solid catalysts. X-ray ptychography is a powerful tool to unravel the textural and structural evolution of catalysts during synthesis, activation, reaction and deactivation.

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Ni-based catalysts for CO_2 methanation probed by X-ray spectroscopy under *in-situ* conditions

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For future sustainable power supply, the long-term storage of energy from renewable resources is a key challenge. A possible approach is the usage of H_2 gained from water electrolysis by application of renewable energy sources in CO_2 methanation. Since the hydrogen gained by these methods can fluctuate due to fluctuations of sunlight or wind, the catalyst must show high stability towards a rather unstable H_2 flow. Potential candidates are supported Ni-catalysts. They are frequently used but tend to deactivate through surface oxidation or sintering. [1] Due to the fine dispersion of active metal centers and a protecting carbon shell, Ni nanoparticles formed out of the thermal decomposition of metal-organic frameworks (MOFs) are promising materials. Regardless of the application, the detailed mechanism and working principles of the catalytic structures are largely unknown, due to the mostly amorphous character of the final structure. Besides the characterization of the pre-catalysts, also the catalytic mechanism itself needs to be investigated especially under dynamic conditions to optimize the catalyst in terms of performance and stability. To investigate the structural changes over the intermediates to the final catalyst XAS should be carried out. Since, XAS is an element specific method both, electronic and structural properties of catalysts can be investigated reliably. [2] X-rays penetrate most materials due to their high energy, hence X-ray-based techniques offer a high versatility in *in-situ* characterization approaches, for example on the methanation reaction with changing stoichiometric gas feed, to mimic the unsteady green hydrogen supply.

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Dynamic operation of Fischer-Tropsch synthesis for power-to-liquid concepts

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Fischer-Tropsch synthesis (FTS) is considered as a power-to-liquid (PtL) storage concept for converting temporally available excess energy into fuels or chemical compounds. Fluctuating energy supply requires a load-flexible energy system. An FTS reactor that operates under dynamic conditions could be advantageous compared to conventional steady-state operations that rely on expensive upstream buffer capacities.

Published literature studies addressing dynamic FTS operation focus on both the design of a reliable and effective reactor that can handle a fluctuating feed (e.g., [1], [2]) and on the possibility of process intensification by imposing fluctuations (e.g., [3], [4]).

Micro-structured reactors, like slurry reactors, have been shown to be promising to efficiently handle the dynamic FTS operation. However, there have been few studies to date and, in particular, results on realistic PtL scenarios are scarce. Many uncertainties remain to be resolved, such as long-term performance, drastic shutdown/re-start scenarios, and economic assessments.

For process intensification, periodic hydrogen pulsing in particular was observed as a potentially beneficial operating procedure to remove accumulated liquid products, restore initial catalyst activity, and increase diesel-range productivity [4]. Hydrogenolysis is considered to be the main responsible reaction mechanism in this regard. All studies show that the applied cycling times have a strong impact on resulting FTS activity and selectivity, but detailed knowledge and useful dependencies are still lacking. To this end, in the present work, activity and selectivity changes are experimentally correlated in a combination of FTS and hydrogenolysis. With a deeper understanding of the phenomena that occur, forced hydrogenolysis could be integrated into a dynamic PtL approach to not only deal with fluctuating feed, but use it for simultaneous process enhancement.

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In situ reaction-induced and externally forced dynamics of Fe-based catalysts in CO_2 hydrogenation

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CO_2 conversion into various chemicals is gaining academic and industrial interest as a promising methodology for CO_2 utilization [1], which does not need fossil raw materials and thus contributes to sustainable development. Due to the inert nature of CO_2, a second co-reactant with higher Gibbs free energy, like H_2, is required. Fe-based materials are suitable candidates for CO_2 conversion to higher hydrocarbons through a tandem hydrogenation network including reverse water gas shift (RWGS) reaction and CO Fischer-Tropsch synthesis [2]. In this context, the electro-catalyzed water splitting with renewable energy (solar, wind, etc.) is the most ideal source of hydrogen. However, the highly fluctuating feature of solar and wind make the supply of H_2 and pressurized CO_2 challenging. Therefore, it is of great importance to study structural changes of working catalysts and their performance under externally driven dynamic conditions. On the other hand, the atmosphere around the working catalyst is extreme complex because of coexistence reducing (CO, H_2 and hydrocarbons) and oxidizing gases (H_2O and CO_2).Depending on their relative partial pressures, various iron-containing phases (oxides, carbides, and metallic iron) are present in the working catalyst. From a fundamental viewpoint, it is also highly needed to investigate the dynamics of reaction-induced catalysts restructuring. To this end, a series of pure and Na-promoted Fe oxide catalysts with same Na/Fe bulk ratio, but different surface ratio, were prepared by different synthetic methods and tested under dynamic reaction conditions. The unique role of Na in protecting the catalysts against restructuring under oscillating reaction conditions was revealed. Additionally, reaction-induced dynamic behavior of product distribution was observed over Mn-doped Fe catalysts. This dynamic phenomenon should be related to restructuring of Fe-containing phases. However, such dynamic phenomenon was absent over 10Fe-0Mn catalyst.

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Metal-organic frameworks derived high entropy sulfides/alloys encapsulated by porous carbon for the oxygen reduction reaction and oxygen evolution reaction

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Developing oxygen reduction reaction (ORR)/oxygen evolution reaction (OER) electrocatalysts with robust performance are essential for achieving the high conversion from renewable electricity to clean energy fuel[1]. We employed a facile intrigue to design high entropy alloys and high entropy sulfides embedded in porous carbon electrocatalyst via one-step calcination of high-entropy metal-organic frameworks. The concept that introducing the high entropy state can change the microstructure, thereby tuning binding energies of oxygenated intermediates of ORR/OER. As a result, the coordination environment of the metal catalytic active center that affects binding energies of oxygenated intermediates and electronic density of metal active was optimized, thus boosting the kinetics for ORR/OER. The optimized FeCoNiMnCu-TDC-BIPY-800 exhibits excellent performance, including ORR and OER. More specifically, the OER process endows an overpotential of 357 mV in the current density of 10 $mA.cm^{-2}$. In ORR, a half-wave potential of 0.75V was obtained. Thus, these composited high entropy alloys and high entropy sulfides nanoparticles hopefully provide catalysts applied in an efficient, sustainable energy storage and conversion system.

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