MAX-PLANCK-INSTITUT
FÜR CHEMISCHE ENERGIEKONVERSION

SCIENTIFIC REPORT
2020 - 2022

MAX PLANCK INSTITUTE
FOR CHEMICAL ENERGY CONVERSION

SCIENTIFIC REPORT 2020 – 2022

Mülheim an der Ruhr, February 2023

REPORT OF THE MANAGING DIRECTOR

DEPARTMENT OF INORGANIC SPECTROSCOPY

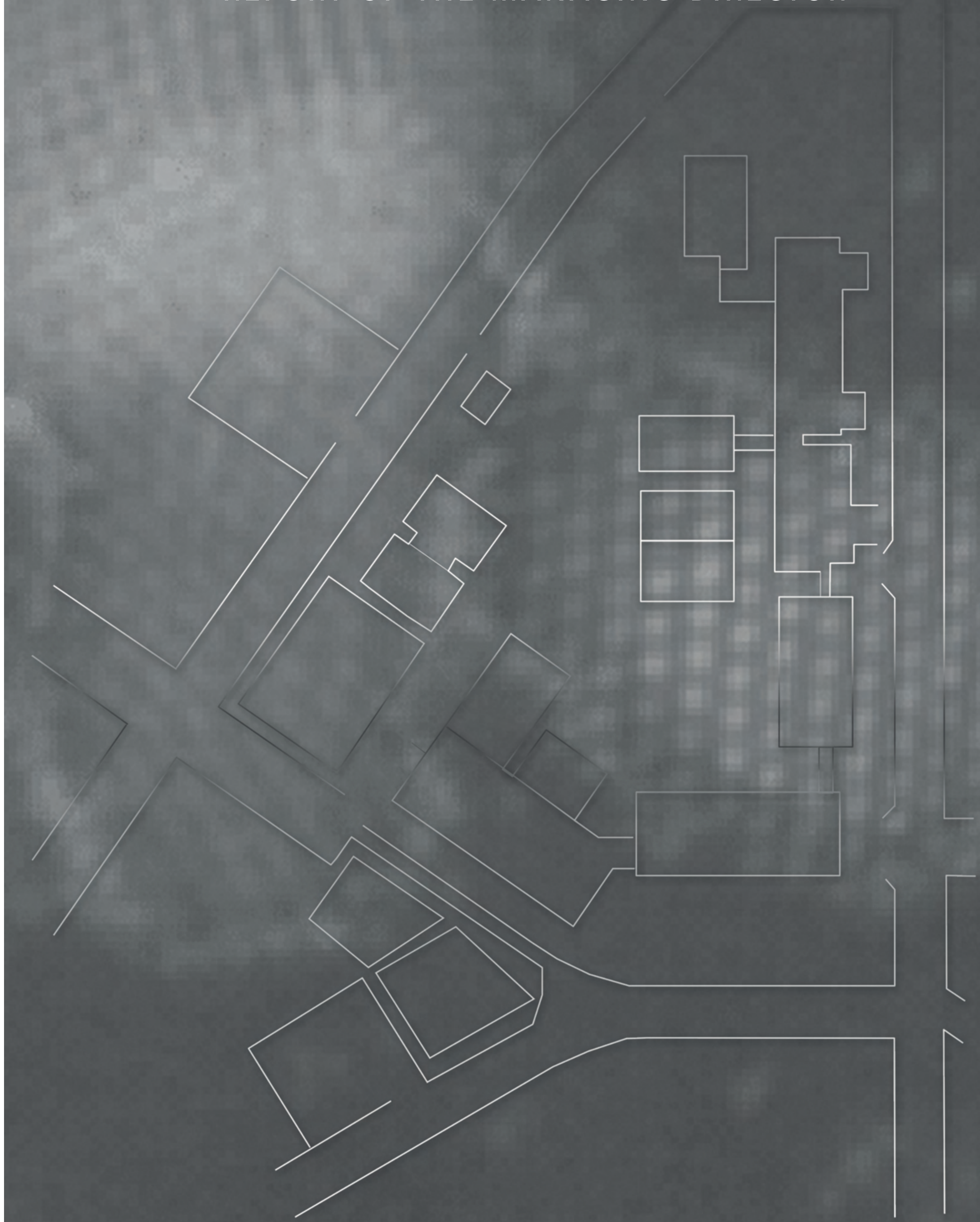
DEPARTMENT OF MOLECULAR CATALYSIS

DEPARTMENT OF HETEROGENEOUS REACTIONS

OTHER SCIENTIFIC ACTIVITIES

MPI CEC IN SCIENTIFIC DIALOGUE

REPORT OF THE MANAGING DIRECTOR



Executive Summary

During this reporting period the MPI CEC has been engaged in forefront research aimed at fundamental understanding of the mechanisms, control factors, and optimization tools for catalytic systems relevant to store and utilize renewable energy in molecules with applications ranging from energy carriers to chemical products. The works of individual scientists and the entire workforce as part of a coherent research framework and an integrative organisational structure have established MPI CEC firmly on the scientific landscape of this highly dynamic and competitive field. This is reflected also in quantitative performance criteria like bibliometric data, awards and recognitions, or projects. With the new buildings becoming fully operational, MPI CEC is ready to foster its success story and to expand in new areas with the appointment of two directors in order to continue its mission according to the Max Planck motto **Insight Must Precede Application.**

Vision, Mission, and Objectives

The future will be renewable. Molecular transformations are essential for the storage, distribution, and utilization of energy from renewable sources, together with renewable feedstocks. The "de-carbonization" of technologies to generate electricity poses challenges, but also opens opportunities for the "de-fossilization" of the other sectors that are vital to humankind's welfare on this planet. At this interface between energy and chemistry, the MPI CEC generates fundamental knowledge, nurtures talent, and engages in collaborative efforts for translation. **The science at MPI CEC is motivated by the unifying goal to understand, control, and design catalytic systems for Chemical Energy Conversion.**

The understanding of the active sites and their dynamic evolvement during activation, reaction and de-activation bridges across molecular, biological, and material catalysts. A particular strength results from the availability and consequent development of a wide range of spectroscopic methods, including their applications both *in situ* and under *operando* conditions. The investigated **control mechanisms range from the molecular to the process-level** targeting multifunctionality and adaptivity in response to variability and fluctuation of renewable energy and feedstocks. The ability to synthesize molecular and material catalysts individually and in judicious combination at the highest technical level is essential in this endeavour. Studying their intrinsic properties in relation to interfacial phenomena continues to be a strategic research area. **The targeted chemical reactions** are chosen as to delineate a system of sustainable processes by integrating the principles of *Green Chemistry* into the energy/chemistry nexus. Small molecule activation to effectively store and release renewable energy, as well as to master value generation through molecular complexity define core competencies. Central chemical processes are hydrogenation and de-hydrogenation, electrochemically driven reactions, and the transformation of CO_2, biomass, and nitrogen-based building blocks.

The research agendas in the departments and projects are focused on knowledge-based rational approaches, often accompanied by data-driven studies for optimization and screening. Integrating experimental and theoretical approaches is greatly facilitated through collaborations within the Joint Work Space on the campus. The adoption of this common strategy on all levels is reflected in publications arising from collaborative efforts of different groups and teams.

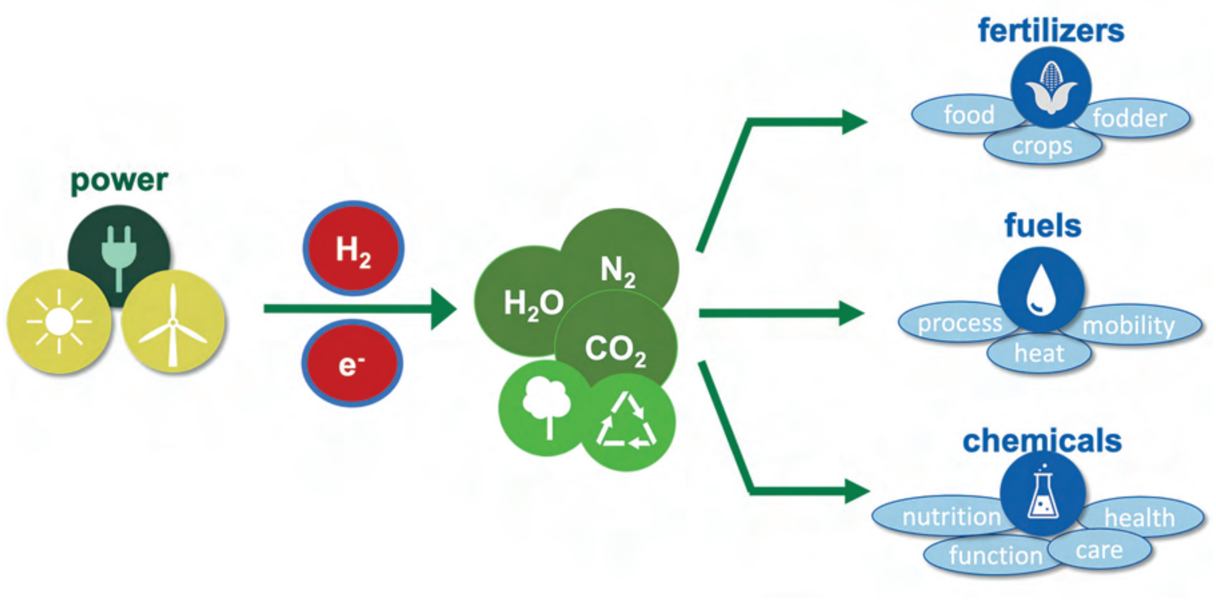


Figure 1. Chemical Energy Conversion as central pillar of a sustainable energy-chemistry nexus: the arrows represent molecular transformations enabled by catalysis science and technology.

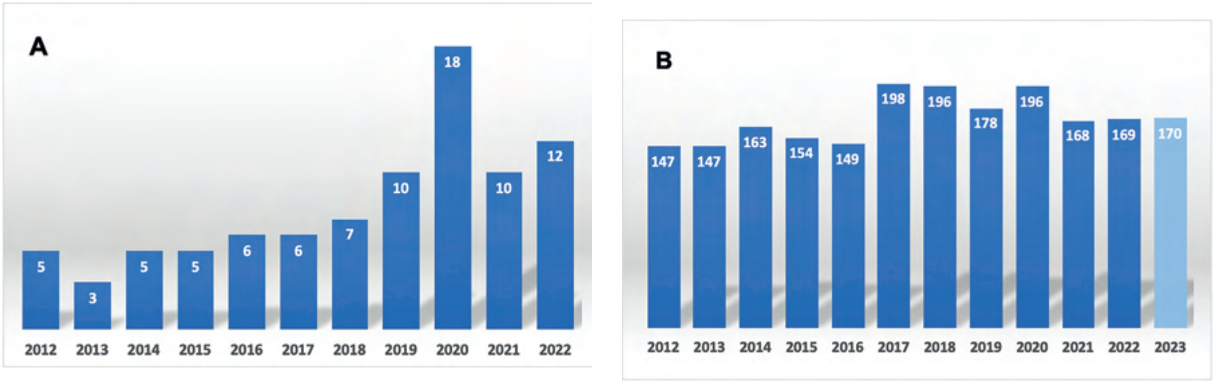


Figure 2. (A) number of PhD examinations and (B) number of publications over the years.

As a general quantitative reflection of the institute's scientific achievements, Figure 2 shows the numbers of completed PhD theses and publications for the present and previous review periods. While the reduction of the activities in the Schlögl Department and the effects of lockdowns during the pandemic are noticeable in both graphics, the institute forecasts to maintain its high level of scientific output in terms of quantity and – even more importantly - quality. This stable development has been rooted in the conceptual research structure of MPI CEC that also forms the basis of the institution's strategic development, as outlined in the next section.

Another reflection of the scientific progress at the CEC are honours and awards that Members of the institute received during the period of this report. It is particularly rewarding to see especially the recognitions for next generation scientists at various career levels. This includes fellowships for incoming researchers (i.a. 7 Alexander-von-Humboldt, 1 Marie Curie, and 1 Fullbright) as well as for outgoing PhDs and Postdocs. The following list exemplifies such recognitions without attempting a fully comprehensive documentation.

Serena DeBeer
Fellow of the Royal Society of Chemistry (2021)
R. J. P. Willian Lectureship, Oxford University (2022)
Malcom H. Chisholm Lecturer, The Ohio State University (2022)
Chair of Metallocofactors Gordon Research Conference (2022)

Ragnar Björnsson
QBIC Society Awards 2021

Nicolas Kaeffer
Member of JACS Au Early Career Advisory Board (since 2022)

Walter Leitner
Prix Binational Franco-Allemand "Georg Wittig-Victor Grignard" awarded by the Société Chimique de France (2020)
Top 3 of the European Innovator Award "Industry" together with Dr. Christoph Gürtler (Covestro AG) (2020)
Top 10 Winners of the Falling Walls Breakthroughs of the Year in Physical Sciences (2020)
Vice-Chairman of the Board of DECHEMA, the German Society for Chemical Engineering and Biotechnology (since 2020)
Advisory Editor of Angewandte Chemie (GDCh, Wiley-VCH) (since 2021)
Chair of the Green Chemistry Gordon Conference (2022)

Wolfgang Lubitz
Vice-President of Council for the Lindau Nobel Laureate Meetings (since 2021)
Honorary Member of EPR section of the German Chemical Society (GDCh) (2022)

Robert Schlögl
Vice-President of National Academy of Sciences Leopoldina (since 2020)
Honorary Doctorate, Darmstadt University, Darmstadt (2020)
Member of National Hydrogen Council (2020-2022)

Jesús Esteban Serrano
Hermann Neuhaus Prize (2020)

Thomas Wiegand
Heisenberg Professorship "Magnetic resonance of complex materials and catalysts" (2021)

James Birrell
Lecturer, University of Essex, UK (2022)

Ragnar Björnsson
CEA Tech, Grenoble, France (2022)

Chenhui Han
Assistant professor at Inner Mongolia University, Hohhot, China (2022)

Deepti Kalsi
Assistant professor at Indian Institute of Technology, Dharwad, India (2022)

Anna Mechler
Professor "Electrochemical reaction engineering", RWTH Aachen (2020)

Patricia Rodriguez Maria
Glasstone Research Fellow, Oxford, UK (2020)

Jesús Esteban Serrano
Lecturer, University of Manchester, UK (2020)

Structure and Development

The year 2022 marked several milestones for the MPI CEC. The **celebration of our 10 Year Anniversary in May** was a fantastic event showcasing our scientific progress to the broader community and fostering our team spirit internally. Integrating the "Frontiers Lectures" for 2021 (Prof. André Bardow, ETH Zürich) and 2022 (Prof. Bert Weckhuysen, Univ. of Utrecht) within a scientific workshop for the departments provided a unique opportunity to exchange scientific ideas and to benchmark our program "live" after two years without the possibility for in-person interactions. The event also marked the transition from the early founding years to a more established, albeit still growing, institute. The **founding director Robert Schlögl formally retired in April** and passed on the duties of managing director to Walter Leitner.

After five years of construction, the **new laboratory and office buildings were opened in July** allowing scientific operation to begin in the new premises (Figure 3). The relocation of the department of "Molecular Catalysis", as well as the continuing project groups form "Heterogeneous Catalysis", to the new buildings was a major effort as the entire laboratory infrastructure including glove boxes, molecular analytics (GC, MS, HPLC, ICP), NMR spectrometer, and high-pressure technology had to be moved and installed. The new setting is characterized by open laboratory and office environment to foster interactions within the regular workflow. While this required significant re-structuring and re-organisation of the day-to-day operation, it has already proven beneficial and has been largely received very positively among the co-workers. The teams from facility management, technical utilities, and workshops are greatly acknowledged for their excellent work. The extremely professional and cooperative interaction between the research teams and service groups is highly appreciated by the board of directors. In collaboration with administration, this ensured a remarkably smooth transition keeping the interruption of laboratory work to an absolute minimum.

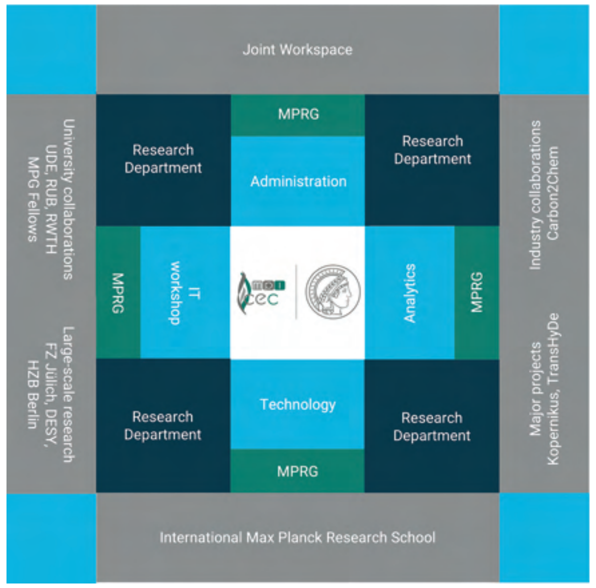


Figure 4. The integrated structure of the MPI CEC as basis for its strategic development.

The integrative **model of the institute's structure** is reflected in the graphical representation shown in Figure 4 and the components are discussed below. The resulting formal framework is depicted in the organization chart in the appendix.

Figure 3. Snapshots from the construction period at MPI CEC 2017-2022.

Departments and Research Groups

Following the original development plan as re-confirmed by the appropriate resource approval through the President of MPG in 2022, the institute will comprise **four Research Departments each headed by a Scientific Member (Director) of the Max Planck Society.** Already in 2017, the appointments of Serena DeBeer for "Inorganic Spectroscopy" and Walter Leitner for "Molecular Catalysis" have fostered this structure synergistically, together with the Department for "Heterogeneous Catalysis" of Robert Schlögl during the reporting period.

The **search process for new Directors has been intensified strongly in 2022.** This is in part a response to the challenges imposed by the pandemic period, which greatly limited the possibility of in-person interactions with potential candidates. The process has included extensive consultations with members of the SAB, colleagues from scientifically related MPIs, and the international community. The scouting office of the Max Planck Society was also actively involved. A dedicated Workshop in July and a Lecture series entitled "*The role of Catalysis for Chemical Energy Conversion: From Molecules to Processes*" covered various aspects of the areas (photo-)catalytic water splitting, heterogeneous catalysis, electrification of chemical synthesis, and systems analysis. As a result, the institute is preparing a nomination for the appointment of a Director to be opened at the meeting of the Chemistry, Physics, and Technology Section of the Max Planck Society in February. Details will be reported by the Managing Director at the SAB meeting.

The MPI CEC is investing strongly in **Max Planck Research Groups (MPRGs)** as important instrument to support the independent career of young scientists and to foster the collaboration with partner Universities. Three MPRGs were created in 2019. Dr. Victor Čolić has established his group at UDE in the NETZ research centre in Duisburg dealing with oxygen electrocatalysis. Dr. George Cutsail set up an MPRG at UDE dealing with advanced EPR spectroscopy and metal organic chemistry. While part of his team is located at UDE, he also uses intensively the EPR infrastructure at MPI CEC and some associated laboratory resources. Dr. Christoph Werlé is associated with RUB developing his program on synergistic organometallic catalysis. Two recently successfully defended PhD theses from his team illustrate *inter alia* the successful collaboration model. In 2021, Prof. Dr. Thomas Wiegand was appointed as MPRG leader and Junior Professor at the Institut für Technische und Makromolekulare Chemie (ITMC) of RWTH. This position is unique as the temporary MPRG is integrated in the Tenure Track program of RWTH Aachen University providing the opportunity for tenure as full professor (W3) at the ITMC. This attractive career path between MPG and a University was established as part of the collaboration of CEC and RWTH within the Cluster or Excellence "The Fuel Science Center".

We are happy to report that the three **former Directors** of the institute's history Kurt Schaffner, Karl Wieghardt, and Wolfgang Lubitz celebrated their 90th, 80th and 70th anniversary during the reporting period. The Emeritus status of Wolfgang Lubitz was extended in 2021 for 2 more years by the Max Planck Society and his activities continue to contribute to the research output and the scientific reputation of the CEC.

The **Max Planck Fellow** programme of the MPG is designed to expand the scientific competence of institutes by formal collaborations with excellent individuals of relevant expertise. The fellow status of Prof. Martin Muhler (Ruhr Universität Bochum) in the field of redox catalysis has been extended for another funding period. Prof. Regina Palkovits (RWTH Aachen University) has been newly appointed in 2019 and Dr. Anna Katharina Beine has started a group on the development of functional materials for the conversion of renewable biomass feedstocks at the CEC as part of this collaboration. A **Max Planck Partner Group** to support early career researchers has also been set up with Dr. Maria Chrysina at the Institute of Nanoscience and Nanotechnology, NCSR Demokritos in Athens, Greece. The fellowship allows her the opportunity to pursue advanced spectroscopic studies at the CEC for her studies on understanding the mechanism of photosynthetic water oxidation

The **Joint Workspace** is now established as a common platform for research between MPI CEC and MPI für Kohlenforschung (MPI KoFo) providing an effective framework for joint research activities despite the formally different legal entities. In particular, it hosts collaborative efforts in spectroscopy with CEC laboratories and the Theory Department of Prof. Dr. Frank Neese from MPI KoFo. During the reporting period, the model has been extended to joint activities from the Molecular Catalysis Department of CEC on catalysis using supercritical fluids in the high-pressure facilities of MPI KoFo. An increasing number of individual projects, often initiated ad hoc under the framework, underpin the success of the model, as demonstrated through high level research publications involving researchers from both institutes.

Scientific Infrastructure

The research within the departments critically depends on the scientific infrastructure providing not only state-of-the-art facilities, but constantly pushing boundaries of methods and instrumentation. The reporting period has seen a very dynamic development and major investments in this area.

An important addition to the scientific infrastructure was the new group **Electron Microscopy and XPS** headed by Dr. Walid Hetaba. In particular, the team accomplished the installation of a new transmission electron microscope (TEM), which has been custom designed with a glove box to allow for the introduction of samples under inert conditions. This powerful instrument has not only greatly de-bottlenecked the measurement of samples, but also allows for analysis of structural and morphological changes of catalyst materials at different times of operations under strictly inert atmospheres. Once the "ELMI Building" as last part of the construction at the MPI CEC will be completed, it is planned to centralize this microscope together with those temporarily located at FHI in Berlin and the XPS techniques in a facility for surface analytics at the campus.

The **EPR** group led by Dr. Alexander Schnegg has established very successfully its operation of advanced electron paramagnetic resonance (EPR) methods to study paramagnetic states in materials and molecules relevant for research within the group and the user community at the campus. The EPR group operates a unique array of 5 advanced pulse/continuous wave multi-frequency (MF-EPR, 3 GHz to 20 THz) EPR spectrometers.

Another new addition to the scientific infrastructure was the installation of a team **Electrochemistry** coordinated by Dr. Ioannis Spanos, dedicated to materials and devices for electrochemical and electrocatalytic processes. The work is focussed on fundamental and applied aspects of water splitting and fuel cells. Most recently, a fully-fledged electrolyzer was acquired allowing for material testing under realistic operation conditions and offering the potential to integrate a realistic water splitting device with hydrogenation reactions to mimic for example fluctuation operations.

The CEC is actively involved in **synchrotron infrastructure** development activities to enable a range of soft and hard X-ray experiments **at both BESSY in Berlin and at PETRA in Hamburg.** CEC staff have been involved in the design and commissioning of both the PINK and CAT beamlines at BESSY. Both beamlines are now in general user operation with privileged access allocations for MPG scientists. CEC staff further support an additional 3 BESSY endstations, with a focus on enabling state-of-the-art X-ray spectroscopic studies of a range of catalytic systems under in situ and operando conditions. While the BESSY beamlines provide a full complement of capabilities in the soft X-ray regime, the facility is not designed for hard X-ray experiments. For this reason, the CEC, together with the FHI, is designing a new hard X-ray "OperandoCat" beamline that will begin operations during PETRAIII and continue to operate following the planned PETRAIV upgrade. This effort is coordinated by Prof. Serena DeBeer at the CEC together with Prof. Beatriz Roldan at the FHI.

The **Catalytic Technology Facility** headed by Dr. Holger Ruland became fully operational in 2021. Consequently, the workshops for equipment design and manufacture, electronics, and glassware have been integrated in its organisational framework. The facility comprises the "reactor hall" providing a highly installed, yet flexible space for equipment and apparatus that are designed to investigate catalytic processes under realistic operation conditions. This enables studies on robustness of catalysts upon long-term operation or exposure to potential impurities in real-world feedstocks, providing important insights into reversible and irreversible deactivation mechanisms. Scaling effects, when moving from the microscopic scale in the laboratory to macroscopic reactor dimensions, can also be investigated. This is particularly valuable in collaborative projects directed towards demonstration, yielding important feedback for the fundamental research on catalyst and process design. Current examples include *inter alia* Carbon2Chem, REDIFUEL, and AmmoRef.

Significant methodological developments and investments have also been made in the area of **Molecular Analytics and Characterization**. The move of the analytical team led by Justus Werkmeister to the new buildings has been accompanied by extension and addition, including the expansion of capacities for inline and online methods. The acquisition of a X-ray diffractometer, under the responsibility of Dr. Thomas Weyhermüller, has been vital to de-bottleneck structural characterization of organometallic complexes and coordination compounds in particular with the opportunity to study highly unstable and sensitive species in a flexible manner.

A systematic process has been initiated to establish a harmonized platform for **Data Management** across all research activities at the institute. The internal process is integrated into the large-scale initiative NFDI4Cat as part of the Nationale Forschungsdateninfrastruktur programme of the Deutsche Forschungsgemeinschaft. The institute is also a partner in the analogous initiative for large scale photon and neutron facilities, known as Daphne4NFDI. A detailed analysis of the institute's requirements and possible technical solutions was conducted and coordinated with the concepts of data lakes and interfaces for data mining as developed within the NFDI initiatives. The broad range of methods and the extensive external activities (e.g. beamline experiments) were identified as important aspects for the MPI CEC, which go beyond the capacity of many standard electronic lab journals. A trial period of beta-testing with several software solutions was therefore initiated at the institute to prepare a set of criteria for a procurement process. After some changes in personnel, Philipp Adamitzki has been appointed as Data Steward and also project leader for CEC's NFDI4Cat activities.

The International Max Planck Research School **IMPRS-RECHARGE** continues to be a highly successful programme for PhD students at the Mülheim Campus and partner Universities. The **Ernst Haage Foundation**, originally placed at the MPI CEC only, has now been extended as a Campus Initiative. The Ernst Haage awards are given in the internal categories for Apprentices and PhDs, and externally to early career academics as National Award. The latter is meanwhile established as a very important recognition for young academics at German research institutions in the field of Chemistry. Most recently, financial support by the **Neuman & Esser Foundation** of the Peters family has enabled to start a Fellowship programme for undergraduate research and internships at MPI CEC.

Technical Infrastructure and Administration

The teams forming the infrastructure backbone of the MPI are of highest competence and motivation. The rapid growth of the institute and the expected new appointments will pose significant challenges on the existing structures. In order to remain highly agile and adaptive to this desired expansions, at least temporary augmentation of resources is foreseen to become necessary in the near future.

The construction work has been an enormous effort in terms of planning, commissioning, and finalizing. The result of the dedicated work of the **Facility and Utility Management** teams coordinated by Kerstin Neurieder and Willi Schlamann (since 2020 as a consultant) internally and in interaction with the MPG as principal constructor and with the various different contractors is finally now visible and has commenced operation this summer. Removing the old laboratory wing and construction of the laboratory for surface analytics ("ELMI") is still ongoing at the time of this review. This large expansion of facilities corresponds to an extension from two to five building units and approximately three times in space relative to the original premises.

The high standards on **Chemicals and Workers Safety** have been successfully translated towards the new setting. Some of the new technical features are still being aligned with appropriate organisational measures. Highest priority is given to this topic and we are very proud of our team that a "zero accident policy" is prevailing.

The **IT Department** of the institute has been responding to increasing risks of cyber-attacks in close collaboration with our **Data Protection Officer** Rolf Trinoga. All new members of the institute obtain training in cyber security upon joining the staff. All new laptops are encrypted and the existing devices have also been updated accordingly. The data back up and emergency plans are currently under further revision.

The **PR and Communications** team has been expanded in response to the growing demand for additional communication channels within the scientific community as well as broader audiences in politics and society.

The highly effective **Administration** of the institute headed by Helga Oppenberg comprises personnel, procurement, and accounting. The workflow is facing growing demands in legal regulations and reporting, especially in view of the increasing importance of third-party funding with the expansion of scientific activities and projects (see below). The collaboration with the **Scientific Coordinator** Dr. Marion Tiedtke is of greatest value in this situation. The interaction with the headquarters of the MPG and in particular the manifold support by our Institutsbetreuer Dr. Christoph Freudenhammer is highly appreciated.

Projects and Collaborations

The MPI CEC aims to act as a "catalyst" for collaborations with Universities and research organisations as well as in translational research with industry through larger projects and coordinated activities. Particularly noteworthy is the initiating role of MPI CEC in the initiative "WissKomm Energiewende" dedicated to communication of the challenges and opportunities associated with the transition into a sustainable energy system to the public. The exhibition was opened under the name Power2Change in the Ruhr Area and is travelling to 5 different museums in Germany.

The list below exemplifies ongoing (with starting year) and new activities, more details are found in the appendix.

Title	*Start*	*Type*	*PI*
Kopernikus – Power-to-X – technologies	2019–2025	BMBF	Leitner
Carbon2Chem – reducing CO2 emissions from industrial plants	2016–2024	BMBF	Schlögl / Leitner
REDIFUEL – Robust and Efficient processes and technologies for Drop in renewable Fuels for road transport	2018–2020	EU	Leitner / Vorholt
E-Tandem – Hybrid Tandem Catalytic Conversion Process towards Higher Oxygenate E-Fuels	2022–2026	EU	Leitner / Vorholt
German National Research Data Infrastructure Projects **NFDI4Cat / Daphne4NFDI**	2020–2025	DFG	Leitner / DeBeer
SFB TRR 247 – Heterogeneous Oxidation Catalysis in the Liquid Phase	2018–2022	DFG	DeBeer / Schlögl
e-conversion – Fundamentals of Energy Conversion Processes	2019–2025	Cluster of Excellence	Schlögl
Fuel Science Center – Adaptive Conversion Systems for Renewable Energy and Carbon Sources	2019–2025	Cluster of Excellence	Leitner / Werlé
CatVIC – Catalytic Valorization of Industrial Carbon	2019–2022	BMBF	Schlögl
TransHyDE – AmmoRef : Reformation of Ammonia	2021–2025	BMBF	Schlögl
H2Giga – PrometH2eus	2021–2025	BMBF	Schlögl
CUBE – Unravelling the secrets of CU-based catalysts for C-H activation	2020–2026	EU / ERC	DeBeer

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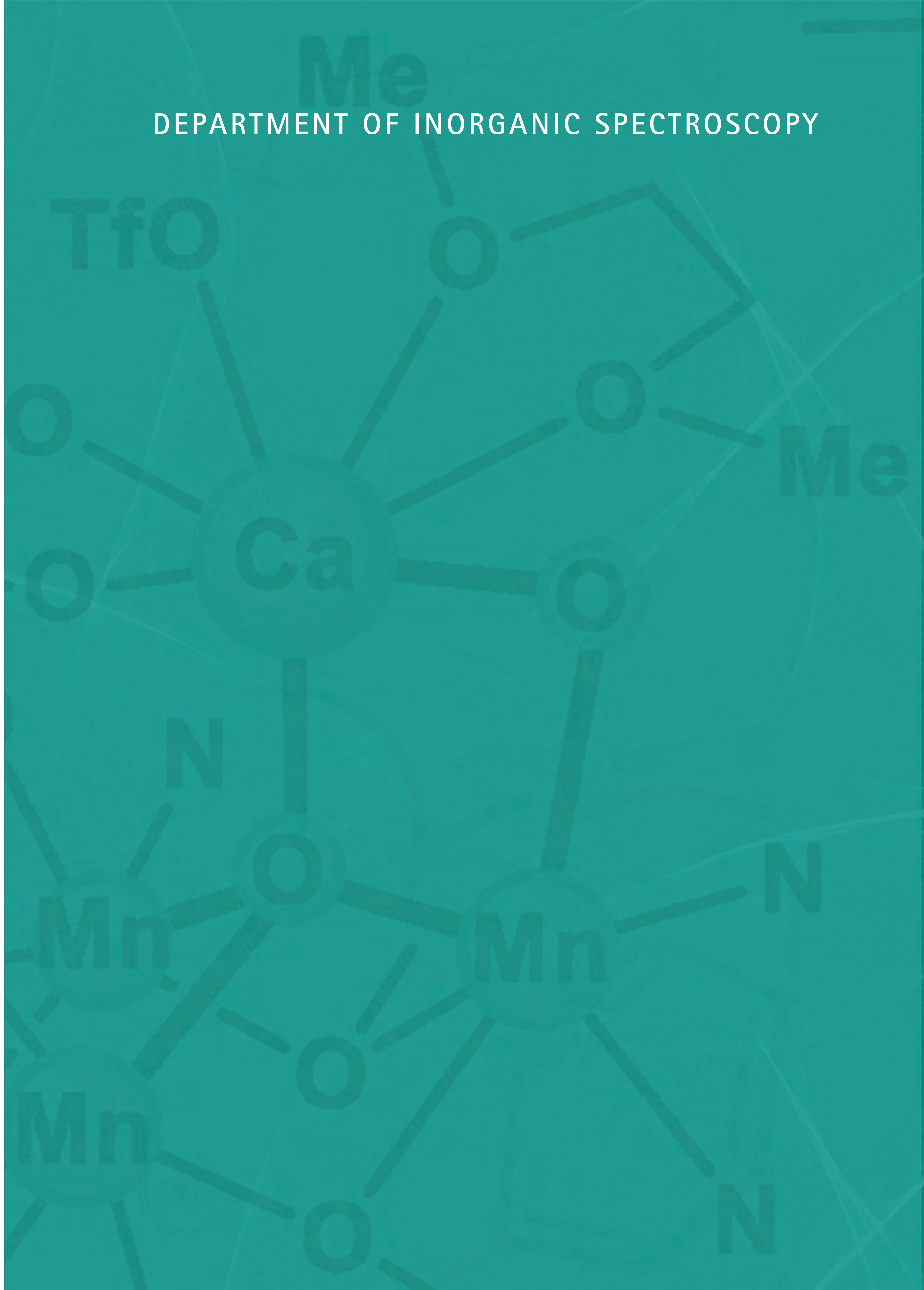
DEPARTMENT OF INORGANIC SPECTROSCOPY



Prof. Dr. Serena DeBeer

Ph.D. (Chemistry) Stanford University (2002)
Beam Line Scientist SSRL, SLAC, Stanford, University (2001-2003)
Staff Scientist SSRL, SLAC, Stanford, University (2003-2009)
Assistant Professor Cornell University (2009-2012)
Research Group Leader (W2) MPI CEC (2011-2017)
Group Leader PINK Beamline, Energy Materials In-Situ Laboratory, Helmholtz Zentrum, Berlin (since 2012)
Adjunct Professor Department of Chemistry and Chemical Biology, Cornell University (since 2012)
Honorary Faculty Ruhr University Bochum (since 2014)
Director Department of Inorganic Spectroscopy MPI CEC (since 2017)

Research in the department of inorganic spectroscopy focuses on the development and application of advanced spectroscopic tools for understanding processes in biological, homogeneous and heterogeneous catalysis (Figure 1, left). The department seeks to understand how earth abundant transition metal-based catalysts can enable challenging energy conversion processes. At present, the department focuses primarily on the key reactions shown in Figure 1 (right) below. Our ultimate goal is to identify the unifying mechanistic principles that are key to guiding rational catalytic design. To this end, we focus on spectroscopic methods, which allow us to obtain detailed obtain a detailed geometric and electronic structural understanding of catalytic active sites. We understand that no single spectroscopic method can provide a complete picture of a catalytic active site. As such, we utilize spectroscopic methods that span the entire electromagnetic spectrum (including EPR, NMR, Raman, UV-Vis, IR, MCD, Mössbauer, XAS, and XES), making use of instrumentation within our own department, as well as within the joint workspace (JWS). We combine our spectroscopic studies with theory (performed both in our own department, as well as in collaboration with the group of Prof. Frank Neese) in order to obtain a more holistic view of electronic structure and mechanism.

We are particularly interested in spectroscopic methods that enable increased selectivity, as it is often the case that a catalytic intermediate of interest may not represent the major component at any given time point. Hence, we are actively involved in developing the full chemical information content of a wide range of X-ray spectroscopic methods. These include X-ray absorption (XAS), X-ray emission (XES), X-ray magnetic circular dichroism (XMCD), nuclear resonance vibrational spectroscopy (NRVS), scanning transmission X-ray microscopy (STXM), and resonant X-ray emission processes (RXES), also known as resonant inelastic X-ray scattering (RIXS) methods. We utilize and develop both in-house and synchrotron-based instrumentation in order to enable a wide range of X-ray spectroscopic studies. Further, we couple our X-ray spectroscopic studies closely with theory in order to develop the full chemical information content of each method.

During the present reporting period, the department has made significant advances in X-ray spectroscopy methodology development and instrumentation development, and the application of these tools to challenging questions in catalysis. In the 2020-2022 period, the department has published more than 165 papers in top journals, including *JACS, Angewandte Chemie, Nature Communications*, and *Nature Chemistry.* In the sections that follow, the department structure and recent staffing changes are first briefly described, followed by recent highlights in both spectroscopic developments and applications.

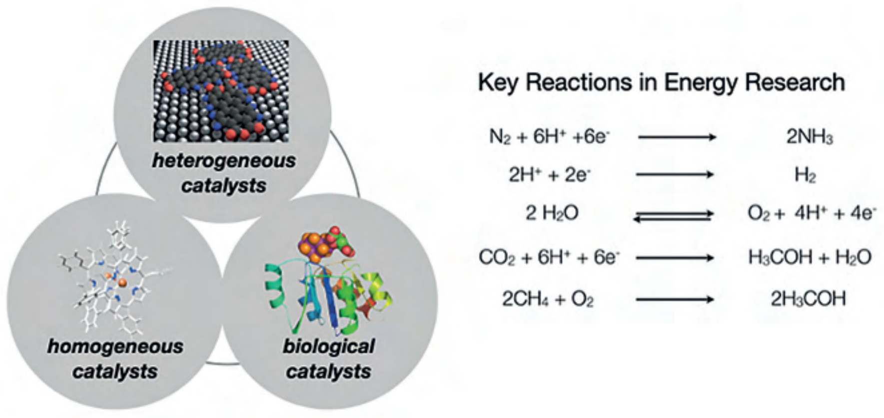


Figure 1. The types of catalytic systems (left) and the key reactions (right) studied by the Department of Inorganic Spectroscopy.

Department Structure

In order to achieve its scientific goals, the department of inorganic spectroscopy must span a wide range of disciplines. We seek a molecular perspective on the mechanisms of catalysts, informed by spectroscopic studies and theory. As such, it is important that our department use molecular complexes as a starting reference point for understanding the full chemical information content of our spectra. Such studies also allow us to assess how rigorously theory can reproduce spectral trends. It then allows us to use our approaches in a predictive fashion when extending our spectroscopic studies to heterogeneous, homogeneous and biological catalysts. Hence, our work flow always requires synthetic, biochemical, spectroscopic, and computational expertise. Further, we have a strong interest in understanding catalytic transformations under operating conditions. This thus requires expertise in kinetics, spectroelectrochemistry, and sample environement/instrumentation design. As such, the members of the department include chemists, physicists, biologists and engineers.

The group leaders' expertise span biological catalysis (Drs. Birrell and Decamps), homogeneous catalysis and molecular synthesis (Drs. Roemelt and Weyhermüller), X-ray spectroscopy instrumentation (Dr. Peredkov), spectroelectrochemistry (Dr. Rüdiger) and computational chemistry (Dr. Bjornsson). At the end of 2021 Dr. Bjornsson, who was on a termed group leader position, accepted a position as a permanent member of the scientific research staff at the Chemistry and Biology of Metals Laboratory at the CEA in Grenoble, France. In the fall of 2022, Dr. Birrell accepted a position as an Assistant Professor in the School of Life Sciences at the University of Essex in Colchester, UK. The department extends our warm congratulations to both of them for making these exciting next steps in their career! The opening in the biochemistry labs left by Dr. Birrell has very recently been filled by Dr. Kushal Sengupta, a previous Alexander von Humboldt fellow in the department, who brings extensive expertise in both biochemistry and spectroelectrochemistry. The position of Dr. Bjornsson remains open, but we are in discussions with a potential group leader candidate, who we hope to recruit in coming months. Finally, there are two project group leaders who are funded by third party funds (from the BMBF and ERC). Dr. Yves Kayser who started in November of 2022 brings extensive expertise in X-ray spectroscopy instrumentation, which is of particular importance given the growing in-house X-ray spectroscopy developments at the MPI CEC. His expertise will allow, in particular, for operando X-ray spectroscopy developments that will be essential for applications with the BMBF funded AmmoRef project. In addition, Dr. Sergio Jannuzzi initially stepped into the role as a group leader in 2020 as a replacement for Dr. Roemelt during her maternity leave. After Dr. Roemelt's return, she requested to limit synthetic laboratory responsibilities and has thus shifted to more computationally-oriented projects. Dr. Jannuzzi thus takes a lead role in the synthetic laboratories with a strong focus on the ERC funded CUBE-based activities. At present, the department is comprised of a total ~40 scientific (including group/project leaders, PhD students and postdoctoral fellows) and technical staff members. During the present reporting period, the department has hosted 7 Alexander von Humboldt Fellows, 1 Marie Curie Fellow, as well as DAAD, NIH and China Scholarship Council Fellows. This indicates that the department has a strong international profile, and we are delighted and privileged to work with such a diverse and talented international team, which allows us to engage in forefront spectroscopic research aimed at addressing key questions in energy research. Recent advances in the 2020-2022 period are described briefly in the sections that follow.

X-ray spectroscopy methodology development

VtC XES

For over a decade, the DeBeer research group has been dedicated to developing and applying valence to core X-ray emission spectroscopy (VtC XES) to questions of interest in chemical catalysis. Highlights include the use of this method to establish the presence of a central carbide in both Mo- and V- nitrogenase, the ability to detect single protonation events at metal active sites and the ability to experimentally probe O-O and N-N bond activation.*(1)* In the 2020-2022 period, new developments included the development of Mo,*(2)* Se,*(3)* P,*(4)* Zn*(5)* and Ru*(6)* valence-to-core spectroscopies. Our report of Mo K-Beta XES in *Angewandte Chemie* in 2020 is among the first applications of this methodology to a second row transition metal.*(2)* We highlight the relative information compared to what has been established for first row transition metal. This information is summarized schematically in Figure 2, highlighting the relative differences in the nomenclature and origins of the respective emission lines. We demonstrated that the K-Beta(2) lines are dominated by spin state effects, while the VtC XES provides information on metal oxidation state and ligand identity. We then went on to show how this methodology could be utilized for applications in (bio)catalysis, particularly for Mo-containing enzymes.

Another method development highlight was a recent *Chemical Science* paper from our group in which we applied P XES to biomolecules for the first time.*(4)* In this study, we showed that P XES is sufficiently sensitive to distinguish ATP from its hydrolysis product of ADP and inorganic phosphate (Figure 3). Despite its importance in biology and in catalysis, phosphorous is notoriously difficult to study due in part to the fact that phosphates are silent in the UV-Vis and while ^{31}P NMR may be useful for proteins the long relaxation times limit time-resolved studies. Our reports suggest that P XES could provide a novel tool for time-resolved studies of biological catalysts. These are studies we plan to pursue in the next evaluation period.

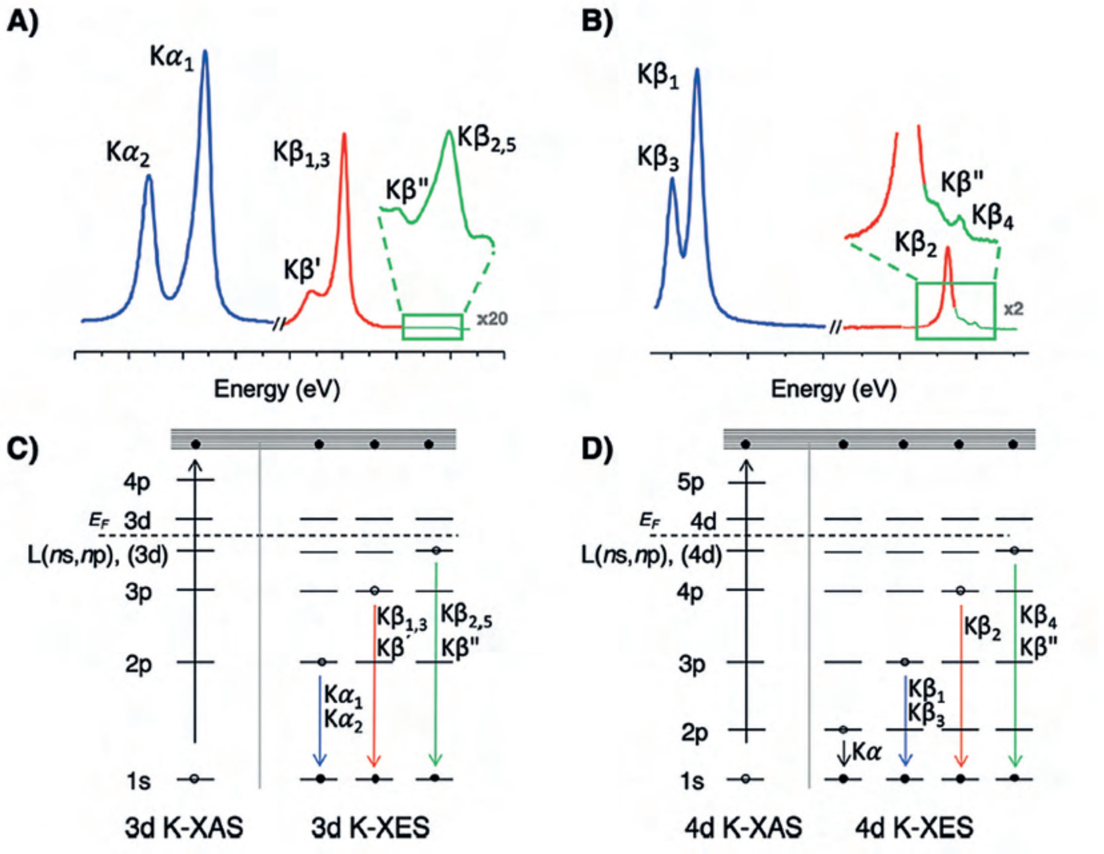


Figure 2. X-ray emission spectra and energy level diagrams of the absorption and emission processes for 3d (A and C) and 4d (B and D) transition metals. Adapted from reference 2.

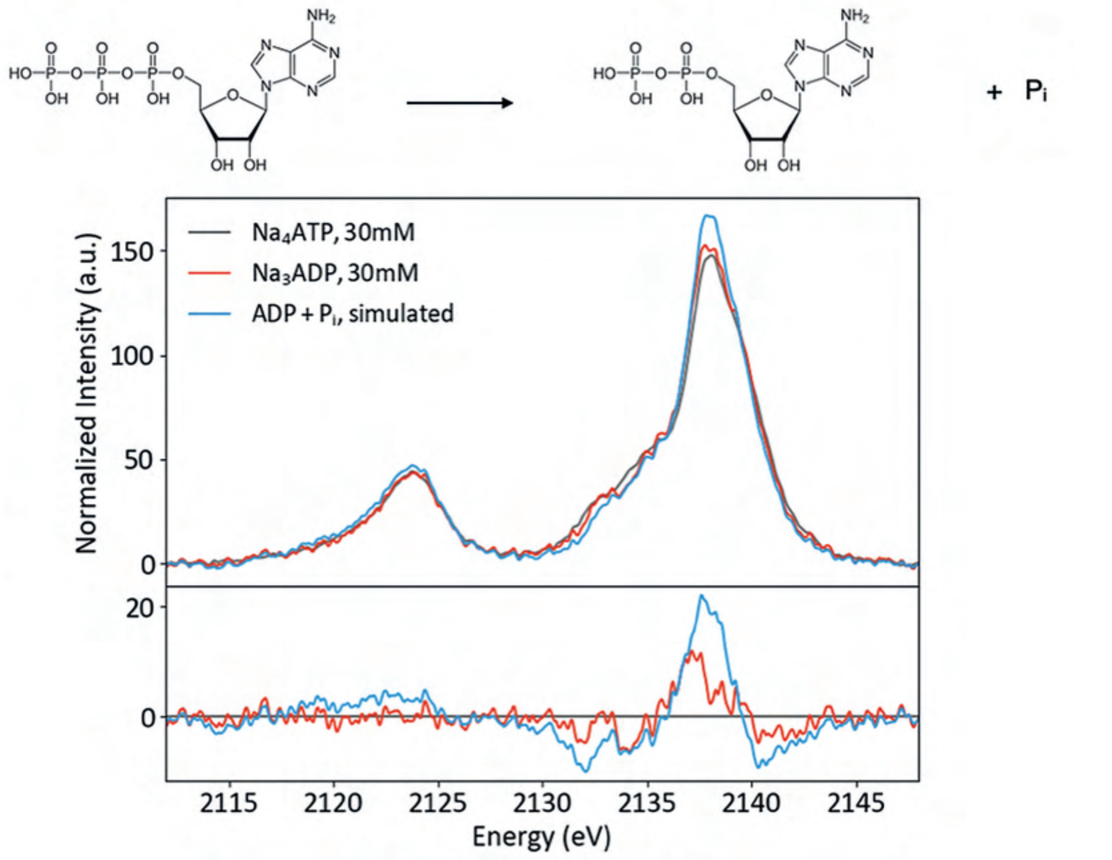


Figure 3. The conversion of ATP to ADP and inorganic phosphate (top). The P XES spectra of ATP, ADP and ADP + Pi, together with the corresponding difference spectra of X – ATP (bottom). Modified from reference 4.

1s3p RIXS (or RXES)

Methods which combine X-ray absorption and X-ray emission spectroscopy in a two-dimensional experiment continue to be a major area of interest for the department. Such methods enable greater selectivity than either method alone and allow us to obtain deeper electronic structural insights. Recently, we have shown that 1s3p RIXS can be utilized to recover physical oxidation state information, which may be lost in conventional XAS and XES spectra due to cancelling effects of d-count and covalency.*(7)* By applying 1s3p RIXS to a series of iron sulfur dimers ranging from diferrous, to mixed-valent to diferric, we have shown that XES spectra that are superimposable in standard non-resonant XES become distinguishable in 1s3p RIXS (also referred to as resonant XES or RXES). This can be best understood by schematically examining the non-resonant vs resonant processes, as shown in Figure 4. In non-resonant XES, an iron 1s electron is ionized to the continuum. Following 3p-1s K-Beta emission, this gives rise to a $3p^5 3d^n$ final state. In contrast, 1s3p RXES (Figure 4, right) involves promotion of a 1s electron to the 3d levels, this gives rise to a $1s^1 3d^{n+1}$ intermediate state, which upon 3p-1s emission results in a $3p^5 3d^{n+1}$ final state. By comparing the multiplet structure of the non-resonant to the resonant XES, one can arrive at a much clearer description of the electronic structure. Further, as full 1s3p RIXS planes allows one to select for specific excited state multiplets of interest, this method could provide a means to examine the energetics of different excited state multiplets. Applications of this method to high-valent iron and manganese oxos to probe two-state reactivity are currently in progress.

We have also continued to pursue method development efforts in 2p3d RIXS, STXM, and NRVS spectroscopies. We note that due to the 2020-2022 period largely overlapping with the COVID pandemic, many of our most challenging synchrotron experiments were not possible. While many facilities eventually allowed for remote access, this was not the case for experiments that involved complex setups or required extensive user intervention, as is the case for many of these development efforts. Nevertheless, four additional papers including RIXS/STXM results are currently in preparation and a paper describing NRVS and QM/MM correlations was recently submitted.

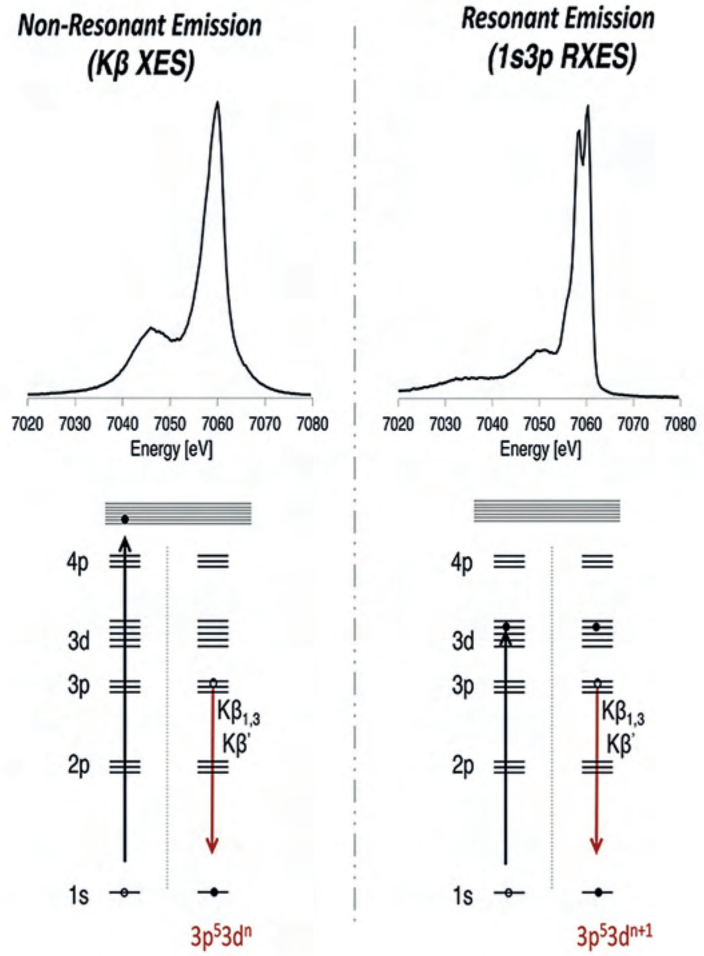


Figure 4. Comparison of the Kβ XES (top left) and 1s3p RXES spectra (top, right) for a high-spin Fe(II) complex, with the corresponding excitation and decay processes shown below each spectrum. Adapted from reference 7.

X-ray spectroscopy instrumentation developments

The DeBeer Department is actively involved in instrumentation developments at both synchrotron facilities and in-house. A brief summary of these efforts during the 2020-2022 timeframe is described below.

Developments at synchrotron facilities

A major development by our department has been the design, construction, and commissioning of the PINK beamline at the BESSYII synchrotron in Berlin. The design and construction was led by Dr. Sergey Peredkov during the previous evaluation period and during the current period the beamline was fully commissioned in "PINK" beam mode and opened to the general synchrotron user community. The beamline spans an energy range of 2-10 keV and utilizes multilayer mirrors to provide an intense source of ∼100 eV band width "pink" beam, which allow for non-resonant emission experiments to be performed with a high incident flux. Dr. Peredkov and his team designed both the control software and the sample environments allowing for facile data collection on beam sensitive samples. As the commissioning of PINK largely overlapped with pandemic shutdowns, Dr. Peredkov utilized this opportunity to improve remote access and automation of data collection. It is now possible for most experiments at PINK to be conducted without the user physically present. However, more challenging setups continue to require a user on site. PINK has already successfully contributed to five publications from the CEC, *(4, 6, 8-10)* with one of these featured as a JACS cover (Figure 5). Several additional papers both from the CEC and from external PINK user's currently in preparation.

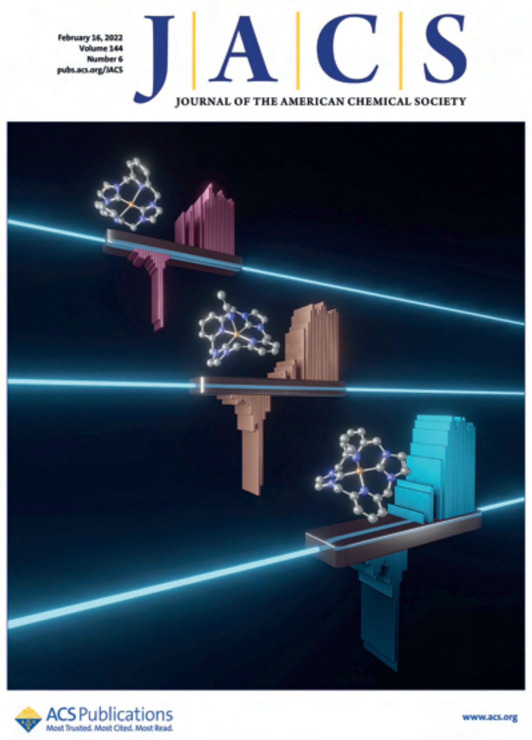


Figure 5. JACS Cover from work at PINK@BESSY. See reference 8 for the full article.

In addition to our activities at PINK@BESSY, the department is also actively involved in the development of a soft X-ray RIXS endstation at UE52@BESSY, known as the Advanced X-ray Spectroscopy at Functional Sites (AXYS) beamline. This is a collaborative effort between the DeBeer group and the group of Alexander Fohlisch. The centerpiece of AXYS is a transition edge sensor (TES) detector, which is funded by an MPG large equipment grant to the CEC and is being built by the US NIST.

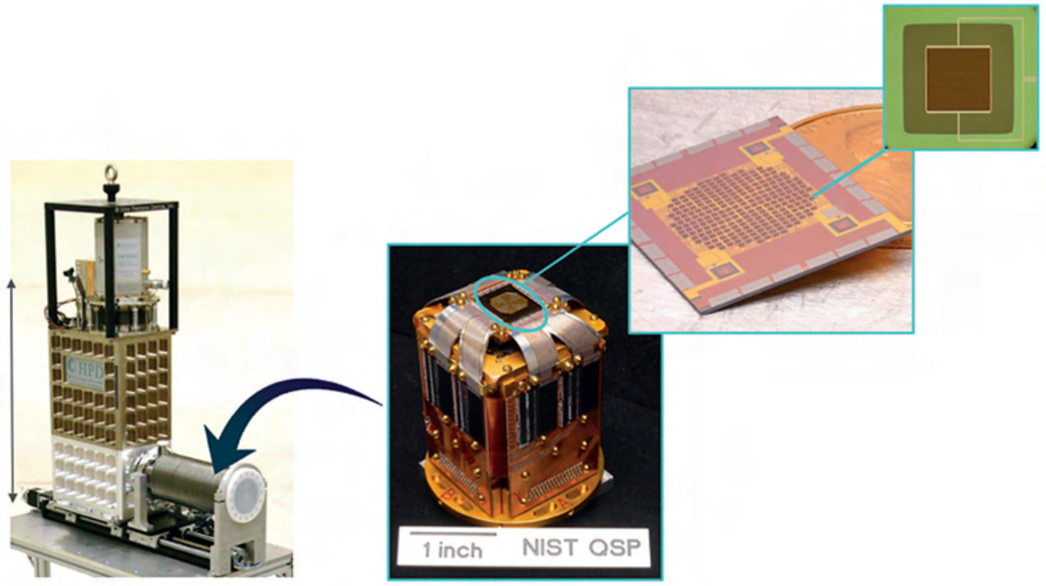


Figure 6. The transition edge sensor (TES) detector that is currently in development by the US NIST for the MPI CEC/HBZ beamline@BESSY.

The TES detector is based on X-ray microcalorimeters, operating at cryogenic temperatures, which measure the energy of fluorescent photons via temperature-dependent resistors (Figure 6). The detector will have 250 pixels, 0.5 eV energy resolution, a 250-1000 eV operating range, an active area of 10 mm2, and estimated solid angle of 11 msr at 3 cm. Importantly, the solid angle of the TES is much larger than what has at typical RIXS grating spectrometer setups and it thus enables us to measure much more dilute samples. This detector builds on a very successful prototype which is currently at Stanford SSRL BL10-1. Test measurements on this setup have shown that 2p3d RIXS of solutions of 0.5 mM Fe can be readily measured with this detector. The TES@BESSY will be similar to that at SSRL, but will have improved resolution (by a factor of 2) and also a larger solid angle of detection. This thus makes the **TES@BESSY the first of its kind in the world** and our completed test measurements clearly show that measurements on dilute biological and homogenous catalysts in solution will be possible. We are designing the chamber to allow for cold transfer of frozen solutions to a cryostat in the main chamber, which should open up a wide range of experiments on both homogeneous and biological catalysts.

Finally, the DeBeer Department has been actively involved in the planning and design of OPERANDOCAT, an MPG funded beamline at the PETRA synchrotron in Hamburg, which will allow for X-ray absorption, X-ray emission and X-ray scattering studies of catalysts, including both spatially- and time-resolved studies. The beamline developments are a collaborative effort with the Roldan group at the FHI. The planned beamline will be initially constructed under PETRAIII, but will be maintained in the PETRAIV upgrade. The beamline energy range will span from 5-55 keV (thus complementing our BESSY activities by enabling higher energy X-ray studies). Importantly the ability to combine spectroscopy studies with scattering studies will allow us to assess local active site changes (from XAS/XES), as well as macroscale interactions (e.g. protein-protein interactions by SAXS), thus enabling us to go beyond the active site and takes steps toward understanding the entire catalytic system.

In situ/Operando Setups for Synchrotron Spectroscopy

During this evaluation period, the department has continued to actively develop and refine our in-situ and operando spectroscopy setups. This has included further development and optimization of our STXM nanoreactor setup including the integration of a mass spectrometer. This setup enables STXM experiments under high pressures (up to 8 bar) and temperatures (up to 800 °C) with simultaneous monitoring of the reaction product composition. This setup was very recently employed for ammonia decomposition studies with the BMBF funded AmmoRef project and was also utilized for studies of dry methane reforming by Ni, Co and Fe based catalysts (in collaboration with Prof. M. Muhler).*(11)*

Another major area of development has been the development of microfluidic mixers. In collaboration with Prof. Lois Pollack (Cornell), we have been developing microfluidic mixers for transient X-ray spectroscopic studies. In order to monitor the formation of intermediates, we have integrated a UV-Vis spectrometer to allow for simultaneous XAS and optical absorption. The optical design and implementation was carried out by Olivia Stepanic McCubbin (a PhD student in the DeBeer group). Extensive test measurements have been carried out at CHESS. In addition, a new setup using a constriction mixer has been designed by the Department and first test measurements are planned at PINK@BESSY in January 2023.

Further, we have continued to refine and optimize our X-ray spectroelectrochemistry setups. These efforts have been led by Dr. Olaf Rüdiger and have resulted in several publications, with several more in preparation. An overview of this work was featured in Faraday Discussion*(12)* and an application to a Ru water oxidation catalyst was featured as a cover in Chemelectrochem (Figure 7).*(13)*

In-house X-ray spectroscopy developments

In addition to our developments at synchrotrons, the DeBeer department is also actively engaged in the development and application of in-house X-ray spectrometers. We presently have an in-house XES instrument that was funded by DeBeer's ERC consolidator grant, and was designed and constructed in collaboration with the Kangießer group at TU Berlin. This instrument allows 2.4-9 keV XES. It has an integrated glove box and a liquid

Figure 7. The cover of ChemElectroChem featuring the department's operando X-ray spectroelectrochemistry on a Ru water oxidation catalysts.

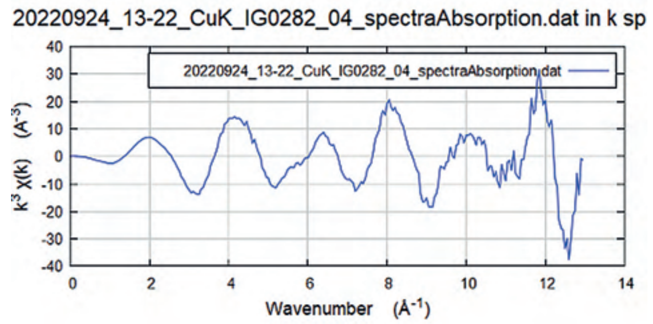


Figure 8. Preliminary EXAFS data from our new in-house spectrometeron a 1% Cu loaded MOF sample.

helium cryostat, allowing for measurements of air-sensitive and temperature-sensitive samples. In addition, the department has a commercial EasyXAFS instrument for XAS and XES measurement in the 5-12 eV region. This setup has some limitations in terms of sample environments and intrinsic source lines from the X-ray tubes, both of which we are working to address.

During the current evaluation period, a new EXAFS instrument was added to our in-house capabilities (again in collaboration with the TU Berlin team). The instrument allows for EXAFS measurements in the 5-15 keV range. The setup was installed in September 2022 and is currently in a commissioning phase. Cu K-edge spectra on a copper-containing MOF at 1% Cu loading is shown in Figure 8, demonstrating the capabilities of the instrument for measurements on dilute catalytic systems.

Currently, measurements are planned for the ERC funded CUBE project, the AmmoRef project, as well as collaborative projects with the KoFo. Funded by AmmoRef, we are designing a reactor setup that will be integrated on an open port of the EXAFS instrument, which was designed to allow for modular and flexible sample environments.

Another exciting development during this period, was the collaborative development (again with the TU Berlin team) of a soft X-ray laser plasma source for time-resolved soft X-ray spectroscopy in the nanosecond time regime (Figure 9). The instrument utilizes a metal target to generate a plasma spectrum that enables transmission measurements in the 240-980 eV range with 3 nanosecond time resolution. A separate pump laser allows for excited state spectroscopy. This instrument was installed at the MPI CEC in October 2022 and is still in a commissioning phase. A liquid flatjet is planned, which will allow for solution measurements of catalytic systems. Installation of this unit is planned for February 2023. The instrument utilizes the same control software design and data file formats as implemented at the PINK beamline in order to streamline future upgrades, as well as data processing and analysis.

Figure 9. In-House time-resolved laser plasma source at the MPI CEC.

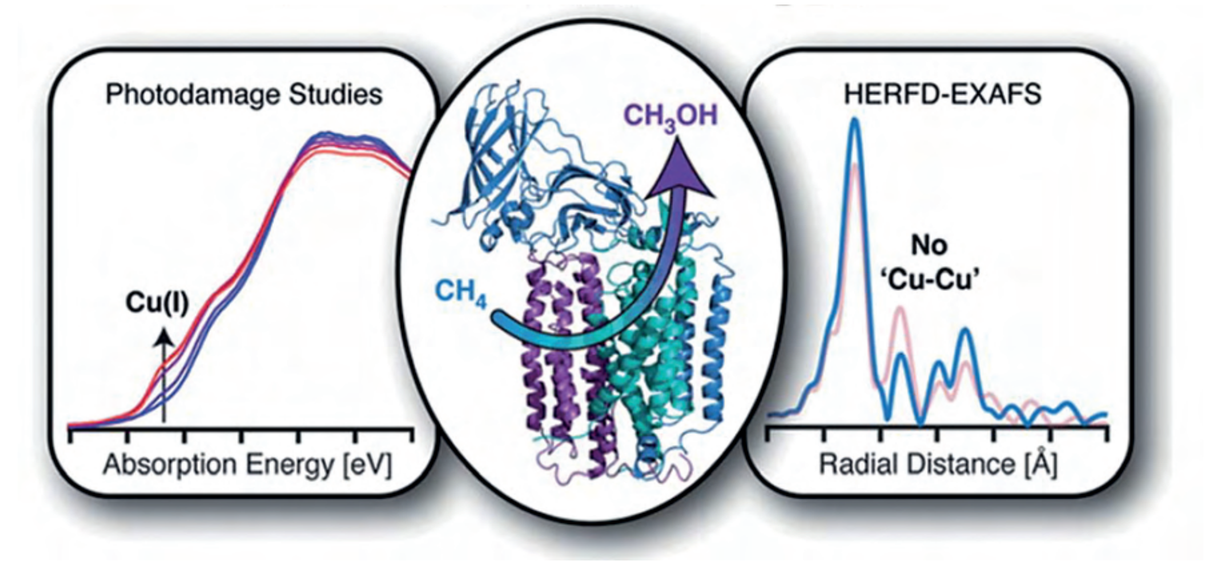


Figure 10. Recent XAS studies of pMMO (reproduced from reference 17). The data show that the pMMO active site is a mononuclear Cu site and that previous studies suffered from photoreduction and background copper contamination.

Selected Research Highlights

The spectroscopic method developments describe in the preceding sections have been utilized in wide range of applications in the 2020-2022 time frame. In the sections that follow we briefly highlight applications in biological, homogeneous and heterogenous catalysis.

Studies of biological methane oxidation

A longstanding interest of the DeBeer group is understanding the mechanism of biological methane oxidation. In biology either copper or iron active sites are utilized to activate the strong C-H bond in methane, with copper sites being found in particulate methane monooxygenases (pMMO) and iron sites being found in soluble methane monooxygenases (sMMO). sMMO's have been studied in far greater detail than pMMO's, however consensus has yet to emerge regarding the nature of their active sites. Building on previous work from our group, we have worked in collaboration with the Neese group to build a unified spectroscopic and theoretical understanding of "Q" the key intermediate for methane oxidation in sMMO. This work was published in JACS in 2021,*(14)* and has been the source of ongoing discussion in the community.*(15)* In order to provide further experimental support for the nature of Q, we have also been pursuing additional studies, including Fe K-Beta XES*(16)* and analogous transient studies using the microfluidic setups mentioned above.

In addition to our sMMO studies, we have also carried out studies aimed at forming a more unified description of the active site in pMMO.*(17)* We have clearly shown that previous studies mistakenly assigned the active site to a dicopper site due to background copper scattering from the beamline components (Figure 10). The interpretation of previous XAS data were further complicated by issues with photoreduction. This new report thus forms a basis for a more rigorous understanding of the pMMO active site. These studies are also informing our ERC CUBE project studies of lytic polysaccharide monooxygenases (LPMOs), which utilize somewhat analogous mononuclear copper sites to enable the activation of strong C-H bonds.

Studies of biological nitrogen reduction

Another area of ongoing interest in the department is understanding biological nitrogen reduction by the nitrogenase family of enzymes. During this period, we wrote two major reviews in this area,*(18, 19)* the former of which has already been cited 85 times and which was featured as a *Chemical Reviews* cover. In addition to these review articles, we have continued to contribute original research in this area. Most notably, we identified the presence of a central carbide in the FeFe-cofactor of Fe-only nitrogenase (Figure 11).*(20)* While no crystal structure is available for the FeFe protein, this information was accessed by Fe VtC XES. Importantly, these data demonstrate that the presence of a central carbide is a common motif in all known nitrogenases, thus further suggesting that it likely plays an essential role in catalysis, most likely enabling structural stability during turnover. Additional key studies in this area have focused on understanding the p-cluster biosynthesis*(21)* and computational studies of nitrogenase intermediates.*(22, 23)*

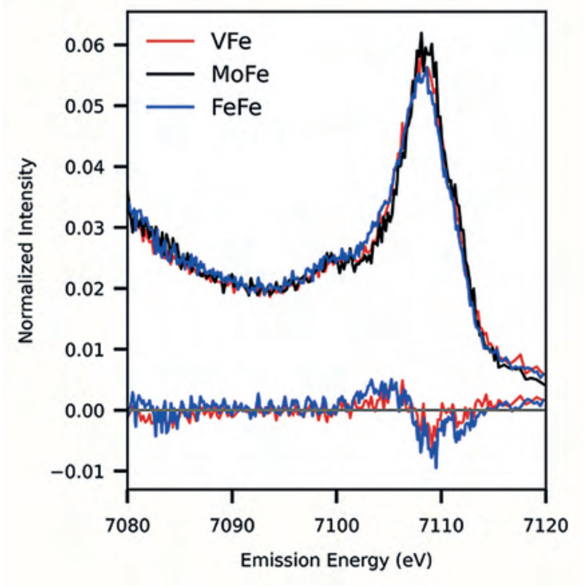


Figure 11. Fe VtC XES spectra of MoFe, VFe and FeFe nitrogenases, showing the presence a a C 2s to 1s feature at ~7100 eV that indicate the presence of a carbide in all three catalytic cofactors. Adapted from reference 20.

Iron-Catalyzed Aminofunctionalization of Olefins

In the area of homogenous catalysis, a particular highlight was a study on iron-catalyzed synthesis of aminoethers from olefins using a combination of theory and spectroscopy. Utilizing a combination of spectroscopic techniques (including Mössbauer, EPR, UV-Vis, XAS, NRVS and resonance Raman), combined with high-level quantum chemical calculations, we were able to obtain insight into the geometric and electronic structure of two of the reaction intermediates.*(24)* The first intermediate was shown to be a high spin ferric species, which decays to an S=2 species that is best described as a high-spin Fe(III) center coupled to an iminyl radical. The later intermediate species was previously unprecedented, but the elongated Fe-N bond, together with the unpaired electron density along the Fe-N vector, is postulated to favor N-transfer reactions onto styrenyl olefins.

STXM studies of a Dry Methane Reforming Catalyst

During this evaluation period, the department has also made a wide range of contributions in the field of heterogeneous catalysis.*(11, 25-30)* This has included in situ and operando studies of oxygen evolution, dry methane reforming, ammonia synthesis and ammonia decomposition catalysts. A particular highlight has been work on a NiCo dry methane reforming catalysts which we studied in collaboration with Max Planck Fellow, Prof. Martin Muhler. This work was featured as the cover of ACS Catalysis (Figure 12)*(11)* and a related hard X-ray study was also published in Nanoscale.*(25)* Using our in-house developed operando STXM setup, we followed the transformation of the catalyst during the reductive activation step and during DMR. During the reduction step, we observed that the NiCo alloy particles become segregated by element with the Co migrating toward the center of the particles and the Ni migrating to the outer surface. This segregated structure is maintained during DMR conditions, suggesting that the formation of this structure is required for optimal catalytic functions. Finally, the formation of Ni-rich branches on the surface of the particles is observed during DMR, suggesting that the loss of Ni from the outer shell may play a role in the reduced stability and hence catalyst deactivation. These findings provide insights into the morphological and electronic structural changes that occur in a NiCo-based catalyst during DMR. Further, this study emphasizes the need to study catalysts under operating conditions in order to elucidate material dynamics during the reaction.

Looking forward, the department is excited to apply our methodological and instrumentation developments to a wide range of catalytic systems. Our new in-house instrumentation and beamline developments, will allow us to delve deeper in our understanding of the geometric and electronic structure of catalytic active sites under operating conditions. In addition, our new developments will also allow us to begin to look at larger macroscale changes, thus spanning from an atomic level description to a broader understanding of the catalytic systems.

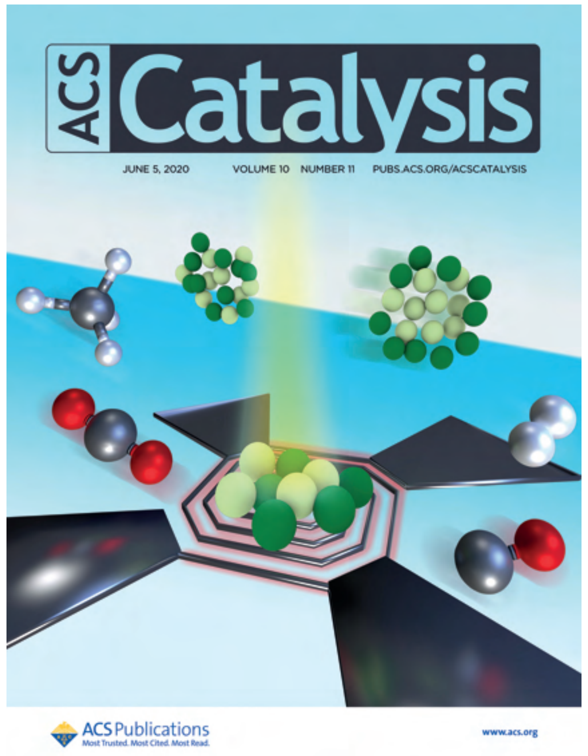


Figure 12. Cover of ACS Catalysis (reference 11) featuring our operando STXM studies of a DMR catalyst.

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Dr. James Birrell

Ph.D. University of Cambridge, UK (2012)
Postdoc MPI CEC (2013-2017)
Group Leader MPI CEC (since 2018)

Summary

Research in my group centres on understanding how metalloenzymes use abundant metals to carry out fundamental reactions like H_2 conversion, as well as how electrons are transferred efficiently over long distances between active site metallocofactors. Knowledge of the detailed geometric and electronic structure of enzyme metallocofactors in various catalytic intermediate states and mechanisms of catalysis allows the formulation of design criteria to build better molecular catalysts. Our work has focused mostly on the mechanism of H_2 conversion by [FeFe] hydrogenases and has been supported by funding from the Deutsche Forschungsgemeinschaft (DFG) and the Bundesministerium für Bildung und Forschung (BMBF). We have also begun to explore large multi-functional metalloprotein complexes that couple H_2 oxidation/production to other reactions. A crucial aspect of this work is the application of a broad range of techniques including spectroscopy, electrochemistry, structural biology and quantum chemical calculations. In the period from Jan 2020 to Dec 2022, my group has published 22 papers including four in *JACS*, two in *ACIE* and one in *Nature Catalysis*. This work has been highlighted in *ChemistryViews* and in the *JACS Early Career Investigators Virtual Issue 2021* and has been presented as talks at several international research conferences including the RSC International Solar Fuels Conference (2021), GRC Metallocofactors (2022), European Bioinorganic Chemistry Conference (2022) and the European Bioenergetics Conference (2022).

The catalytic cycle of [FeFe] hydrogenase

[FeFe] hydrogenases are highly active and reversible enzymes, achieving turnover frequencies of 10,000 s^{-1} for H_2 production and 150,000 s^{-1} for H_2 oxidation. Their active site cofactor, the H-cluster (Figure 1A), is composed of two parts: a canonical [4Fe-4S] cluster and a unique [2Fe] cluster, coordinated by carbon monoxide, cyanide and 2-azapropane-1,3-dithiolate ligands. Recent efforts, particularly from our group and collaborators, have provided enormous insight into the catalytic mechanism [1] and culminated in a model for the catalytic cycle (Figure 1B).

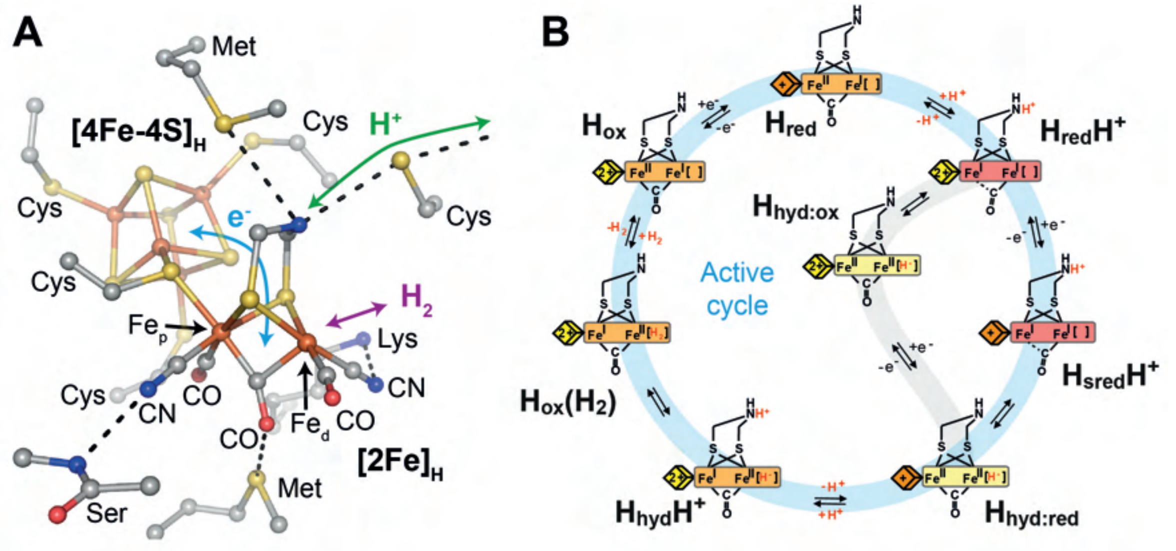


Figure 1. (A) The H-cluster and surrounding amino acids in [FeFe] hydrogenase. Blue, green and purple arrows indicate the pathways for electron, proton and gas transfer, respectively. **(B)** Putative catalytic cycle for the [FeFe] hydrogenase. The [4Fe-4S] sub-cluster of the H-cluster is represented by an orange cube and the [2Fe] subcluster is represented by a light orange rectangle. The terminal CO and CN^- ligands are omitted for clarity.

Early in 2020, we published variable temperature infrared (IR) spectroscopy and nuclear resonance vibrational spectroscopy (NRVS) results supporting a model in which bridging hydride containing intermediates do not play a role in the catalytic cycle [2] in contrast to proposals from another group [3]. Furthermore, we showed with pH-dependent IR spectroelectrochemistry that the $[4Fe\text{-}4S]_H$ subcluster in [FeFe] hydrogenase did not have a pH dependent redox midpoint potential [4], again contradicting previous findings from another group [5]. An important difference between these two studies was the exclusion of the non-physiological reducing agent sodium dithionite (NaDT) in ours. We then followed up this study with a detailed examination of the role of NaDT, and how its oxidation products, particularly SO_2 give an artifiactual pH dependent redox midpoint potential for the $[4Fe\text{-}4S]_H$ subcluster [6]. Furthermore, after directly demonstrating the presence of a terminal Fe-hydride bond in a catalytic cycle intermediate of [FeFe] hydrogenase using NRVS measurements in the previous assessment period [7], we went on to demonstrate the importance of vibrational coupling between the Fe-H bond and the rest of the [2Fe] cofactor and the protein matrix [8]. This clearly demonstrated the intimate relationship between the active site co-factor and the protein environment and how the latter finely tunes the properties of the former for efficient catalysis.

Protection of [FeFe] hydrogenase from oxygen using sulphide

[FeFe] hydrogenases are generally highly O_2 sensitive, although exceptions are known, including the periplasmic [FeFe] hydrogenase (*Dd*HydAB) from the sulphate reducing bacterium *D. desulfuricans*. This enzyme can be purified under air in an inactive state, which can be reactivated under reducing conditions. We speculated that this state contained an additional ligand bound to the H-cluster, blocking oxygen binding. In the previous assessment period, we discovered that addition of Na_2S to *Dd*HydAB under oxidising conditions led to protection from O_2 [9]. In the current assessment period, in collaboration with Prof. Ingrid Span (Friedrich-Alexander-Universität Erlangen-Nürnberg), we crystallised the O_2-stable state and solved its structure [10], revealing an additional ligand bound, which anomalous scattering determined to be a sulphur (Figure 2).

At the same time spectroscopic data (in collaboration with Prof. Serena DeBeer, Prof. Stephen Cramer (SETI) and Dr. Ingo Zebger (TU Berlin)) and calculations (in collaboration with Dr. Ragnar Bjornsson (CEA, Grenoble)) agreed with an HS^- ligand bound to an Fe(II)Fe(II) diiron site. This project has been extended to study the structure of additional catalytic cycle intermediates with funding from the DFG as part of the SPP1927 "Iron-sulfur for Life: Cooperative Function of Iron-Sulfur Centers in Assembly, Biosynthesis, Catalysis and Disease" priority program.

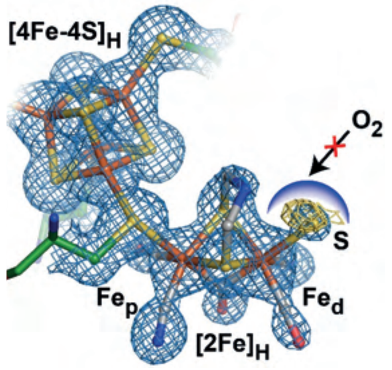
The ability to protect [FeFe] hydrogenases from O_2 damage has allowed for facile implementation of these enzymes into electrode materials for fuel cells [11] and electrolytic cells [12], in collaboration with Prof. Nicolas Plumeré (TU Munich). Together with Prof. Nicolas Plumeré and Prof. Volker Sieber (TU Munich), Dr. Michael Richter (Fraunhofer Institute) and Dr. Tobias Gärtner (ESy-Labs), we were awarded funding from the BMBF to develop hydrogenase-based electrochemical materials into commercial devices.

The electron-confurcating [FeFe] hydrogenase (HydABC) from *Thermotoga maritima*

My group has also been investigating the structure and mechanism of a multifunctional [FeFe] hydrogenase complex (HydABC) from the hyperthermophilic bacterium *Thermotoga maritima*, whose metabolism involves the anaerobic fermentation of carbohydrates producing CO_2 and H_2. A crucial component is the electron-confurcating [FeFe] hydrogenase, which oxidises NADH and ferredoxin produced during metabolism and uses the electrons to make H_2. It is thought to do this using electron confurcation, in which electrons enter the enzyme from two sites at different electrochemical potential and are combined and sent down a pathway at intermediate potential. However, very little is known about the mechanism of HydABC or about electron confurcation in general.

In early 2020, my group demonstrated the production of HydABC in *E. coli*, determined that it was a heterododecamer with a molecular mass around 600 kDa, characterized its activity, and spectroscopically investigated its redox cofactors, including the active site H-cluster [13].

Figure 2. X-ray crystal structure of an O_2 stable state of an [FeFe] hydrogenase. X-ray crystal structure of [FeFe] hydrogenase in the O_2 stable state, showing the native electron density in blue mesh and the anomalous sulphur density of the additional ligand in the open coordination site in yellow mesh [10].



These results already indicated that the enzyme contained just one FMN and that the H-cluster is probably not the electron-confurcation site. In collaboration with Dr. Jamie Blaza (University of York, UK) we solved the structure of HydABC using cryoEM, to 2.3 Å resolution [14]. This revealed an extended electron transfer pathway in each $Hyd(ABC)_2$ heterohexamer composed of iron-sulphur clusters connecting the two FMN and two H-clusters (Figure 3).

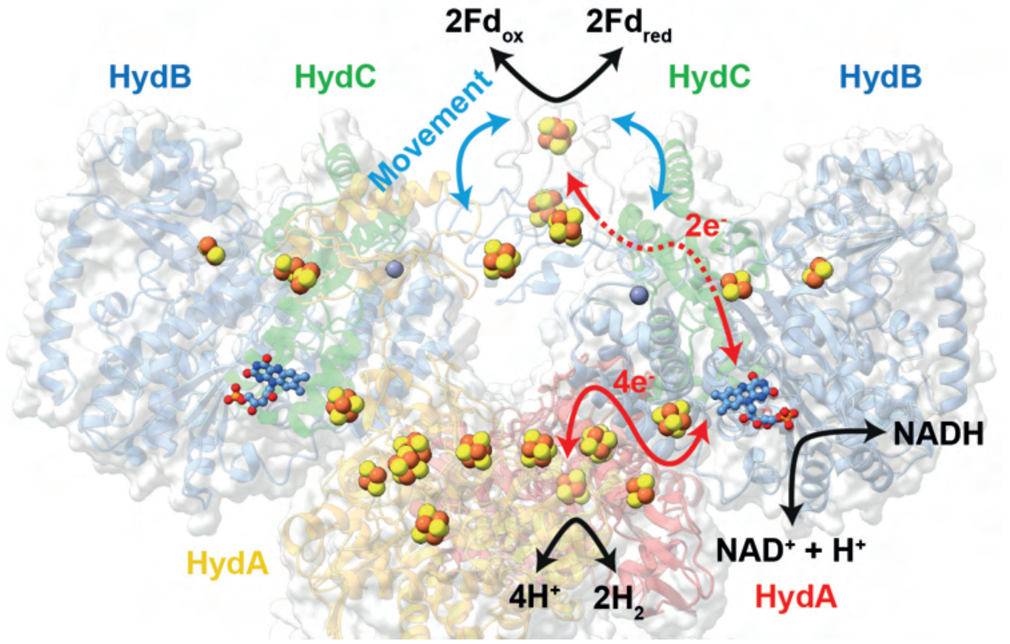


Figure 3. Structure of HydABC from *Thermotoga maritima*. One half of the $Hyd(ABC)_4$ heterododecamer is shown as a grey surface overlayed with a ribbon model of a $Hyd(ABC)_2$ hexamer (HydA in red/yellow, HydB in blue and HydC in green). The iron-sulphur clusters and zinc are shown as spheres and FMN are shown as balls and sticks. Two conformations of the C-terminal iron-sulphur domain of HydB (HydB-CT) are shown, one in which it is in a "closed-bridge" state contacting the C-terminal domain of HydA (HydA-CT) in an adjacent trimer, and another in which the HydB-CT is in an "open-bridge" state.

Two additional iron-sulphur clusters are located on the opposite side of the FMN from the main electron transfer pathway, possibly for exchanging electrons with ferredoxin. We were also able to solve three additional structures in which regions of HydB and HydA had different conformations forming a "bridge" feature that is observed in a "closed" and "open" state, where a Zn site appears to function as a "hinge" (Figure 3).

Carbon monoxide dehydrogenase from *Carboxydothermus hydrogenoformans*

In nature, CO_2 is reversibly reduced to CO by a class of CO dehydrogenase enzymes containing an unusual [Ni-4Fe-4S] cluster (called the C-cluster). In order to better understand how earth abundant metals such as Fe and Ni can be tuned to perform this exquisite chemistry so efficiently as well as to understand how this unique metallocofactor is assembled, my group has been producing several CO-dehydrogenase enzymes (CODH-I, II and V) from the hyperthermophilic bacterium *Carboxydothermus hydrogenoformans*, as well as the maturase CooC3, which is thought to be involved in Ni insertion.

Preliminary results indicate that all four of these proteins can be produced heterologously in *E. coli*. CODH-II gave a fully active enzyme, while CODH-I had only a fraction of the expected activity and presented with unusual spectroscopic properties, and CODH-V could only be produced in small amounts and appeared to have no activity at all. In collaboration with Prof. Wolfgang Schuhmann (Ruhr University Bochum we have incorporated CODH-II into a "gas-breathing" electrolytic cell for CO_2 reduction to CO [15]. Meanwhile, continuing research is aiming to understand the unusual properties of CODH-I and V. It is likely that CODH-I requires the putative Ni-insertase CooC3 for full activity. Accordingly, we have been investigating the metal and adenosine nucleotide (ATP/ADP) binding properties of CooC3 and its interaction with CODH-I.

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Dr. James Birrell has moved to University of Essex, UK as an Assistant Professor in September, 2022.
Dr. Kushal Sengupta has taken charge of his group since November, 2022.

Dr. Ragnar Bjornsson

Ph.D. University of St Andrews, UK (2012)
Postdoc MPI CEC (2012-2014)
Research assistant professor University of Iceland (2014-2018)
Group Leader MPI CEC (2018-2021)

Computational Chemistry

The research in my group involves computational chemistry with multiscale modelling techniques to gain insight into complex chemical systems related to enzymatic and molecular catalysis. We use quantum chemical methods based on density functional theory as well as single-reference and multi-reference wavefunction theory together with hybrid quantum mechanics / molecular mechanics (QM/MM) methods to study complex systems within their solution, solid or protein environment. A primary research topic in the group has been to gain electronic structure insights into how Nature accomplishes biological nitrogen reduction. This reaction, catalyzed by the nitrogenase enzymes, is studied via detailed theoretical modelling and calculations of spectroscopic parameters, working in close collaboration with experimentalists at the MPI CEC.

From Jan 2020 to Dec 2022 we published 14 scientific articles. In 2021 I was the recipient of the QBIC (Quantum BioInorganic Chemistry) Society award for my research into the electronic structure of the cofactors of nitrogenase.

Studies into Biological Nitrogen Reduction

Nitrogenases are the only enzymes in nature that catalyze the conversion of dinitrogen to its active form of ammonia, a critical reaction in the nitrogen cycle. This reaction remarkably proceeds at ambient temperatures and pressure using electrons and protons directly, and has been difficult to mimic synthetically. Nature utilizes complex multi-nuclear iron-sulfur cluster chemistry to achieve this difficult conversion but the details of the reaction mechanism remain enigmatic.

Modelling of reduces states of the FeMo cofactor: E_2 state

Characterizing the molecular and electronic structures of the reduced states of the Lowe-Thorneley kinetic cycle of Mo nitrogenase is critical to being able to unravel the catalytic mechanism of nitrogenase. The E_2 state of the FeMo cofactor has acquired 2 electrons and 2 protons compared to the resting E_0 state and is known to relax back to E_0 via H_2 evolution if trapped in this state. This reactivity suggests that the E_2 state probably contains a metal-hydride and this has been inferred from photolysis experiments. Two distinct S=3/2 EPR signals have also been found, suggesting two E_2 isomers to co-exist.

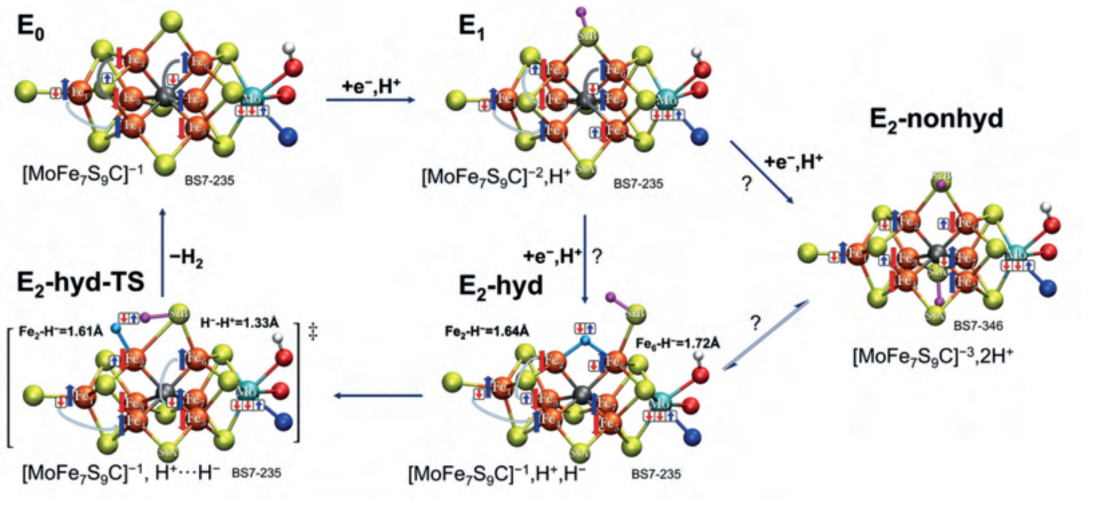

Figure 1. Electronic structure diagrams of the calculated E_0, E_1, **E_2-hyd**, **E_2-nonhyd** states as well as the transition state for H_2 evolution (**E_2-hyd-TS**).

We performed a detailed QM/MM study of the E_2 state potential energy surface[1] using our previously validated QM/MM model. We found that the most stable E_2 isomer is a bridging hydride structure between Fe2 and Fe6 but with the protonated S2B sulfide bridge having converted into a terminal sulfhydryl group on Fe6. Additionally, a non-hydride doubly protonated S2B and S5A sulfide bridge structure was found to be very close in energy. A transition state for H_2 evolution was located and the activation barrier was found to be strongly dependent on the treatment of the surroundings with the protein environment raising the barrier compared to a model without. The study was published in *Chem. Eur. J.* in 2021.[1]

Modelling of the initial CO-binding to the FeMo cofactor

The binding of alternative substrates and inhibitors has been found to highly useful in nitrogenase research, revealing spectroscopic properties or reactivity data otherwise difficult to obtain. CO is an inhibitor for nitrogen reduction and is known to react with an earlier Lowe-Thorneley state than the E_4 state that binds N_2. As CO ligands can be conveniently probed by IR spectroscopy, considerably more spectroscopic data is available for CO than other substrates/inhibitors. The electronic structure changes due to binding of a pi-acceptor ligand to the high-spin Fe ions in a weak-field sulfide environment of FeMoco may be of relevance to N_2 reduction, but different nitrogenase variants have also been found to be capable of converting CO into hydrocarbons through a mechanism which is not understood either. In a collaboration with Prof. DeBeer and Prof. Neese (MPI-Kofo) we performed a systematic QM/MM investigation into the initial steps of CO binding, comparing binding to the E_0 and E_1 states.[2] The results suggest that initial CO binding may take place in the E_1 redox state of the cofactor and that sulfide bridge opening appears to be critical part of the initial CO binding geometry. A bridging CO isomer was also located in the calculations, a potential intermediate prior to sulfide loss which is known to ultimately occur in CO inhibition. The results were found to be strongly dependent on the treatment of the protein environment. The study was published in *Inorg. Chem.* in 2021.[2]

Vanadium nitrogenase

The vanadium nitrogenase is an alternative nitrogenase that is expressed under Mo-deficient conditions. The iron-vanadium cofactor was believed for a long time to simply be a V analogue of the iron-molybdenum cofactor. A recently described X-ray structure, however, surprisingly revealed a 4-atom ligand (CO_3^{2-} or NO_3^- proposed) to replace the S3A sulfide compared to FeMoco. Additionally, the Fe and V oxidation states and the overall charge of the iron-vanadium cofactor resting state are not well established. We performed a systematic QM/MM investigation[3] into vanadium nitrogenase, comparing calculated QM/MM structures to the 1.35 Å crystal structure (assumed to be of the resting state). The 4-atom ligand was revealed to most likely be a CO_3^{2-} and a BS7-235 spin isomer was found to be the most stable for all calculated charge states. A reduced $[VFe_7S_8C(CO_3)]^{2-}$ charge state was found to be the only charge state in good agreement with the X-ray structure. The study was published in *Inorg. Chem.* in 2021.[3]

Benchmarking of density functional methods for structures of spin-coupled Fe/Mo-sulfur dimers

The cofactors of nitrogenase present unique challenges to contemporary quantum chemistry with their large number of unpaired electrons, antiferromagnetism, delocalization and unique ligand environment. Currently, due to the size and complexity of the cofactors we are limited to the use of broken-symmetry density functional approaches. A much-discussed problem in the literature is the appropriate density functional approximation to describe these cofactors. In a study[4] published in *J. Chem. Theory Comput.* we systematically investigated the capability of state-of-the-art density functional theory to describe the molecular structure of well-defined spin-coupled Fe-Fe and Mo-Fe dimers. We found that metal-metal distances in sulfur-bridged spin coupled dimers are particularly sensitive to the DFT-level used (unlike closed-shell dimers) and this is found to correlate with the calculated metal-ligand covalency of the bridging ligands. The Fe-S covalency is particularly important and we find that these trends carry over to the case of the larger cluster FeMoco, allowing one to rationalize which theory level should be used to describe the iron-sulfur clusters of nitrogenase. The study was published in *J. Chem. Theory Comput.* in 2022.[4]

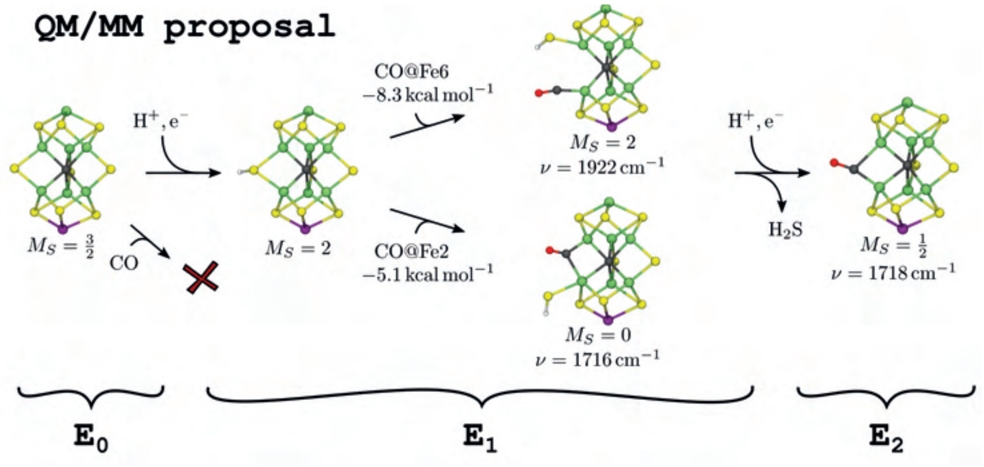

Figure 2. The proposed mechanism for CO binding to FeMoco from QM/MM calculations.

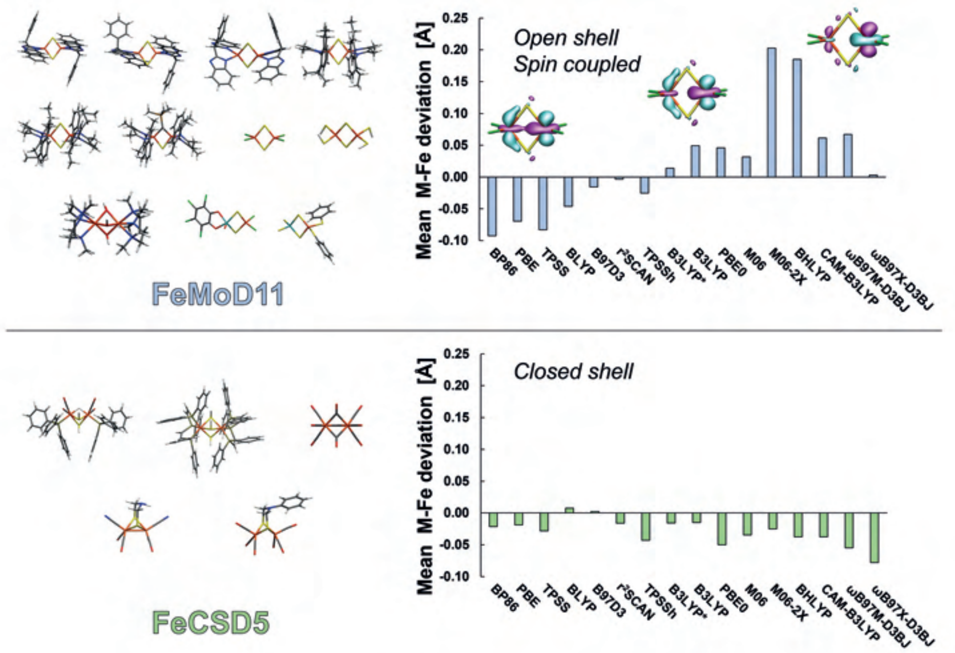

Figure 3. Deviations in M-Fe distances (Å) for with different density functionals for spin-coupled dimers (FeMoD11) vs. closed-shell dimers (FeCSD5).

Various collaborations

In addition to our primary research objects, my group engages in experimental collaborations in various areas: contributing computational insights into: the chemistry of fragmentation of molecules by low-energy electrons (collaboration with Oddur Ingólfsson, University of Iceland)[5,6], magnetic coupling of single-molecule magnets (collaboration with T. David Harris, Northwestern University)[7], how gels are formed (collaboration with Prof. K. Damodaran, University of Iceland)[8], conformational properties of fungal inhibitors (collaboration with Dr. T. Kramer, Maynooth University)[9], the nature of a sulfide-bound inactive form of [FeFe] hydrogenase (collaboration with Dr. James Birrell).[10] We have also contributed to the development of a nudged elastic band implementation[11] in ORCA (collaboration with Prof. Hannes Jónsson, University of Iceland) and help shed light on the complicated localization-delocalization equilibrium of a diamine cation by multireference wavefunction calculations (collaboration with Prof. Hannes Jónsson, University of Iceland)[12].

Dr. Ragnar Bjornsson has moved to the CEA (the French Alternative Energies and Atomic Energy Commission) in Grenoble, France as a permanent research scientist, in December 2021.

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Biochemistry of Metalloproteins

Our group combines biochemical and spectroscopic methods to understand complex processes in metalloproteins. We focus on two major iron-sulfur cluster systems: nitrogenases and the [Fe:S] biogenesis SUF system.

1) Nitrogenases: studies on the cofactors and the P-cluster

Nitrogenases catalyze the challenging reduction of dinitrogen (N_2) in ammonia (NH_3), which involves successive electron transfer steps from the [4Fe:4S] cluster of the reductase moiety (Fe protein) to the [8Fe:7S] P-cluster in the catalytic moiety (MFe protein, in which M = Mo, V, or Fe) and then to the FeM-cofactor where the reaction takes place. [1] Questions related to the structures of these enzymes and their cofactors, their biosynthesis, or the reaction mechanism, remain open.

a) Methods

Our group focuses on the nitrogenases of the soil bacterium *Azotobacter vinelandii* (Figure 1), which is a genetically tractable organism. In order to investigate the role of specific residues in these proteins, we produced several single-codon as well as gene deletion mutant strains via mutagenesis and recombination techniques. The DeBeer department uses and develops cutting-edge spectroscopy techniques to understand the properties of metallocofactors, however sample concentration is often a limiting factor for studies of metalloproteins.

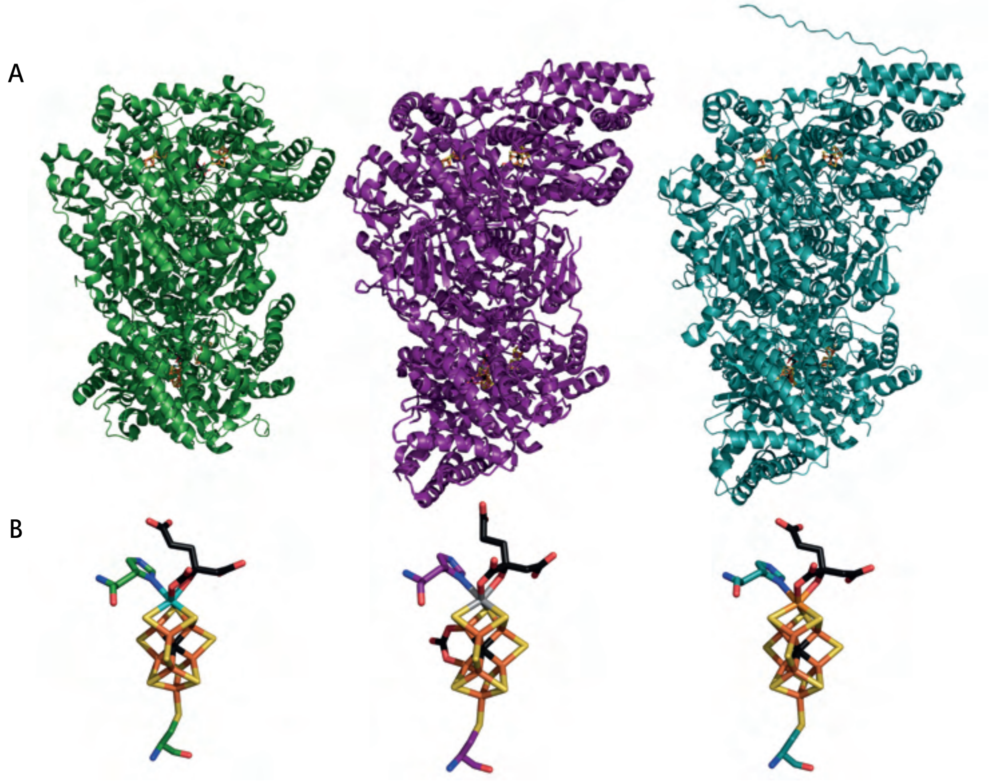

Figure 1. Structural models of A) the MoFe (green), VFe (purple), and FeFe (teal) proteins of *A. vinelandii*; B) the FeMo-, FeV-, and FeFe-cofactors (orange: iron, yellow: sulfur, teal: molybdenum; grey: vanadium; red: oxygen, blue: nitrogen; carbon atoms are either in black or of the color of the protein chain). The structure of FeFe has not been elucidated experimentally and the model shown here was produced by AlphaFold calculations.

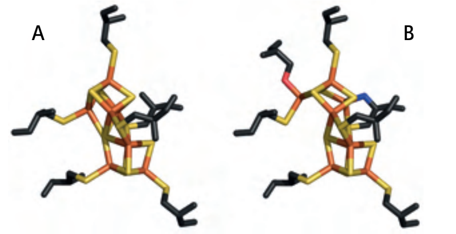

Figure 2. Structural model of the P-cluster and its coordinating residues in MoFe of *A. vinelandii*, A) in the fully-reduced P^N state; B) in the 2-electron oxidized P^{2+} state (orange: iron, yellow: sulfur, black: protein side chain; the amide of α-Cys88 and the hydroxyl function of β-Ser188 are shown in blue and red, respectively).

To circumvent this issue and enable studies on solid nitrogenase, we lyophilized the MoFe and Fe proteins, and performed EPR and X-ray Absorption Spectroscopy (XAS) measurements on the lyophilized samples. While the proteins showed minor distortions, the redox and spins states were maintained, and catalytic activity could be recovered after resolubilization, showing that lyophilisation is a viable option for spectroscopic studies of nitrogenases. [2]

b) A Fe_6C core in all nitrogenases

Three types of nitrogenases have been described, corresponding to distinct proteins encoded by different set of genes: Mo, V, and Fe nitrogenases. Mo nitrogenase is produced by every diazotroph, and the V and Fe nitrogenases are therefore considered as alternative nitrogenases. Valence-to-Core X-ray Emission Spectroscopy (VtC XES) experiments by the DeBeer department, followed by crystallography measurements by others, revealed that the FeMo- and FeV-cofactors share a similar structure with a unique Fe_6C core. This μ_6-C^{4-} binding mode is not observed anywhere else in nature. Although all nitrogenase cofactors are predicted to share a similar biosynthesis pathway, with the NifB-co cluster being a common precursor, the structure of FeFe and its cofactor FeFe-co have not yet been elucidated. To check if FeFe-co also contains a carbide, we produced and isolated FeFe of the *A. vinelandii* DJ2241 strain by growing these bacteria on a medium deprived of Mo and V, and performed VtC XES measurements on the purified protein. The obtained spectrum is superimposable with those obtained for MoFe and VFe, showing that the Fe_6C core is a property of all nitrogenase cofactors (Figure 1). [3] The role of the carbide in N_2 reduction by nitrogenases is not clear, and it has been proposed that it is structural, maintaining cofactor structure during the reaction. Numerous spectroscopy and structural studies have led to suggest that N_2 binds on Fe center(s) of the Fe_6C core following hydride formation. Carbide coordination may influence the Fe centers to adopt an $S = 3/2$ intermediate spin state, which would greatly impact substrate binding. This will be assessed via 1s3p RIXS measurements (collaborative project with Prof. DeBeer).

c) The role of the accessory protein NifW in P-cluster maturation

Substrates can bind on the active site of nitrogenases only after enough electrons have been sequentially transferred to the cofactor from the P-cluster, located at the interface of the α- and β-subunits of the MFe proteins (Figure 2). This [8Fe:7S] cluster is formed *in situ* on the MFe protein from the fusion of two [4Fe:4S] cubanes, each coordinated by either the α- or the β-subunit. The last step of P-cluster maturation precedes the insertion of the FeM-cofactor and is catalyzed by the Fe protein, however the maturation process is far from understood. Genetic methods have proven to be essential in the study of P-cluster biosynthesis, with deletion mutants being used to assess the role of maturation factors. After the isolation of MoFe protein species carrying immature P-clusters when produced in Δ*nifH A. vinelandii*, the group of Prof. Dennis Dean (Virginia Polytechnic Institute and State University, USA) identified several subspecies distinguished by the maturation factors they interact with. To elucidate the role of the maturation factor NifW, we performed EPR and XAS studies on Δ*nifH* Δ*nifZ* MoFe complexes bound or not to NifW, in two redox states (dithionite-reduced and IDS-oxidized). In both species, we identified the clusters as two sets of $[4Fe:4S]^{2+/1+}$ cubanes, suggesting that NifW is not involved in the fusion process, which must then occur after NifW binding. These spectroscopic studies revealed subtle differences between the clusters contained in these species: in Δ*nifH* Δ*nifZ* MoFe bound to NifW, the clusters show an additional coordination to a light atom, and the distance between them is decreased. This led us to suggest that NifW plays a conformational role in P-cluster maturation, with its binding to MoFe allowing the clusters to be in close vicinity before their fusion (Figure 3). [4] The biosynthetic steps preceding NifW binding remain to be elucidated.

d) The P-cluster of V nitrogenase

The structure and the electronic properties of the MoFe P-cluster have been thoroughly investigated and the crystal structure of VFe suggested an identical structure for its P-cluster. However, discrepancies have been observed regarding its electronic properties. In the fully-reduced P^N state, the P-cluster is diamagnetic and therefore EPR-silent. In the 2-electron oxidized P^{2+} state, it has an integer spin $S = 3$ or $S = 4$ and displays an EPR signal in the parallel mode at $g \sim 12$. Previous studies have failed to report such a signal for the P-cluster of the VFe protein. To understand the origin of this discrepancy, we produced and isolated VFe and apo-VFe (protein containing the P-cluster but no FeV-co) from the *A. vinelandii* strains DJ2253 and DJ2256, which allow rapid purification of these proteins via affinity chromatography. Our electrophoretic studies after purification revealed a significant imbalance in the β-/α-subunit ratio in those proteins. Apo-VFe samples nearly contain 4 times more β- than α-subunits, suggesting they contain up to 3 times more [4Fe:4S] cubane (P-cluster precursor) than mature P-cluster. Surprisingly, parallel-mode EPR studies of IDS-oxidized VFe showed an intense signal at $g \sim 12$, while it could not be detected in IDS-oxidized apo-VFe, suggesting that the P-cluster of VFe is similar to that of MoFe, but that significant structural changes may occur upon FeV-co insertion. [5]

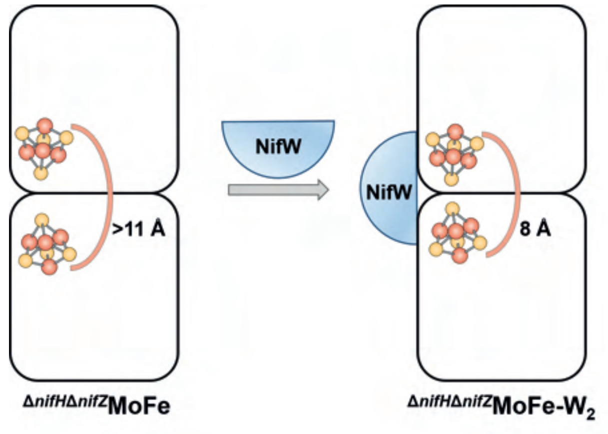

Figure 3. Role of NifW in P-cluster maturation. The distance between the [4Fe:4S] clusters decreases upon NifW binding.

e) Electron transfer to FeMo-co: role of the β-Tyr98 and β-Phe99 residues

Substitutions help understanding the properties of specific protein residues, but can also significantly alter enzymatic activity. It was reported that substituting the β-Tyr98 and β-Phe99 residues of the MoFe protein with a histidine enables a faster electron transfer from the P-cluster to FeMo-co (Figure 4). To understand how these substitutions may affect the electronic or structural properties of the metalloclusters, we produced the variant MoFe proteins from the *A. vinelandii* strains DJ939 and DJ1956, respectively. In collaboration with Dr. Kushal Sengupta, we measured the acetylene reduction activity of these variants and recorded EPR spectra. While the β-His98 variant showed decreased acetylene reduction activity, the β-His99 variant showed a similar activity to native MoFe. However, both variants exhibited different behavior upon thionine oxidation. In order to investigate the effect of the substitutions on the sole P-cluster, we are building an *A. vinelandii* strain to produce these variants without cofactor.

2) Iron-sulfur cluster biogenesis: the minimal SUF system of methanogenic archaea

Three systems are responsible for the biosynthesis of [2Fe:2S] and [4Fe:4S] clusters in prokaryotes: the ISC, NIF and SUF systems. Those systems are essential for the maturation of key energy-converting enzymes such as hydrogenases or nitrogenases. They share a similar general mechanism, with the cluster being assembled on a scaffold before being transferred to target proteins via a chaperone. Although a structural model is available for the $SufC_2BD$ complex of *Escherichia coli*, the mechanism of cluster assembly on the bacterial heterodimeric SufBD scaffold is not understood, in particular the role of the homodimeric $SufC_2$ ATPase in the reaction. The SUF system of methanogenic archaea represents an attractive model as it is composed only of the SufB and SufC proteins. We produced the SufC protein of the hyperthermophilic archaeon *Methanococcus jannaschii* and characterized its ATPase activity. [6] The activity is optimal at high salt concentrations and high temperatures that reflect the environmental conditions of the archaeon. Interestingly, the enzyme can use either Mg^{2+} or Mn^{2+} as a cofactor. To follow the conformational changes during the ATPase reaction, we established a cooperation with the group of Prof. Thomas Wiegand to perform solid-state NMR studies on SufC with various ATP analogues. Preliminary ^1H-NMR measurements showed that this enzyme is an adequate model for these challenging analyses. SufC also represents an attractive model for P K XES studies (project in cooperation with Dr. Sergey Peredkov).

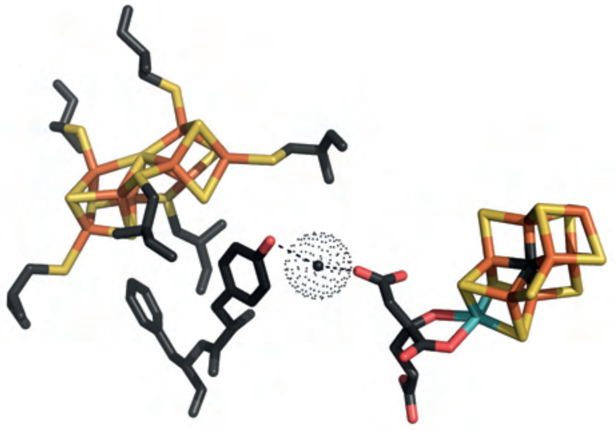

Figure 4. Position of residues β-Tyr98 and β-Phe99 in the MoFe protein of *A. vinelandii*, between the P-cluster and FeMo-co. The hydroxyl function of β-Tyr98 and the homocitrate ligand coordinate the same water molecule.

A)

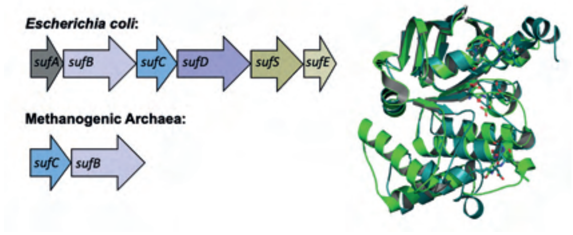

Figure 5. A) *suf* operons in *E. coli* (top) and methanogenic Archaea (bottom). The order and simplicity of the *suf* operon is conserved through methanogens, making this system an attractive target for biochemistry studies. B) Structural alignment of SufC of *E. coli* (green, PDB ID: 2D3W) and SufC of *M. jannaschii* (teal, AlphaFold prediction). The alignment reveals a few differences in the secondary structures, notably in the size of helices. However, the ATPase motifs (Walker A, Walker B, ABC signature, in stick representation) seem structurally conserved.

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Spectroscopy and reactivity of small molecular catalysts

Numerous natural and man-designed transformations of fundamental importance to our daily lives are enabled by transition metal molecular catalysts in solution. Built on the fundamentals of coordination chemistry, synthetic chemists push the development using abiotic scaffolds and reaction conditions as in the case of organometallic chemistry or drawing inspiration on biological systems in bioinorganic chemistry motivated by life-sustaining reactions performed by enzymes. Large efforts are dedicated to harness in molecular catalysts the key features that allows for challenging transformations in energy conversion such as C-H and O-O activation. Although reactivity studies enables our grasp on novel transformations, it has limited ability to provide deeper insights into key structural and electronic features to drive rational catalyst design.

Spectroscopy overall provides the means to interrogate not only reactants and products, but also the nature of reactive species responsible for the desired reactivity. The methods offered by MPI CEC spans over a wide range of the electromagnetic spectrum, thus enabling in-depth investigation on different fronts. The spectroscopic observables are often not clearly mapped to the atomic structural domain as a consequence of intricate quantum mechanical selection rules of light-matter interaction. To close the loop, molecular modeling is essential to provide chemical insights and to propose electronic structural descriptions consistent with experimental data. This make quantum chemical calculations and the Orca program[1] invaluable allies to tackle the scientific questions.

Our group employs the synthesis-spectroscopy-theory tripod to drive fundamental research on the key characteristics that enable first-row transition metals to perform C-H functionalization and O-O activation.

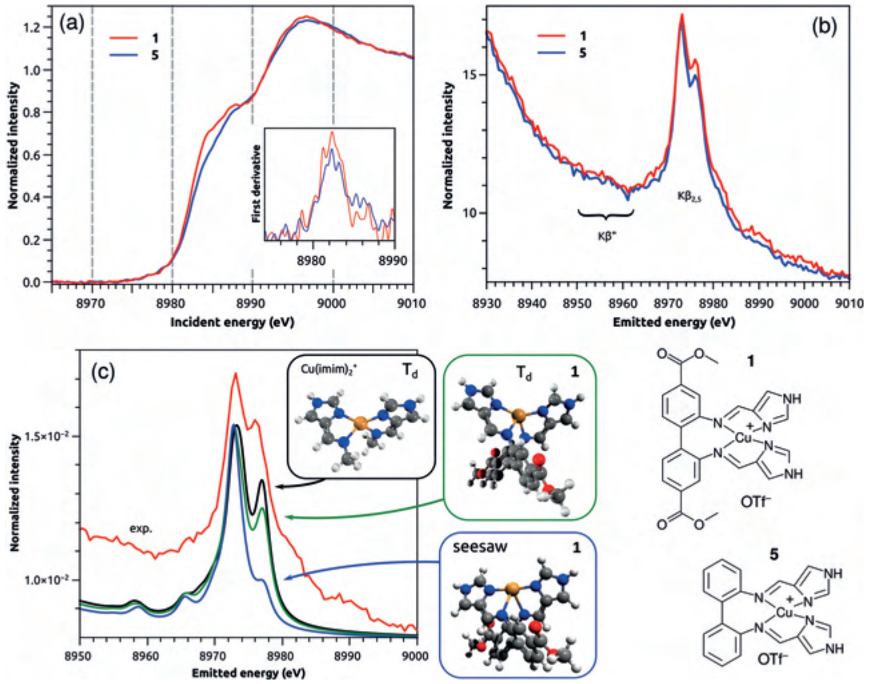

Figure 1. **(a)** Cu K-edge XAS and first derivative (inset), **(b)** Experimental VtC XES and **(c)** calculated spectra for three structural models. The best agreeing model relative to the peak at 8978 eV in the VtC XES data – $Cu(imim)_2^+$ – has geometry incompatible with the strain imposed by the biaryl backbone, indicating that the each imine-imidazole group derives from different ligands in a polinuclear chain.

Copper complexes and their incorporation to metallorganic frameworks towards C-H activation

Within the framework of the ERC-funded synergy project "CUBE", we engaged in a collaborative work with the group of Prof. Dr. Unni Olsbye at the University of Oslo. She together with Prof. Dr. Serena DeBeer (MPI CEC), Silvia Bordiga (University of Turin) and Vincent Eijsink (Norwegian University of Life Sciences) are the principal investigators of this ERC grant. Jointly, we investigated Cu(I) complexes designed to integrate a metallorganic framework (MOF) with the perspective of application to catalysis. Prior to the incorporation in the solid scaffold, nuclear magnetic resonance (NMR) experiments indicated the formation of high-molecular weight aggregates in solution. The investigation in the solid state using X-ray absorption spectroscopy (XAS) on the Cu K-edge supported the description of a tetracoordinated site in near tetrahedral local symmetry around the copper center. The X-ray emission spectroscopy (XES) revealed two emission lines in the valence-to-core (VtC) region whose relative intensity could not be explained computationally by a mononuclear species, which is consistent with the aggregation behavior in solution. Finally, the complementarity between Cu K-edge XAS and VtC XES was highlighted with quantum mechanical calculations to track the spectral intensities to the molecular orbital composition as a function of the site symmetry.[2] In this work, we used our in-house X-ray spectrometer *easyXES100-extended* for the XAS, and for XES the department's tender X-ray beam line "PINK"@BESSY developed and maintained by Dr. Sergey Peredkov, a group leader in the department. Importantly, this work laid the foundations for our current ongoing efforts in the development of Cu-impregnated MOFs, in which the immobilization on well-defined sites on the scaffolds is expected to isolate the Cu centers. On the methodological aspect, the tools and the knowledge employed here will be used to characterize the structure of these sites.

High-valent iron chemistry

Nature employs not only copper, but also iron to activate strong C-H bonds in oxygenase enzymes. As we move left in the first row of the transition metals, the stabilization of terminal oxo and nitrido species enables the direct investigation of the isolated reactive species in which the metal is an unusually high oxidation state. In our group, the spectroscopic investigation of high-valent iron molecular systems in pursued.

In a collaborative work with Jun.-Prof. Dr. Alicia Casitas of the Philipps-Universität Marburg, we characterized an Fe(IV)-cyanide complexes by ^{57}Fe Mößbauer spectroscopy and their ferric precursors by electron paramagnetic resonance (EPR).[3] Unlike in oxos and nitridos, the Fe(IV) center investigated is not stabilized by strong π bonds with the terminal functional group (O and N respectively), but solely by strong σ bonds with the ancillary ligand, rendering a very reactive bond with the terminal group, allowing for potential applications in organometallic catalysis.

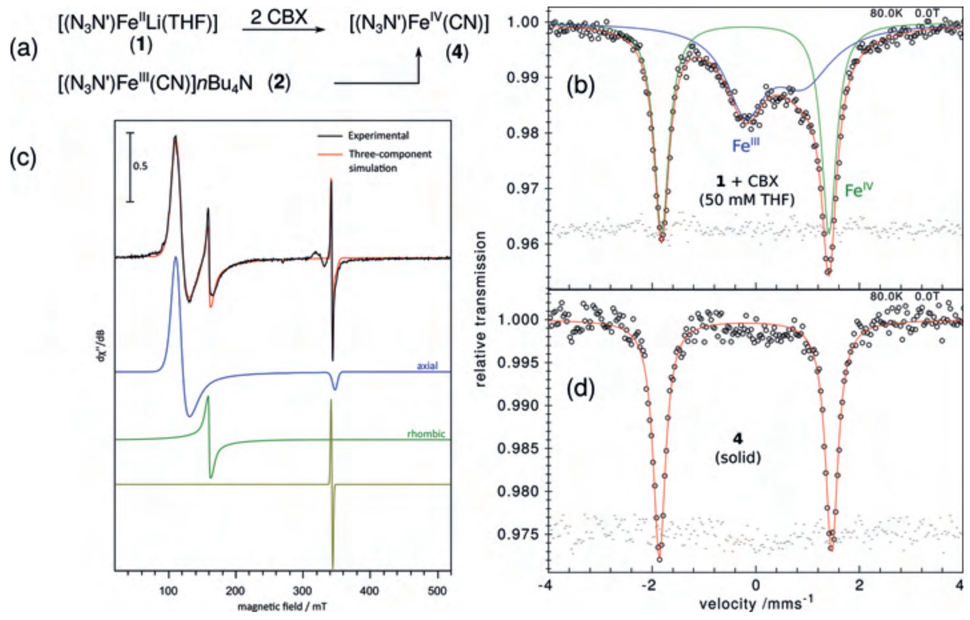

Figure 2. **(a)** Reaction scheme leading to the formation of the Fe(IV)-cyanide complex **4**. **(b)** ^{57}Fe Mössbauer spectrum of a freeze-quenched reaction between the ferrous precursor **2** and 2 equivalents of the hypervalent iodine reagent (CBX) shows a mixture of the ferryl and ferric species, thus revealing the ability of CBX to perform single electron transfer and group transfer reactions. **(c)** X-band EPR of a freeze-quenched reaction between **1** and 1 equivalent of CBX showing the formation of a major axial species associated with complex **2** and an unknown rhombic species. (d) ^{57}Fe Mössbauer spectrum of **4** prepared by one-electron oxidation from **2**.

The negative isomer shift (–0.20 mm/s at 80 K) and the large quadupole splitting ($|\Delta E_Q|$ = 3.32 mm/s) combined with the diamagnetism found in NMR support the electronic configuration in which the four d electrons are paired in a doubly-degenerate molecular orbital. The use of applied-field Mößbauer revealed an symmetric electric field gradient around the three-fold symmetry axis of the complex. The synthesis of this complex from a ferrous precursor employing a hyper-valent iodine reagent forms transiently a ferric species captured by freeze-quench Mößbauer. The EPR investigation of the ferric intermediate after isolation and purification show a clear axial species with small zero-field splitting, which is typical of high-spin Fe(III) and with the axial symmetry expected from the crystal structure. However, freeze-quenced reaction with the iodione reagent revealed ca. 20% of a rhombic species whose structural interpretation is still ongoing.

In another study in collaboration with Prof. Dr. Karsten Meyer from the Friedrich-Alexander-Universität Erlangen-Nürnberg we employed X-ray absorption spectroscopy (XAS) in transmission mode and in high-energy resolution Kβ-detected mode (HERFD XAS) at the Fe K-edge to study a series of adamantylimido complexes supported by a tricarbene ancillary ligand. This was one of the rare cases in which the ligands are able to stabilize a wide range of metal oxidation state: from +II up to +V. The interpretation of the pre-edge absorption peaks according to time-dependent density functional theory (TDDFT) revealed the interplay of π-backbonding in the low-valent limit and π-donation as the oxidation state increases.[4]

Complexes with non-innocent ligands

Depending on the energy level of the ligand- and metal-based molecular orbitals and the redox properties of both, the unpaired electrons at the valence shells can shift between the metal and the ligand. For example, the interaction between a metal M in the oxidation state n with a ligand L can result in a M^{n}(L) or a M^{n-1}(L$^{+\bullet}$) species. The ability to employ spectroscopic techniques to differentiate between isoelectronic species is important to understand their reactivity and which factors favor each species. In the case of an oxidation or reduction, the differentiation between a metal-centered or ligand-centered redox event is very informative on the mechanism and properties of the formed species.

In a collaborative work with Prof. Dr. Karsten Meyer from the Friedrich-Alexander-Universität Erlangen-Nürnberg, [5] we employed high-energy resolution Kα-detected X-ray absorption spectroscopy (HERFD XAS) at the Co K-edge to assess whether the one-electron oxidation of a Co(III)-mesitylimido yielded a Co(IV)-imido or a Co(III)-imidyl, being the latter a ligand radical species. The differentiation has implications in metal-catalyzed *N*-group-transfer chemistry. The position of the rising edge and the first moment of the pre-edge peak at nearly the same energy indicated that both Co(III)-imido and its one-electron oxidation product had metal centers with similar effective nuclear charges, hence the same oxidation state. The spectra calculated by TDDFT showed great agreement with the experimental data, which motivated their use in the data interpretation. The low-energy side of the pre- edge peak of the oxidized product is largely a transition from Co 1s to N-radical bearing a spin-up electron, further corroborating the imidyl assignment.

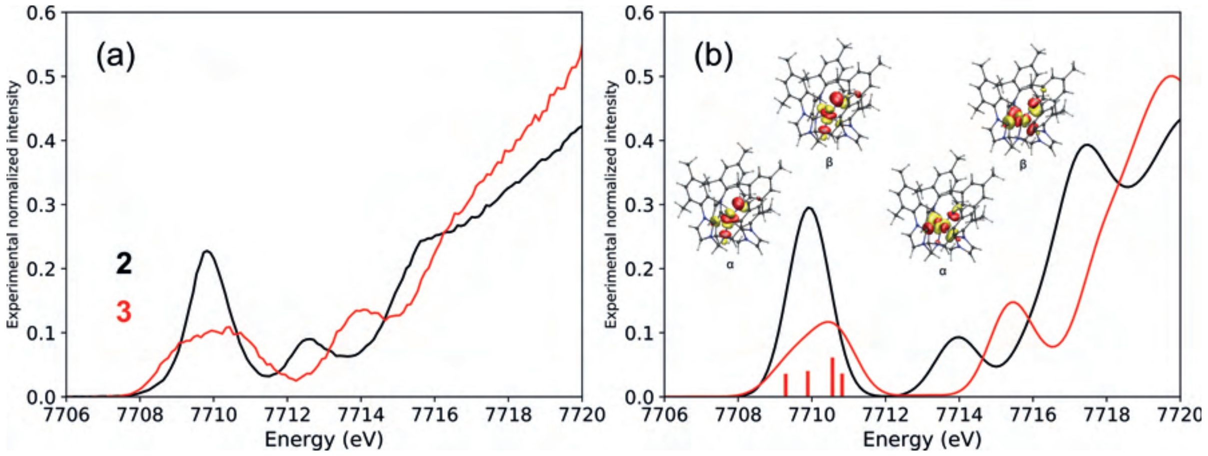

Figure 3. **(a)** Experimental Co K-edge HERFD XAS of the Co(III)-imido complex **2** and Co(III)-imidyl **3**. **(b)** Calculated spectra by TDDFT with acceptor natural transition orbitals associated to the transitions in the pre-edge of **3** shown as red sticks. Energy shift: 93.2 eV, lineshape: Gaussian, line width: 1.3 eV.

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X-ray Spectroscopy Instrumentation

Introduction

In studies of complex catalysts and metalloproteins, X-ray emission spectroscopy (XES) and X-ray absorption spectroscopy (XAS) play major roles in describing the local geometric and electronic structure. XES studies in the Kß main line and valence -to-core (VtC) regions attract particular interest because these spectra can provide element selective information about spin states and coordination environments, respectively. Recent experiments showed that analysis of weak VtC spectra can help to identify ligands surrounding the probing atom and overcome many of the limitations associated with EXAFS and XANES techniques [1,2,3]. Another perspective approach is enhancement of XAS features by recording fluorescence from VtC emission events [4].

During the last years, the Department of Inorganic Spectroscopy extensively enhanced capabilities of in-house tools for spectroscopic analytics. The research in the X-ray Instrumentation group is focused on the development of new instruments and methods for x-ray emission and absorption spectroscopies.

PINK: a new tender x-ray facility for an x-ray emission spectroscopy

The goal of the PINK project is to offer world-class capabilities for studying complex catalysts with a strong emphasis on non-resonant XES in the tender X-ray energy region (2-5 keV). An important component of the design of PINK has been the capabilities high sample throughput and time-resolved (0.1s-10s) measurements.

Construction of the PINK branch at the EMIL beamline (BESSY II synchrotron source) in Berlin was completed in late 2019. It is designed to operate in the tender x-rays regime with energies ranging from 2.2 to 9.5 keV. This energy range provides access to XES and XAS studies of transition metals ranging from Ti to Cu (K*α*, Kβ lines) and light elements P, S, Cl, K, Ca (K*α*, K), as well as Zr to Ag (L*α*, Lβ)I lines. The beamline (see Figure 1) is operated in two modes. In the high flux mode, a multilayer (ML) monochromator (E/ΔE≈30÷80) focuses beam in a 30μmx500μm

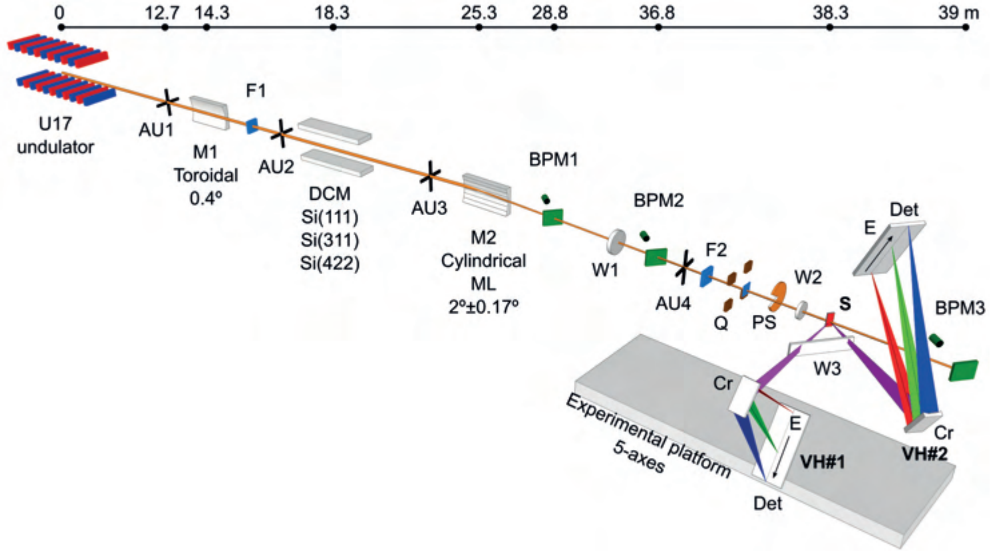

Figure 1. Layout of the PINK instrument. Beamline optics: toroidal mirror M1, optional double crystal monochromator (DCM), cylindrical multilayer monochromator M2. Apertures: AU1, AU2, AU3, JJ. Filters: F1 - water-cooled diamond attenuators, F2 – 3 sets by 6 attenuators each (C, Al and Ta). Optical beam position monitors: BPM1, BPM2 and BPM3. Quadrant I0 monitor: Q. Photon shatter: PH. Vacuum windows: W1, W2, W3. Sample holder: S. Atmospheric von Hamos spectrometer: #VH1: (analyser crystal – Cr, detector – Det). Vacuum von Hamos spectrometer: #VH1

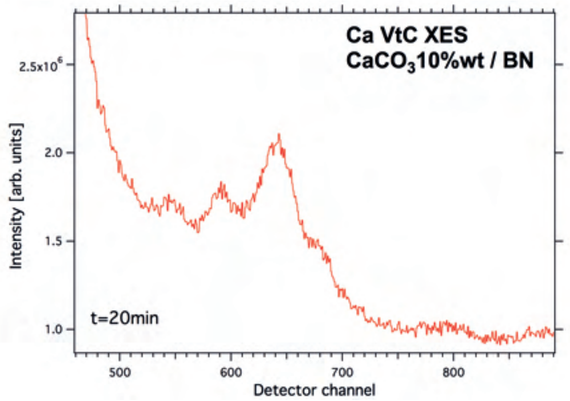

Figure 2. Ca VtC XES of CaCO3 10%wt/ BN powder mixture.

(VxH) spot and provides high photon flux (10^{14} ph/s @ 2-5 keV) allowing non-resonant XES measurements of very dilute substances. Fluorescent X-rays can be analyzed by two in-house designed short radius von Hamos crystal spectrometers. High energy resolution of ΔE=0.4-1.2 eV was achieved by using eight diced Si, Ge and quartz crystals optimized for operation at large (82°-55°) Bragg angles. Delivered in the beginning of 2022 a Si(311) crystal now allows VtC XES measurement of Ca complexes at more favorable Bragg angle of 69-71° (Figure 2). Both spectrometers can be run independently, thus we are able to record non-resonant XES spectra for two elements simultaneously - so called "two-color" experiments. XANES and high energy resolution fluorescence (HERFD) techniques are available in the second - high monochromatic mode ($E/\Delta E \approx 10000 \div 40000$) with the help of a DCM monochromator, which results in reduced photon flux intensity [5].

Commissioning of the high flux mode was done during the 2020-2021 timeframe. Since the beginning of 2022, the station is also opened for external users via the BESSY general user "GATE" platform [6]. Commissioning of the high-monochromatic mode is planned in 2023.

The PINK staff (Perdekov and Pereira of the MPI CEC) provides full user support for both internal (CEC) and external researchers. The Covid-19 pandemic introduced many restrictions on traveling and user access. Early in 2020, we have started extensive activities to enable experiments at the PINK via remote access or/and with limited personnel. We provided live automatic upload of the experimental data to the cloud server and access to an electronic logbook containing all measurement parameters. The ongoing experiment can be monitored via web browser.

Another substantial improvement in the PINK beamline IT infrastructure is transfer of the control system to docker containers, which make it more user friendly and facilitate maintenance and backup processes.

Development of the sample environment at the PINK

Due to the high photon flux available at PINK, radiation damage is a significant issue and requires focused design strategies in order to reduce the dose on a sample. One such strategy is the continuous scanning of the sample with a high speed in order to reduce the radiation dose on any given a spot. Recent measurements of $[Ru(NH_3)_6]Cl_3$ complex showed radiation damages already after 0.2-0.5 s under incoming photon flux of 10^{13} ph/s (Figure 3). By increasing the sample scanning speed, we can reduce instantaneous irradiation time down to 50 ms, thus enabling data on a undamaged sample to be obtained.

There are two more ways allow to decrease radiation damages of the specimens: using high flow rate liquid cells and putting samples at cryogenic temperatures. Low temperatures also help to stabilize very reactive intermediate complexes. We designed in-house two sample environment vacuum chambers (SEC) for the PINK setup. The first chamber operates at room temperature and can accommodate up to 4 solid samples and a liquid flow cell or an electrochemical cell. This chamber has been extensively used for the PINK set-up commissioning and studies of ruthenium and phosphorus complexes (see Figure 4) in solid and liquid states [7,8].

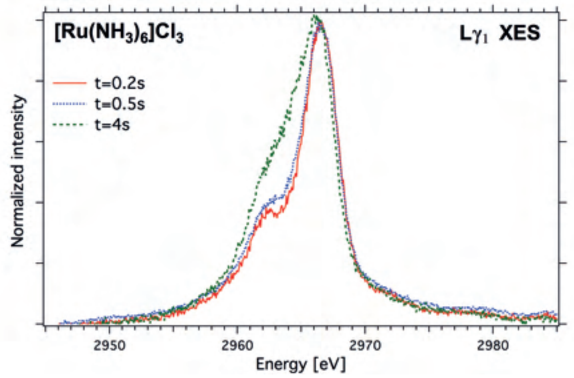

Figure 3. Radiation damage of $[Ru(NH_3)_6]Cl_3$ under 10^{13} ph/s photon flux.

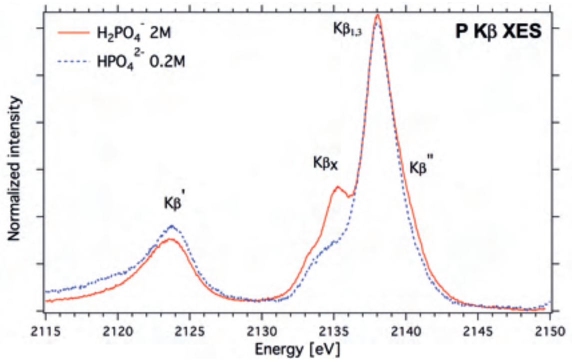

Figure 4. P Kβ spectra of NaH_2PO_4 and Na_2HPO_4 in solution.

Recently, we extended the capabilities of the electrochemical experiments by installing a LED light source. These developments were made for an external group from University of Zürich (research proposal 221-11206-ST), who performed unprecedented two-color experiment on photo-electrocatalytic water oxidation on iron titanate (Fe_2TiO_5) photoanode. Another external research project uses Pd Lβ VtC XES for studies of N-heterocyclic carbene bond formation in palladium (research proposal 222-11710-IN/OT).

The second - cryogenic chamber - designed in collaboration with the Sample Environment Group (HZB) accommodates up to 8 samples at temperatures down to 15K. Large efforts were undertaken to utilize graphenic carbon windows as the material for vacuum windows in the low temperatures cryo-SEC as opposed highly toxic beryllium windows, which are often used in such setups. Using this chamber, we have performed Kβ VtC XES measurements of S, Fe, Co, Ni, Cu and Ru(Lβ VtC) complexes in the form of powders and frozen solutions with concentrations down to 10mM/l [9,10, 11, 12]. At this stage, there have already been 5 publications resulting from work at PINK, with several more in progress [7-14].

New projects have started in 2022

Beside the PINK project the X-ray Spectroscopy Instrumentation group takes part in other infrastructure projects within the Department of Inorganic Spectroscopy.

- In the middle of 2022 a new project of building of a multi-technique P63 beamline at PETRA (Hamburg) for studies of catalysts was started. Our group takes part in development of XES and SAXS tools, as well as planning of sample environment.
- During 2022, we have been responsible for development and installation of the control and acquisition systems for the newly constructed experimental facility for the time-resolved soft X-ray XAS at the CEC MPI. The key strategy was unification of the hardware and software used at the facility with the control system at the PINK beamline. This allowed us to decrease drastically resources needed for the software development and will make maintenance of the control system easy and reliable.
- During this reporting period, we were also involved in the design of a new end-station for soft x-ray XAS using a TES detector at the UE52 beamline at the BESSY-II synchrotron source (Berlin). This work in progress in close collaboration with HZB.

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Investigation of Trends and Intensity Mechanisms of Transition Metal Halides by X-Ray Emission Spectroscopy

The elucidation of catalytic cycles and the understanding of mechanisms within a catalytic cycle are most crucial towards understanding how the structure of a catalyst can influence the performance and the selectivity of a reaction. Not only the electronic structure of the transition metal center but also the ligand environment (first and second as well as higher coordination spheres) are key factors which govern reactivity. A variety of spectroscopic methods gives insight into the geometric and electronic structure of a metal center, but only few spectroscopic methods directly probe the ligands that are bound to that metal center. Valence-to-Core X-Ray Emission Spectroscopy (VtC XES) gives insight into the nature of bound ligands due to probing transitions from mainly ligand based ns and np orbitals into metal 1s orbitals (Figure 1).[1]

VtC transitions are known to gain intensity by mixing of the ligand donor orbitals with metal p orbitals.[2] One factor influencing the amount of this p orbital admixture is the bond length, which increases from MCl_4 to MI_4, thus explaining the correlation between shorter bond lengths and higher intensities with constant metal center. Further, we were able to show that the origin of p contribution stems almost exclusively from metal 4p orbitals by analysis of orbital coefficient matrices (c^{mol}, c^{atom}) and orbital overlap matrices in addition to Loewdin population analysis.

However, there must be other factors contributing to the observed intensities. It was found that, when looking across the metal series ($MnCl_4$ → $ZnCl_4$), the bond length

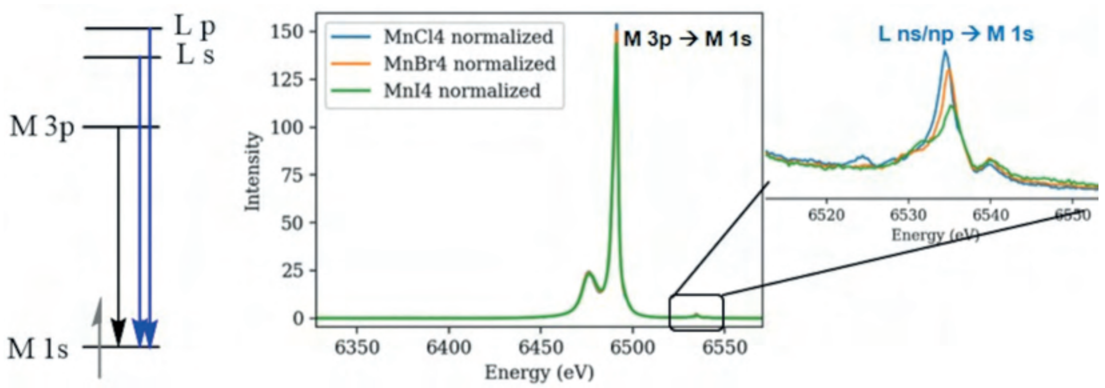


Figure 1. Origin (left) and shape of X-Ray Emission Spectra (VtC region enhanced, right).

It is not yet fully understood what mechanisms govern the intensities of these valence-to-core transitions. Within this project, our research provides insight in the experimentally observed trends in intensities within the Mn – Zn halide series $[MX_4][NEt_4]_2$. Further, computational studies were conducted in order to corroborate our observed trends and to investigate the mechanisms contributing to the VtC intensities. DFT calculated VtC areas and experimentally observed VtC areas show excellent correlation, while several trends were found. Within a series MCl_4 → MBr_4 → MI_4, a decrease in intensity (VtC area) is observed (Figure 2, left, right, see next page).

decreases, therefore the metal 4p contribution increases but, at the same time, the intensities of the VtC transitions decrease (Figure 2, right). Thus it is clear that, when looking at complexes with different transition metal centers, not only observables like the bond length but also the chemical environment (different 1s orbital contractions, different bonding environments) have an impact on the transition dipole moments. Identification and quantification of these factors is subject of our current research.

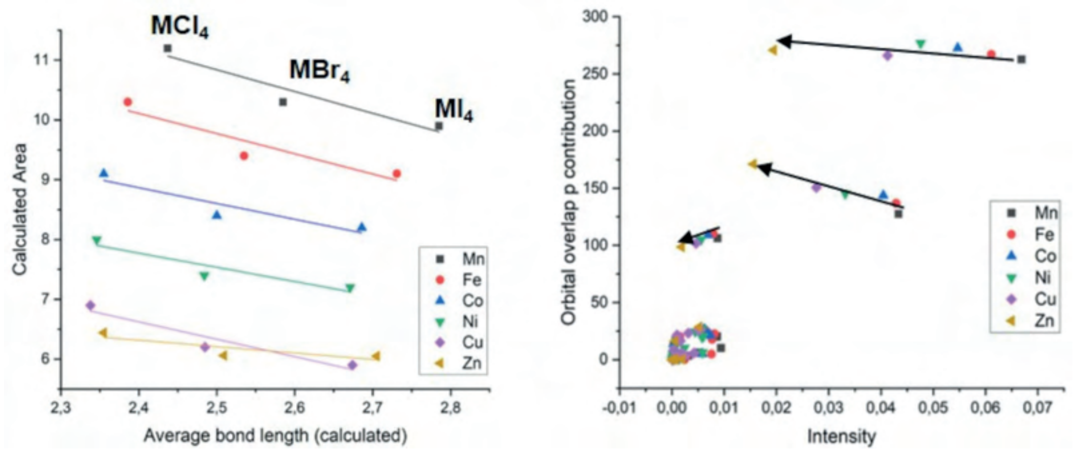


Figure 2. Left: Correlation between bond length and VtC area. Right: Correlation between the intensity of transitions and metal p contribution.

Electronic Structure Determination of Transition Metal Catalysts by Combining Experimental and Computational Studies

Low-coordinate Ni(I) complexes bearing chelate ligands have widely found application in catalytic C-C and C-X bond forming reactions.[3] α-Diimine (DI) Ni(I) complexes have been used in C,H activation and HIE reactions, where Chirik and co-workers were able to isolate rare monomeric [^{ipc}ADI-NiX] complexes (Figure 3, left) bearing bulky substituents for stabilization.[4] Fully evaluating the electronic structure of these compounds is crucial towards elucidating the full mechanistic cycle of catalytic reactions. Spectroscopic data obtained for [^{ipc}ADI-NiX] render an S=1/2 ground state (SQUID, EPR). For α-diimines and related ligands, e.g. PDI, the bond distances a – c (Figure 3, right) are crucial indicators for the redox state of the ligand.[5] The observed bond lengths are consistent with a neutral ligand and thus Ni(I) d^9 electronic ground state.

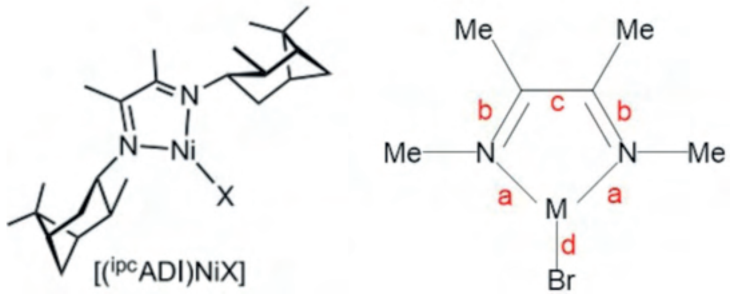
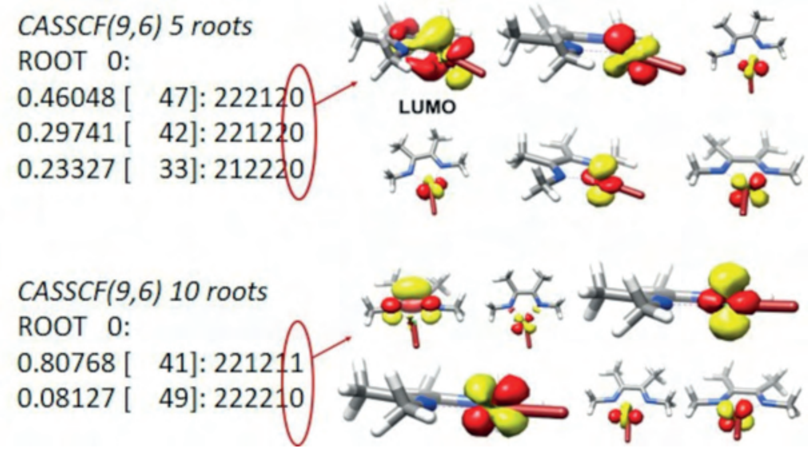


Figure 3. Structure of [^{ipc}ADI-NiX] (left) and the truncated system ^{Me}ADI-NiBr (right).



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CASSCF(9,6) 5 roots
ROOT   0:
0.46048 [    47]: 222120
0.29741 [    42]: 221220
0.23327 [    33]: 212220

CASSCF(9,6) 10 roots
ROOT   0:
0.80768 [    41]: 221211
0.08127 [    49]: 222210
```

Figure 4. CASSCF results of the ^{Me}ADI-NiBr system.

Simple DFT calculations (B3LYP/x2c) on the truncated system ^{Me}ADI-NiBr support the Ni(I) d^9 formulation. However, when more complex, multiconfigurational (CASSCF) or coupled cluster (DLPNO-CCSD(T)) computational methods are employed, the system seems to be less straightforward. Depending on the chosen input, for example the number of roots requested in a CASSCF calculation, both the Ni(I) d^9 (5 roots) and a ligand radical (10 roots) were obtained as electronic ground state (Figure 4).

The complete elucidation of the composition of the ground state wavefunction using our manifold of available methods (CASSCF-ICE and MRCC in addition to CASSCF and DLPNO-CCSD(T)) is topic of our current research on this project.

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Spectroelectrochemistry

In our group we combine electrochemistry with spectroscopy in order to elucidate complex reaction mechanisms or understand materials electrocatalytic activity. We put our effort to measure spectroscopy simultaneously with the electrochemistry using *in situ* or *operando* conditions. We have developed a series of spectroelectrochemical setups that allows us to measure UV-Vis, FTIR, EPR and X-ray spectroscopy under redox potential controlled conditions. Using these techniques, we have studied water oxidation catalysts (both molecular and heterogeneous) and enzymes (hydrogenases).

Hydrogenases

Hydrogenases are the most efficient noble-metal-free catalysts for H_2 production or oxidation. These enzymes use earth abundant metals in the active site (such as Ni or Fe) and work at almost no overpotential under mild conditions (Lubitz *et al. Chem. Rev.* 2014). Our group has extensive experience in protein film electrochemistry (PFE) and we have supported the group of James Birrell with such experiments. In brief, we investigated the dependence with the temperature of the electrocatalytic activity of the [FeFe] hydrogenase from *Thermotoga maritima.*[1] In another study we showed how the [FeFe] hydrogenase from *Desulfovibrio desulfuricans* (*Dd*H) lost its electrocatalytic current for hydrogen oxidation when exposed to sodium sulfite (Na_2SO_3) at low pH values.[2] In that work we propose that the use of sodium dithionite (NaDT), a common reducing agent in enzymatic work, has to be handled with extreme care, since one of the oxidation products of NaDT is Na_2SO_3. At low pH values, this will generate SO_2, which reacts with the hydrogenase, to generate some redox states ($H_{ox}H$ and $H_{red}'H$) that have been previously assigned by others (Stripp, S. *et al. Acc. Chem. Res.* 2018) as catalytically relevant states. Our experiments indicate that these states are just an artifact, and explain why the solution activity assays reported by their research group, contradicted the PFE experiments published by many other groups. Solution activity assays use NaDT as electron source to trigger H_2 evolution by the enzyme. These experiments showed maximum activity at pH 7, and almost no activity at pH<5, while PFE shows a constant increase of activity as the pH is lowered to pH 4 (at lower pH values, the enzyme is not stable anymore and it is denatured).

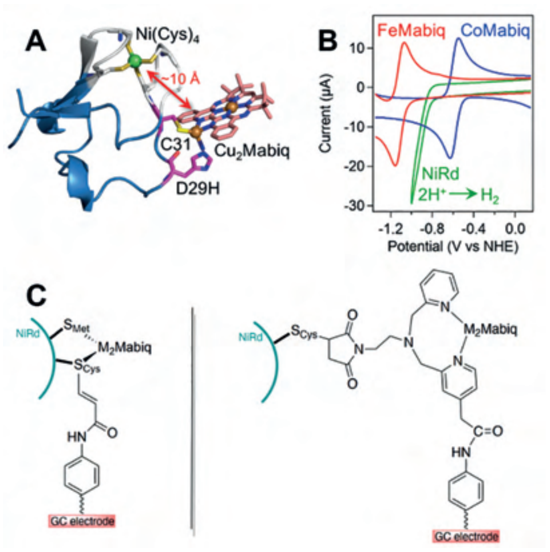

Figure 1. NSF-DFG proposed research. The project aims to study Mabiq-NiRd constructs **(A)**, where the Mabiq will mimic the iron-sulphur clusters of the native enzyme. The redox potential of Mabiq, can be tuned by varying the loaded metals **(B)** or an additional ligand that can be incorporated to the external metal and that can be used to link the hybrid construct to the electrode.

Our group has been also awarded with a DFG-NSF collaborative grant, were in collaboration with the groups of Prof. Hannah Shafaat from Ohio State University, and Prof. Corinna Hess from the Technische Universität München, we will be studying the mechanism of H_2 formation in a hybrid semisynthetic hydrogenase (**Figure 1**). Our main contribution to the project will be the spectroscopic studies of the different components as well as the design of electrode-linker-artificial enzyme constructs to allow spectroelectrochemical (EPR, X-ray and infrared spectroscopies) measurements.

We have further collaborated with James Birrell and Nicolas Plumere (Ruhr University Bochum-Technical University Munich) to show how we could reactivate the sulfide-protected *Dd*H inside a redox polymer film, which expanded the practical application of such systems from strictly anaerobic conditions to much less demanding conditions.[3] We also showed how by fine tuning the redox properties of the redox relay in the conductive redox properties of the redox relay in the conductive polymer, the bias of the system could be tuned from only H_2 oxidation (Plumere, N., Rüdiger O. *et al. Nat. Chem.* 2014, *Oughli, A.A. et al. Ang. Chem. Int. Ed.* 2015) to a reversible H_2 oxidation/evolution system.[4]

Since one of the new directions of the group has been to incorporate X-ray absorption spectroscopy to our repertoire of spectroelectrochemical (XAS-EC) techniques, we have explored the possibilities XAS-EC on protein systems, using a [NiFe] hydrogenase entrapped in a redox polymer electrode as a model system. The use of a polymer allowed to increase the enzyme concentration per surface area, allowing the collection of Ni K-edge XAS. By careful analysis of low temperature (20 K) reference samples, with the room temperature data from operando measurements, we could determine the maximum X-ray dose we could use to without photoreduction of the enzyme. To prevent beam damage, we defocused the beam and applied filters to attenuate the flux. Once this was optimized and we could observe changes with the applied potential on the edge and pre-edge positions, suggesting enzyme reduction at the most negative potentials. Nevertheless, the experiments proved to be challenging, and we summarized them in an article in Faraday Discussions, where we also reviewed the present literature on molecular X-ray spectroelectrochemistry and provided a list of recommendations for future experiments.[5]

Spectroelectrochemistry of Molecular Catalysts

We have designed a couple of spectroelectrochemical cells for freely diffusing molecular systems that can be used for XAS and for EPR. We used these cells to study a pentadentate Py_2^{Me}tacn Ru water oxidation complex. The XAS experiments showed a shift of the Ru K-edge as the potential was increased in aqueous electrolyte, consistent with an increase of the oxidation state of the metal. Interestingly, when we repeated the same experiment in anhydrous organic solvent, starting with the isolated Ru(IV)=O complex we could see an additional increase of the absorption edge. Repeating the same experiments on the EPR cell, we showed the formation, of a paramagnetic species in aqueous electrolyte as expected for a Ru(III) intermediate. But when we oxidized the Ru(IV)=O complex of a new paramagnetic species was observed, consistent with the formation of a Ru(V) species, which could not be observed in water, in agreement with the X-ray observations. The article was chosen as front cover for the Wolfgang Schuhmann Festschrift at *ChemElectroChem*.[6]

In a collaboration with the group of Antoni Llobet (ICIQ, Tarragona, Spain), we showed the importance of in situ spectroelectrochemistry, when we could follow the electrochemically induced changes on different molecular Ru water oxidation catalyst. EPR spectroelectrochemstry could identify the intermediates during the activation process of this catalyst upon repetitive cycling. The Ru(III) spectra changed the fitted g-values after the activation process, which was consistent with a reorganization of the ligand sphere. Moreover, after activation, the catalytic mechanism changes, shifting the redox transitions to lower potentials, and making possible the observation of a Ru(V) intermediate, since after activation, catalysis requires the formation of Ru(VI) **(Figure 2)**.[7]

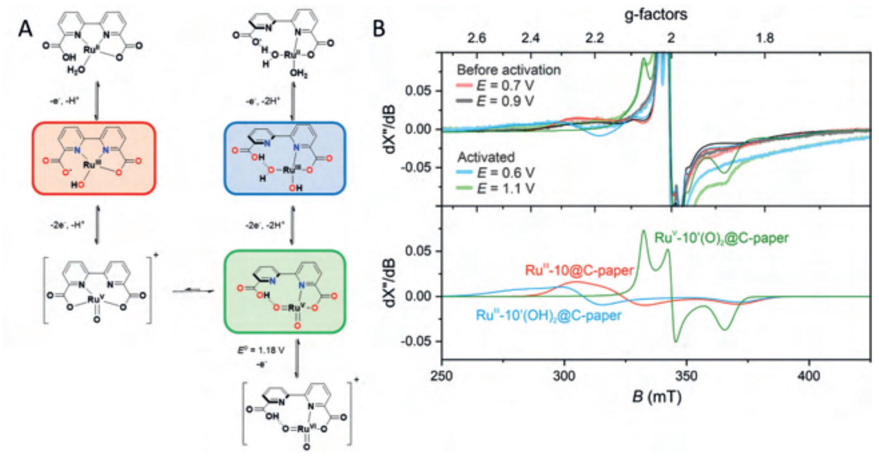

Figure 2. **(A)** Proposed mechanism based on the electrochemical results. The shaded squares indicate the paramagnetic species that could be measured by EPR. **(B)** EPR spectra (upper panel, thick shaded traces) measured in situ before and after electrochemical activation (by running 50 CVs between 0.2 and 1.2 V), on a carbon paper electrode functionalized with 10 (10@C-paper). The spectra can be simulated with a combination of two main components, a signal centered around g = 2.0, assigned to the carbon paper, and the anisotropic Ru signals plotted on the lower panel (present only after catalyst adsorption). Spectra were measured at 10 K in 0.1 phosphate buffer (pH 7.0).

In continuation with this line, we just started in 2022 to investigate a series of Co and Fe molecular complexes for CO_2 reduction, using a combination of electrochemistry, with EPR and X-ray spectroscopies.

Heterogeneous Cobalt-Iron oxides for water oxidation.

As part of the DFG Collaborative Research Center / Transregio 247 we are currently investigating Co/Fe oxides for water oxidation using a combination of soft and hard X-ray emission (XES) techniques to investigate the synergistic effect of these metals in catalysis. In particular we want to interrogate the electronic structure of these using these techniques, in order to understand better the observed catalytic properties. We investigated Fe-substituted spinel materials obtained by nanocasting[8] as well as the effect of laser-pulse post-processing treatment on these materials.[9] We also studied the effect of combining these materials with boron during its synthesis and how this changed the electronic structure around the Co.[10] We also provided similar XAS/EXAFS support in two more publications within this collaborative network.[11-12] For more details see the separated report on the CRC/TRR 247 project.

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Synthesis of Model Compounds

Research in my group focuses on the synthesis of small molecular model complexes for spectroscopic investigations. Systematic variations of structural and electronic features in a series of compounds of similar composition allows to correlate the spectroscopic response with structure. Our samples are typically analyzed by standard methods and their structure determined before they are further investigated (Mössbauer, EPR, SQUID, XAS, etc.). The combination of exact structural data with high-quality spectroscopic measurements of model compounds makes it possible to test and improve quantum chemical methods which in return help to interpret data obtained from catalytically active systems.

Model Systems for Nitrogenase

We have been working on modeling the catalytically active site of nitrogenase for some time. This bacterial enzyme catalyzes the conversion of atmospheric nitrogen to NH3 under physiological conditions. Ammonia is the primary source for the biosynthesis of essential nitrogen compounds in these bacteria and of plants which live in symbiosis with such organisms.

The chemical activation of nitrogen is extremly challenging since the triple bond of molecular nitrogen is the most inert small molecule one could think of. We have learned a lot about the chemistry and structure of nitrogenase but the exact electronic structure in the reaction cycle, the catalytic mechanism and the function of the interstitial carbon atom[1] in the molybdenum cofactor remain unclear. The metallic cofactor FeMoco in nitrogenase has been identified to be the active site of the enzyme where nitrogen binds and ammonia is released. It is basically composed of seven iron-, a molybdenum-center, nine sulfides, and a central carbide ion (see structure of framework in Fig. 1).

We are particulary interested in the chemical function of the carbide ion in the cluster and have therefore tried to synthesize model systems that show similarities to the natural example.

We have investigated a series of carbon bridged dinuclear iron complexes which are accessible by reaction of bis(diphenylthiophosphinoyl)methanediide^{2-} with FeCl2 in THF.[2] Figure 1 shows the composition and structure of complex 1 and demonstrates resemblance with FeMoco.

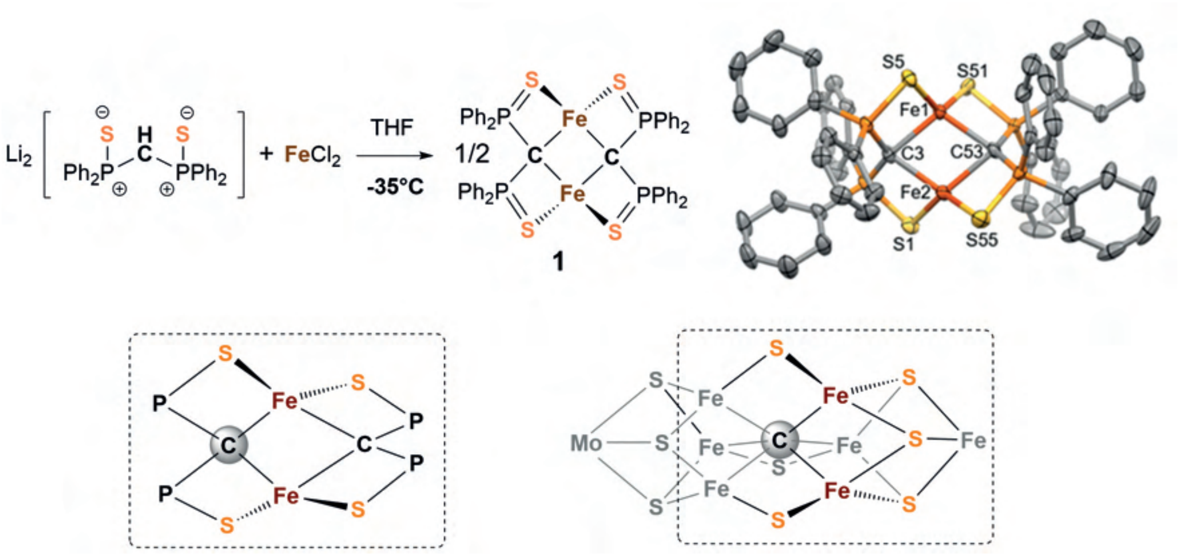


Figure 1. Synthesis and structure of **1** (top); Framework of **1** (bottom left) and FeMoco (bottom right).

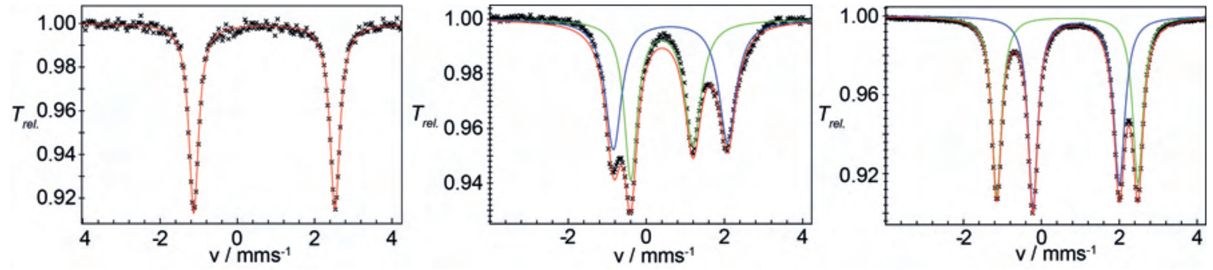


Figure 2. ^{57}Fe-Mössbauer zero-field spectra and simulations (color) of **1** (left), **2** (middle) and **3** (right) at 80 K in the solid.

Compound **1** can be reversibly electrochemically or chemically one-electron oxidized to form the mixed-valent Fe(II)Fe(III)-complex **2**. Figure 2 shows the zero-field ^{57}Fe-Mössbauer spectra of **1** and **2** which clearly show that the iron centers in the complexes are high-spin Fe(II)Fe(II) and Fe(II)Fe(III) ions, respectively.

Complex **1** can bind suitable substrates by expansion of the coordination number from 4 to 5 at one iron site. Figure 3 shows the change of the UV/vis spectrum upon addition of dimethylaminopyridine (DMAP). Spectrometric titration and x-ray structure anaylsis of the product reveal that **1** can exactly bind one molecule DMAP to form compound **3**. The ^{57}Fe-Mössbauer spectrum shown in Figure 2 (right) clearly indicates the inequivalence of the two Fe(II) sites in **3**.

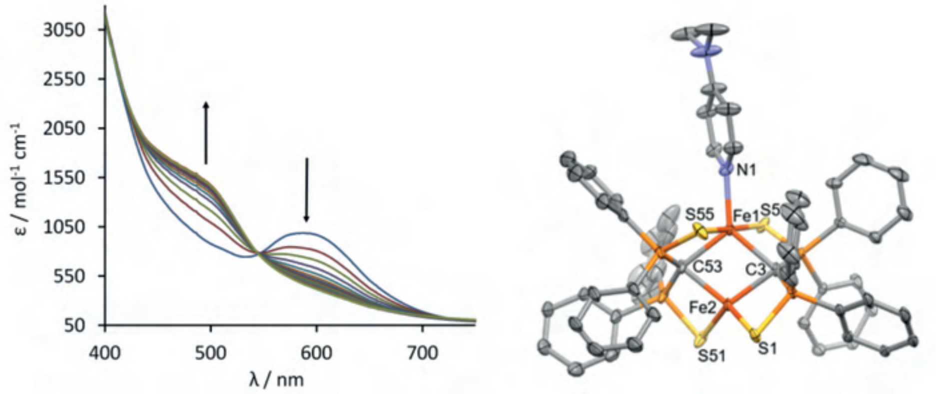
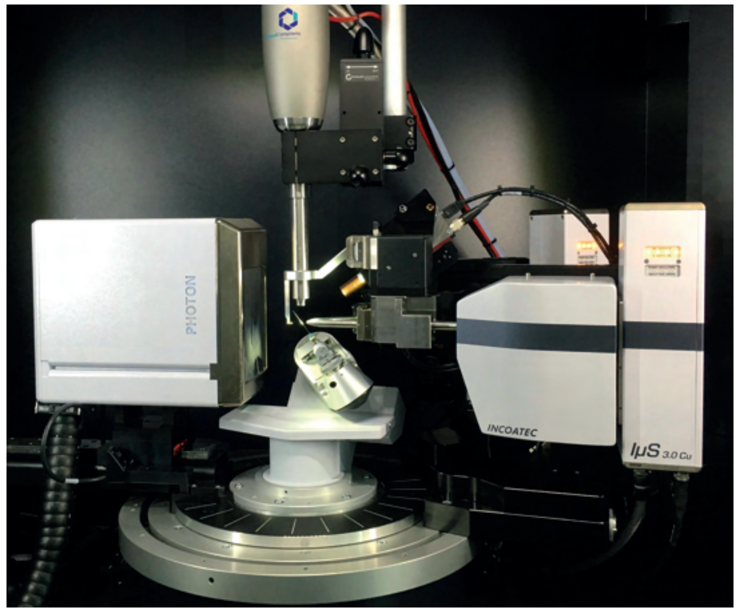


Figure 3. UV/vis spectrometric titration of **1** with DMAP (left) and crystal structure of **3** (right).

The work in my group focuses on the structure elucidation of small and medium-sized molecules using X-ray diffraction and NMR spectroscopy. Research on molecular transition metal compounds for catalysis relies on structure determination by means of X-ray diffraction on single crystals, since self-organization effects often dominate coordination chemistry and targeted synthesis of compounds is only possible to a limited extent. It is often not easily possible to determine the structure using other methods, such as NMR spectroscopy, since high-resolution NMR spectra cannot normally be obtained in the presence of paramagnetic metal centers. Independently of this, the X-ray structure analysis of the single crystal provides highly precise information about the three-dimensional arrangement of atoms and produces precise bond lengths and bond angles, which are of fundamental importance for understanding the chemical properties of a compound. However, the prerequisite for determining the structure using this method are single crystals, which are not always easy to obtain, sometimes not at all. NMR spectroscopy is very well suited for determining the structure in solution. It provides detailed information about the connectivity of atoms in molecules in diamagnetic compounds, but cannot determine exact values for bond lengths and angles. However, it is an excellent and indispensable tool, especially for the rapid assessment of synthetic intermediates and for the characterization of target compounds.

X-Ray Structure Determination

Knowledge of the precise three-dimensional structure of the model compounds and catalytically active compounds studied in our departments is of great importance to understand the properties and reactivity of these molecules. The determined structure of the metal complexes also forms the basis of quantum mechanical calculations on these substances, which in turn serve to understand the reactivity and spectroscopic properties that are investigated in the department "Inorganic Spectroscopy" and the "Joint Workspace".



A Bruker D8 Venture with microfocus Mo- and Cu-Kα radiation, INCOATEC X-ray optics, Photon III detector and OXFORD Kryostream 800 (80-500K) is available for single crystal diffractometry.

A Bruker Avance III HD 500 MHz spectrometer with Prodigy cryo-probe (-40 to +70 °C) is used for NMR investigations. The probe allows the acquisition of 1D and 2D spectra of most relevant nuclei (1H, 19F, 13C, 15N, 29Si, 31P, ...)

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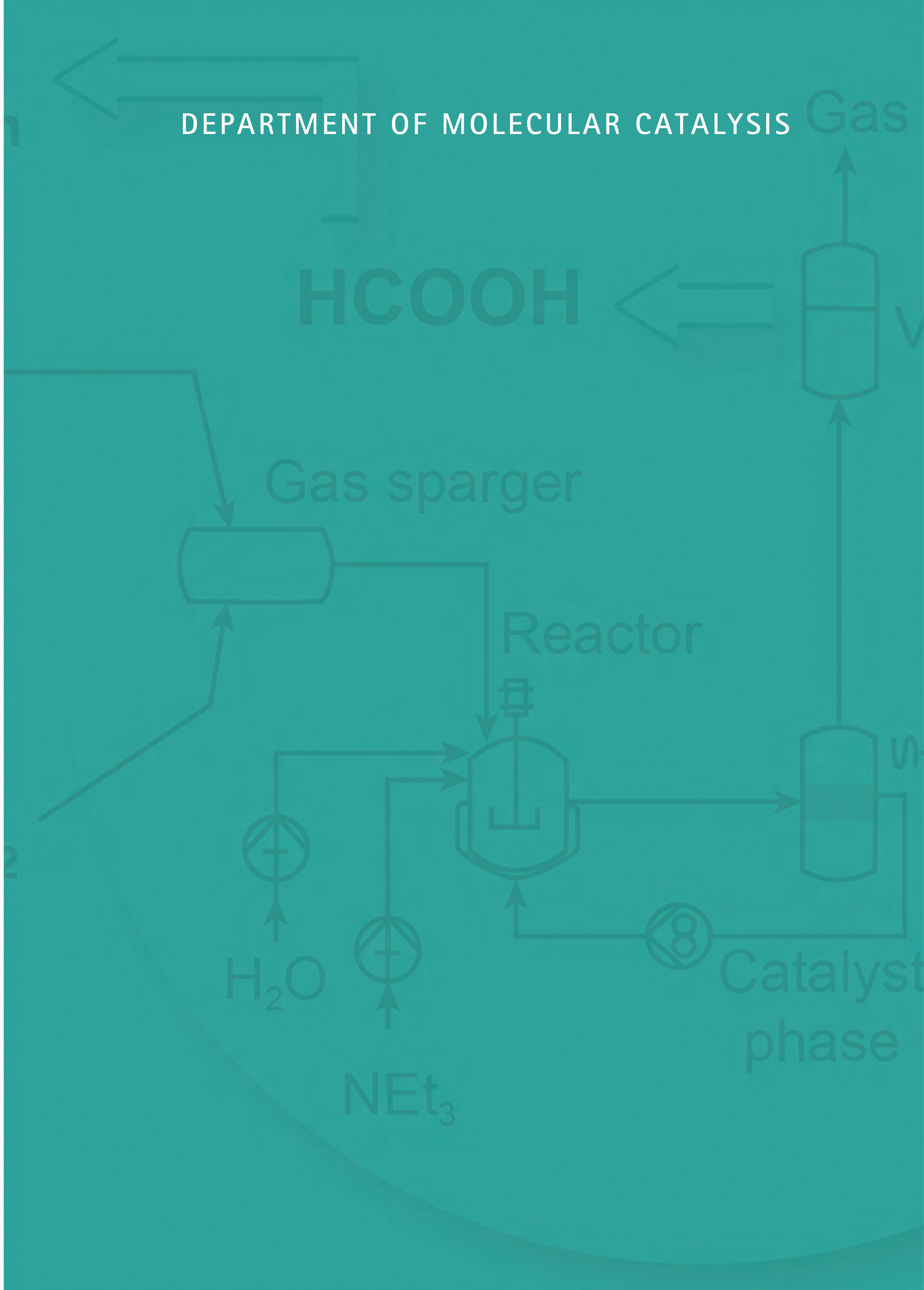
DEPARTMENT OF MOLECULAR CATALYSIS



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Research Concept of the Department „Molecular Catalysis“

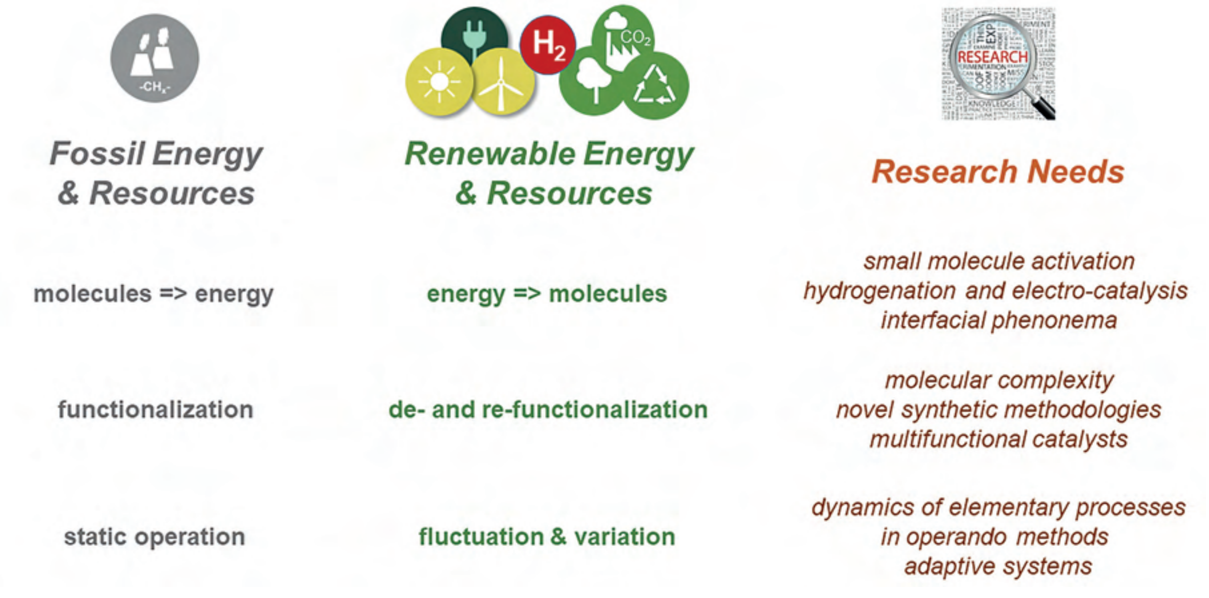
The long-term vision of our scientific activities is to contribute to a sustainable development at the interface of energy and chemistry by generating fundamental knowledge in catalysis. The advancement of specific expertise and know-how in our team is embedded in the framework of Green Chemistry, viewing the challenges associated with the transition into a de-carbonized energy system as an opportunity for a sustainable, de-fossilized chemical value chain, as summarized in Figure 1[1]. Potential synthetic targets range from liquid fuels as energy carriers, through large volume base chemicals, to high-value products of the chemical industry. Small molecule activation and reductive transformations for the de- and re-functionalization of renewable carbon resources define a common scientific framework across the individual activities. In particular, this requires understanding and mastering the dynamics of concerted or cascaded catalytic cycles and of interfacial processes in multiphasic systems.

Our research activities embrace (i) the design of catalysts, (ii) the exploration of synthetic pathways, (iii) the use of reaction media and interfaces as strategic control parameters, and (iv) the development of reaction engineering concepts. The scientific and methodological progress is firmly rooted in the molecular principles of organometallic chemistry. A primary goal within the reporting period and beyond is to expand these principles into neighboring areas such as materials catalysis or electrocatalysis. Identifying similarities and differences in the molecular principles of these sub-disciplines of catalysis is attempted by overcoming presumed boundaries often imposed through differences in traditional wording or conceptual descriptions of common phenomena.

Recent Developments and Trends

Catalyst Design

Activities in this area comprise the design, synthesis, characterization, and evaluation of molecular and nanoparticle catalysts. The developments follow a rational approach based on mechanistic knowledge, often integrated with and even guided by computational analysis.



Fossil Energy & Resources	Renewable Energy & Resources	Research Needs
molecules => energy	energy => molecules	small molecule activation hydrogenation and electro-catalysis interfacial phenomena
functionalization	de- and re-functionalization	molecular complexity novel synthetic methodologies multifunctional catalysts
static operation	fluctuation & variation	dynamics of elementary processes in operando methods adaptive systems

Figure 1. Research objectives of the WL team derived from the vision of a de-fossilized energy-chemistry nexus embracing the principles of Green Chemistry.

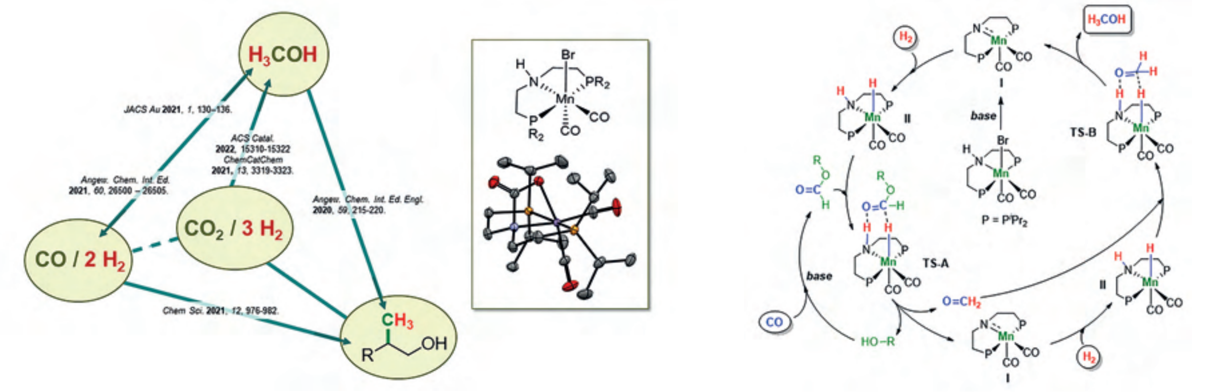


Figure 2. Catalytic interconversions of CO_2 and H_2 with CO, methanol, and methyl groups using Mn^{1+} catalysts as a useful manifold for chemical energy conversion and the mechanistic rationale for Mn catalysts involving P-N-P pincer-type ligands for metal-ligand cooperation. The X-ray structure (unpublished) shows a CO_2 adduct of the active catalyst I, which is most likely a dormant off-cycle species during CO_2 hydrogenation with this catalyst.

In organometallic catalysis, the pragmatic concept of exploiting the diagonal relationship between Ru^{2+} and Mn^{1+} in the periodic table in the quest for efficient catalysts based on 3d metals has proven highly prolific. In particular, the interconversion of CO_2 and H_2 with CO, methanol, and methyl groups using the Mn-MACHO framework has been systematically explored (Figure 2). The highly endothermic reverse water gas shift (rWGS) reaction shown as the dashed line can be circumvented by opening novel connections between the individual corners of the tetrahedron shown in Figure 2. This includes some remarkable transformations, such as the catalytic hydrogenation of CO [2] and CO_2 to methanol [3], as well as the dry reforming of methanol to CO and H_2 [4]. The latter reaction allows using methanol as a liquid transportation form of synthesis gas. Detailed experiment and computational analysis of the underlying reaction mechanisms [5] revealed the importance of formaldehyde, typically masked as (hemi-)acetals, as a common intermediate. This knowledge was exploited, *i.a.,* for novel synthetic methods for C-methylation [6-8].

During the reporting period, silanes R_3Si-H for challenging reduction reactions were also investigated in collaboration with the MPRG of Christophe Werlé. While our interest was initially sparked by using the polarized Si-H bond as a proxy for heterolytic cleavage of the H-H bond, several synthetically highly interesting applications have emerged from the MPRG’s contribution [9,10].

Notably, it was found that a Cobalt complex developed in the Werlé group allowed fine-tuning the reaction conditions to arrive at either the formate ($2e^-$), formaldehyde ($4e^-$), or methanol ($6e^-$) reduction level of CO_2 selectively [11]. In collaboration with the Neese group within the IMPRS research school, a mechanistic rationale for this adaptive performance of the catalyst could be derived [12] and expanded most recently to a volcano-plot analysis using the hydricity of the M-H bond as a key descriptor in collaboration with Prof. Clémence Corminboeuf [13].

The concept of “adaptivity” has intrigued our efforts in catalyst design during the reporting period. It allows the development of catalytic systems that flexibly adjust to fluctuations and variations in future energy and feedstock supply. A major pre-requisite for fully adaptive systems is that catalysts can be switched between two (or more) different states in a reversible, rapid, and robust manner: we call this the *R^3*-rule. This challenge was tackled based on the rapidly growing progress in our approach to catalytically active nanoparticles on molecularly modified surfaces (NPs@MMS), as summarized in a recent *Accounts of Chemical Research* article [14] and the report of the team of Alexis Bordet. The development has greatly benefitted from collaboration with the DeBeer and Schlögl departments regarding the characterization of the complex multifunctional materials, as well as with Prof. Bruno Chaudret at LPNO in Toulouse.

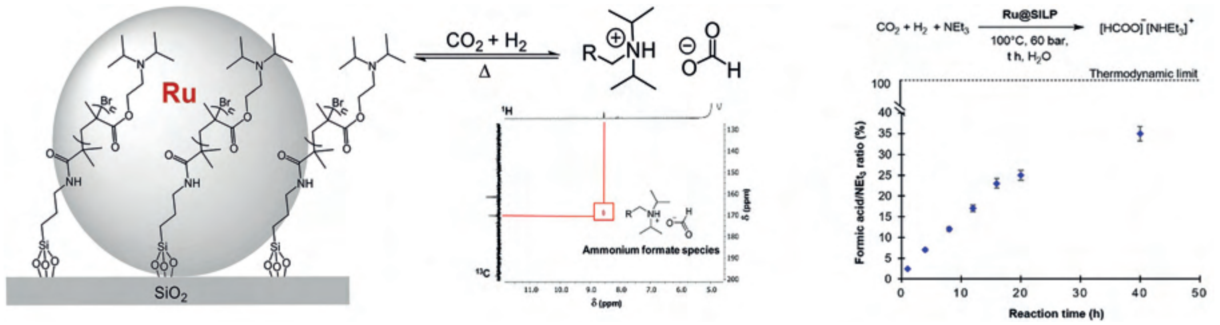


Figure 3. Switching of the surface properties due to reversible CO_2 hydrogenation to formate as the basis for the “adaptivity” of Ru-based catalytic system (for synthetic application and other adaptive systems, see the report by A. Bordet) and systematic development of a heterogeneous catalyst for CO_2 hydrogenation based on this serendipitous finding.

To enable "adaptivity," we proposed to modify a silica surface with a molecular unit that enables fully reversible interactions with CO_2 to change the chemical composition of the surface. The resulting equilibrium was hypothesized to modulate and ideally "switch" the catalytic performance of Ruthenium nanoparticles deposited on this matrix. The desired surface modification was achieved in collaboration with Prof. Philipp Jessop at Queens University in Canada, grafting on silica the PGS materials developed for CO_2 switching in his laboratory. Indeed, the selectivity of Ruthenium nanoparticles for hydrogenation reactions of different functional groups could be controlled and reversible with high precision and in almost real-time through the absence or presence of CO_2 in the hydrogen feed gas [15]. Detailed mechanistic studies showed, however, that the effect did not result from the CO_2/bicarbonate equilibrium as hypothesized in the design. Instead, the reversible hydrogenation of CO_2 to formate was identified as the molecular trigger (Figure 3, left). This unexpected finding is exploited more broadly for "adaptive" catalytic reactions. Notably, it also allowed us to design an exceptionally active heterogeneous catalyst for CO_2 hydrogenation to formate solutions as products (Figure 3, right), a reaction hitherto dominated mainly by homogeneous catalysis [16].

Synthetic Pathways

The main focus of this area is the exploration and evaluation of new synthetic methodologies for the toolbox of industrial chemistry. A longstanding program focuses on using CO_2 as raw material as a most attractive way to harness renewable energy into chemical energy carriers and value-added products (for example, see Figure 2). The selective synthetic conversion of lignocellulosic raw materials and platform chemicals continues to be an active field of activities, particularly as part of the Cluster of Excellence "The Fuel Science Center." A generic scientific challenge in this area is the controlled reduction of the oxygen content in the starting materials and its integration with C-C and C-X bond formation processes to build molecular complexity.

A new research line that was started with the implementation of the department at the CEC is the field of organometallic electrocatalysis. The corresponding team has been coordinated since 2020 by Dr. Nicolas Kaeffer, and recent progress is outlined in his report. As a basis for developing this research line, we attempted to harmonize the mechanistic concepts for CO_2 reduction in organometallic chemistry and electrocatalysis. The major review article covering nearly sixty pages in *Angewandte Chemie* has gained significant attention from both communities [17]. In this article, the pathways for CO_2 reduction with highly reduced metal complexes were characterized according to the elementary processes responsible for electron transfer as "electrons through metal (ET_M)" and "electrons through hydrides (ET_H)" mechanisms. In the ET_M pathway, the electrons are directly transferred into empty orbitals of CO_2 upon coordination either in a η^2(C=O) (Aresta type) or η^1C (metalla carboxylate) mode, followed by a proton attack (Figure 4). In the ET_H pathway, the highly reduced metal complex reacts first with protons to form a metal hydride, followed by CO_2 insertion into the M-H bond, similar to hydrogenation catalysis. Current activities focus on the elucidation of classical organometallic approaches to control these pathways [18] and their exploitation in synthetic transformations towards molecular diversity beyond C1 products by incorporation of additional substrates (electron through the substrate, ET_S), as highlighted in the report by N. Kaeffer.

The insertion of CO_2 into M-H or M-C bonds is a central elementary step for its use as a building block. While CO_2 chemistry is often associated with "CO_2 activation", we know from numerous studies in the literature and our contributions in this field that these steps are often facile and not rate-limiting [19]. Nevertheless, they are crucially important because they define the desired connectivity [20]. However, the main kinetic challenge to arrive at a catalytic cycle is often the cleavage of the resulting M-O bond under regeneration of the reactive M-H/C bond. Current activities, often in collaboration with Dr. Markus Hölscher at ITMC of RWTH Aachen for DFT analysis of the elementary steps and catalytic cycles, are directed to achieve such transformations directly, in addition to recently established pathways to use CO_2 as a building block via formaldehyde or CO as reactive intermediates (see also section 2.1). A CO-based pathway to the C2 product acetic acid starting from CO_2 and H_2 was demonstrated using methyl formate as an intermediate [21]. The complex catalytic system for the formal "isomerization" of methylformate comprising base-catalyzed decomposition to CO and MeOH and Pd-catalysed recombination to $MeCO_2H$ was optimized using a design of experiment approach increasing the TON from initially 11 to over 43000. The power of statistical data analysis and algorithm-based optimization is currently developed further as a broadly applicable tool as part of the activities in the NFDI4Cat consortium.

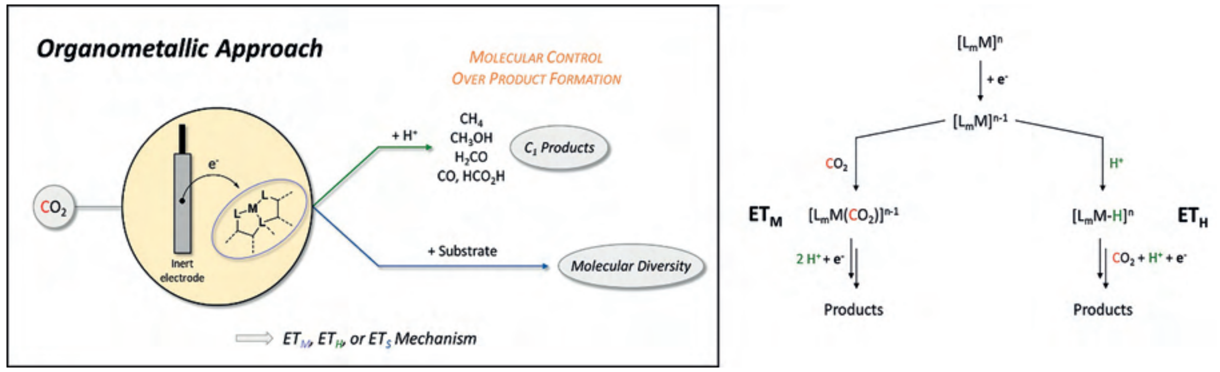


Figure 4. The concept of organometallic electrocatalysis for CO_2 reduction and utilization as a synthetic building block towards molecular diversity.

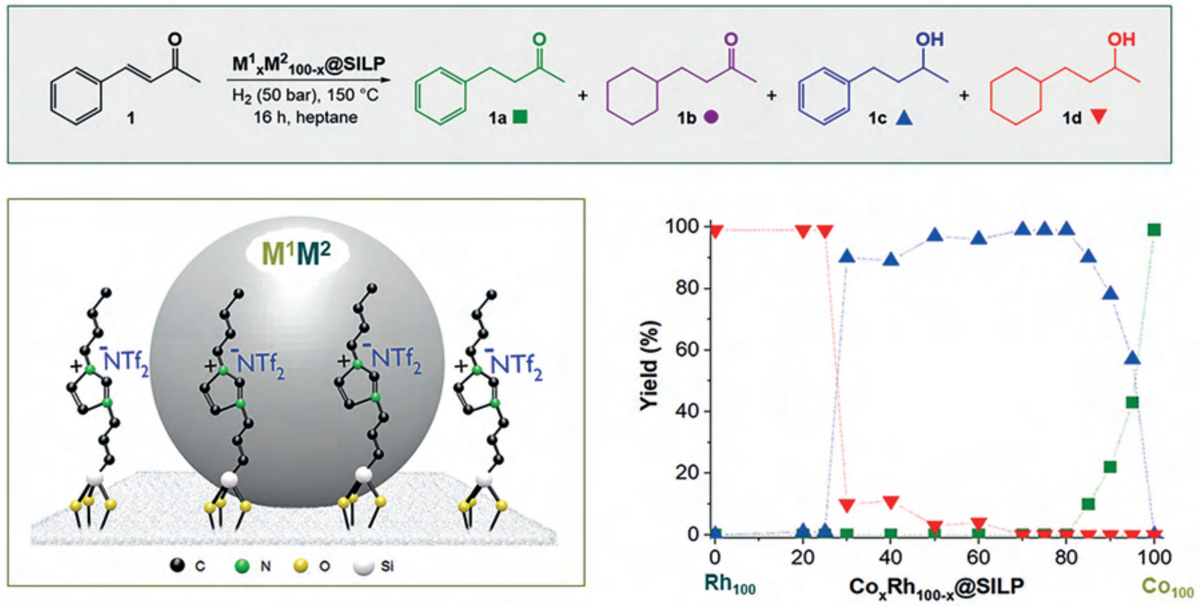


Figure 5. Selectivity control in multifunctional substrates through the defined composition of bimetallic metal nanoparticles in NP@MMS systems (M^1 = 3d metal, M^2 = 4d or 5d metal).

Another line of research continues to be the development of catalytic systems based on the NP@MMS catalysts to control the H-H bond cleavage from homolytic to heterolytic for the formal transfer of $2H^\circ$ or H^-/H^+ [xiv]. A range of unprecedented activities and selectivities [14] in hydrogenation and hydrogenolysis reactions has been achieved with catalysts explicitly designed for this approach (see the complete list of references in the report by A. Bordet). The possibility to generate bimetallic nanoparticles with precisely defined ratios of noble and non-noble metals has been particularly beneficial in this context. Figure 5 shows an example of Co_xRh_{100-x} catalysts demonstrating the remarkable sharp selectivity inversion around the $Co_{30}Rh_{70}$ ratio [22]. This effect has already been applied to many synthetically valuable reactions and expanded to other metal pairs such as Fe_xRu_{100-x} and Co_xRu_{100-x} [23,24]. The exploration of the approach is still ongoing, including the combination of metal nanoparticles with Lewis acids [25] or molecular complexes [26].

Reaction Media and Interfaces

Chemical transformations involving organometallic catalysts are typically carried out in the solution phase; hence, the solvent or reaction medium influences both the molecular transformation and the overall process. Of particular relevance in our research agenda are multiphasic systems involving liquid/liquid or solid/liquid interfaces. Research in this area aims to use the interactions and dynamics as strategic control parameters for the chemical transformations as well as separation and catalyst recycling processes.

A notable example of the influence on reactivity is the hydrogenation of fluorinated aromatics using NPs@MMS, where the interplay of low surface and solvent polarity proved crucial for high selectivities [27]. Supercritical carbon dioxide ($scCO_2$) was demonstrated to be a particularly attractive solvent for this reaction in collaboration with Nils Theyssen at the KoFo Technikum within the Joint Workspace [28]. Supercritical CO_2 was also shown to allow effective catalyst recycling in the newly developed amine-based catalyst system for reductive hydroformylation in the team of Andreas Vorholt [29,30].

An important methodological development to study the kinetic coupling of phase transfer processes and catalytic turnover was the design of a borescope technique to measure droplet sizes under operando conditions, even for high-pressure reactions in the Vorholt team. This novel analytic tool revealed a striking non-linearity in the kinetics of long-chain olefin hydroformylation in biphasic media resulting from the interference of the formed product aldehyde with the mass transfer across the interface. The resulting paper [31] received the remarkable result of both reviewers enthusiastically recommending "publish as it is," noted as unprecedented by the editors.

Crossing an aqueous/organic phase boundary is a significant challenge also in electrocatalytic processes with organic substrates. In a collaborative effort, Nicolas Kaeffer and Alexis Bordet were most recently able to devise a CNT-supported Pd nanoparticle catalyst achieving simultaneously the stabilization of Pickering emulsions and electrocatalytic proton reduction mediating H-transfer to hydrogenate olefins in the organic phase [32]. This opens new avenues for harvesting electrons directly for complex organic synthesis in electrocatalysis.

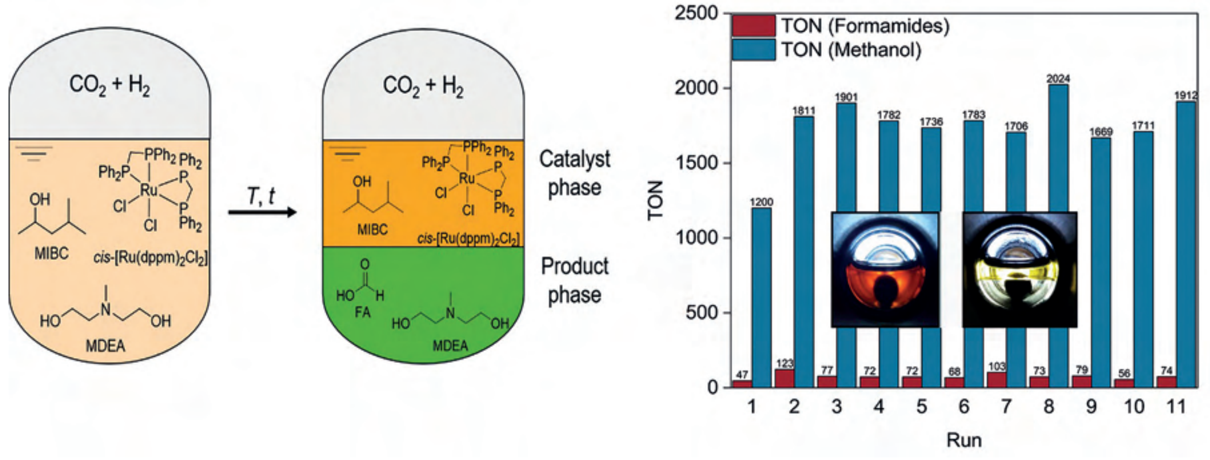


Figure 6. Self-separating systems for catalytic CO_2 hydrogenation. On the left, the concept is exemplified for hydrogenation to a formic acid/amine adduct; on the right are pictures of the two stages and recycling data for the hydrogenation to methanol.

In CO_2 hydrogenation, the products are often highly polar compared to typical solvents employed for dissolving the organometallic catalyst. By judicious choice of catalyst structure and solvent, it was possible to devise reaction media that self-separated into a product and a catalyst phase as the reaction proceeded. Efficient catalyst recycling was demonstrated for the hydrogenation of CO_2 to formic acid/amine adducts [33] and even methanol [34]. Current efforts are directed towards implementing (semi-)continuous processes based on similar latent and permanent multiphasic systems (see also section 2.4).

Reaction Engineering Concepts

A continuing goal of the research activities in this area is developing a flexible methodological platform to investigate molecular catalytic processes throughout their entire lifetime from activation to deactivation upon integration of the chemical transformation with the downstream processing, especially for catalyst deactivation [35]. Software-based monitoring, control, and data analysis coupled with increasing levels of automatization are part of the technical progress. Figure 7 shows the current array of available operando techniques and a picture of a corresponding experimental set-up as designed and developed by the team of Andreas Vorholt.

The teams working on this project typically comprise chemistry and chemical engineering expertise. The high degree of flexibility allows adapting the technical solutions quickly to newly emerging chemical transformations, as demonstrated, for example, by the implementation of magnetic inductively activated catalysis under continuous-flow conditions [36].

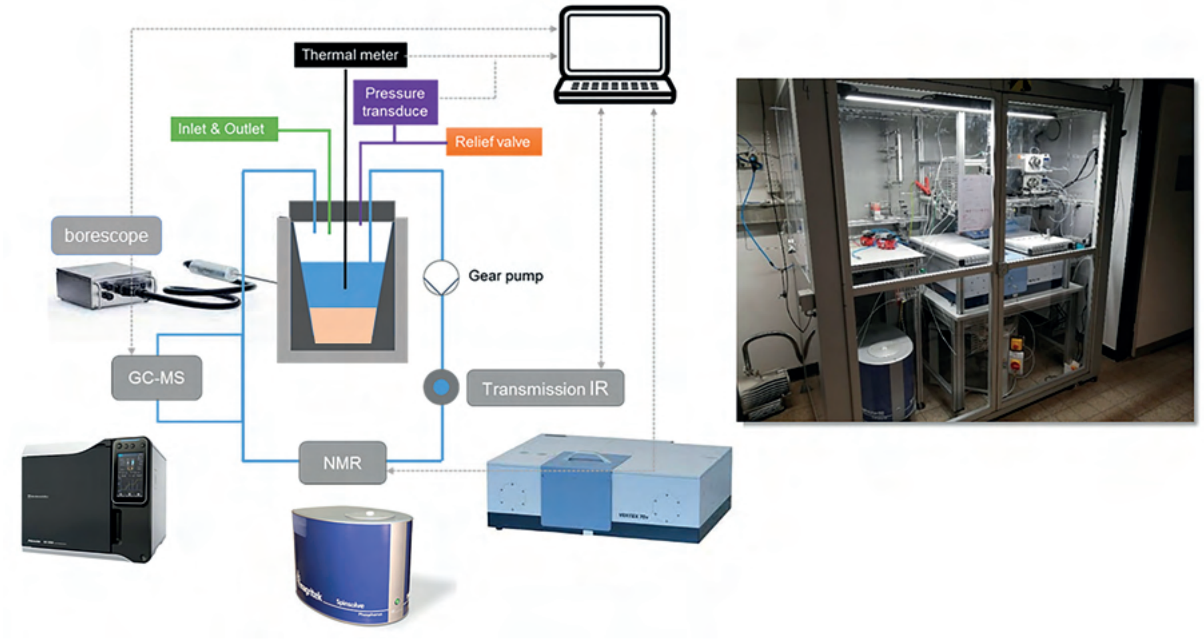


Figure 7. Flexible platform for operando studies of multiphasic molecular catalysis to monitor and control the dynamics of catalyst activation and deactivation, desired and undesired reaction pathways, and phase behaviour.

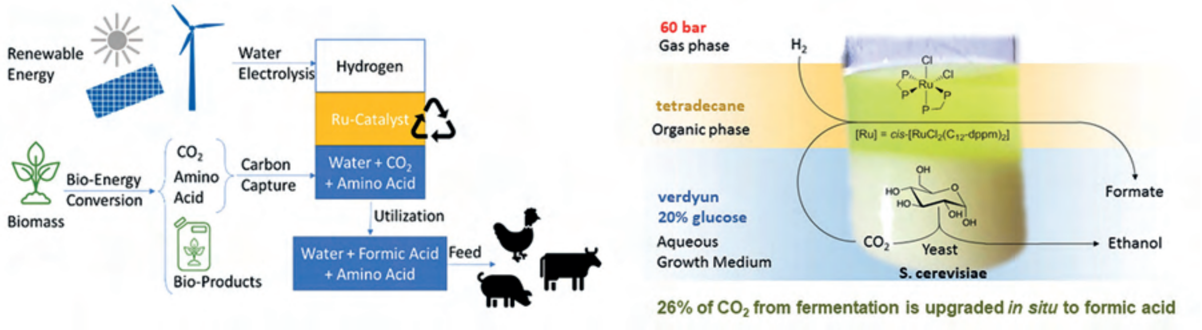


Figure 8. Integration of CO_2 hydrogenation with biogenic CO_2 sources (bioenergy conversion with carbon capture and conversion, BECCU).

The competence in multiphase catalysis allows the integration of sequential catalytic reactions to tandem and cascade processes of increasing complexity. Given the large potential of synthesis gas from renewable sources at the energy-chemistry interface, the Vorholt team focused on reaction sequences involving hydroformylation as a key step [37,38]. This included strategies for producing fine chemicals and advanced fuel blends [39,40].

The integration of reaction and separation steps is particularly important for value chains based on biomass-derived product streams. While many such process schemes are reported, there must be more systematic and model-based guidelines for solvent selection. An attempt to use predictive tools for solvent properties in this context was undertaken in collaboration with Dr. Jésus Esteban Serrano at Manchester University [41]. Reactive distillation was also envisaged as an alternative to this field's more widely studied extractive processes [42].

Biomass for energy applications such as biogas generation or ethanol fermentation is inevitably coupled with CO_2 generation. Using this biogenic CO_2 as a carbon source can contribute to genuinely carbon-neutral and even carbon-negative processes. The term bioenergy conversion with carbon capture and utilization (BECCU) has been coined for such processes that are particularly attractive for decentralized local value chains. In the team supervised by Giancarlo Franciò in the laboratories of the ITMC at RWTH Aachen, we have started to envisage this potential based on our competence in CO_2 hydrogenation and multiphase catalysis as part of our activities within the Fuel Science Center. Two concepts were developed to achieve maximum integration to avoid energy-intensive separation and purification steps. In one case, aqueous amino acids were used for CO_2 capture and as product solutions in combination with the generated formate, because both formic acid and amino acids are used as nutrients for animal feed [43]. It was demonstrated that the designed Ru catalyst was effectively retained in a special biphasic organic/water system, allowing for efficient recycling and avoiding metal contamination in the product solution. In the second approach, it was even possible to use the biphasic system for the integration of CO_2 hydrogenation directly with glucose fermentation [44]. The challenge to find reaction conditions compatible with both the chemo- and bio-catalytic transformation was tackled in collaboration with the group of Prof. Lars Blank in the Biology Department at RWTH Aachen. Remarkably, up to 20% of the CO_2 formed as a stoichiometric coupled product in fermentation could be upgraded to formate by catalytic hydrogenation in a single reactor unit.

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Multifunctional Catalytic Systems

Objectives

Harnessing renewable energy *via* hydrogen (H_2) as the essential molecular pivot allows the conversion of non-fossil carbon feedstocks (CO_2, biomass, recycled polymers) and opens new synthetic strategies for the production of fuels, fine chemicals, agrochemicals, and pharmaceuticals. Catalysts are essential to control the activation and transfer of H_2 defining a central pillar in science and technology for chemical energy conversion. While catalysts are traditionally developed to fulfill one specific task with maximum activity and selectivity, flexibility and adaptivity will become increasingly important in the future to cope with the dynamics of alternative energy resources and quality variations of chemical feedstocks. At the same time, adaptive systems are able to respond to rapidly changing market demand for products and enable decentralized and customized production. The fundamental principles to design, prepare, and control catalysts and catalytic reactions in a highly flexible or even adaptive manner are, however, very poorly developed.

Results

In our team, we approach this challenge using an organometallic approach to generate metal nanoparticles (NPs) on molecularly modified surfaces (MMS) as multifunctional catalytic systems for the activation and transfer of molecular hydrogen (H_2) (Figure 1). This produces NPs@MMS systems that are fully tunable, and which reactivity can be controlled through the rational choice of the individual parameters (composition of the metal nanoparticles, structure of the molecular modifier, nature of the support). We have recently highlighted this approach in an account,[1] and published several research papers on this topic in the past three years.[2a-i]

While the developed catalysts present often outstanding properties regarding their dedicated tasks, their performance is typically optimized to remain static. However, the flexible molecular toolbox for the generation of such materials appeared promising to push the boundaries towards adaptive catalytic systems - referring here to materials that offer control over their reactivity by external stimuli in a fully reversible manner and in almost real time under operating conditions.

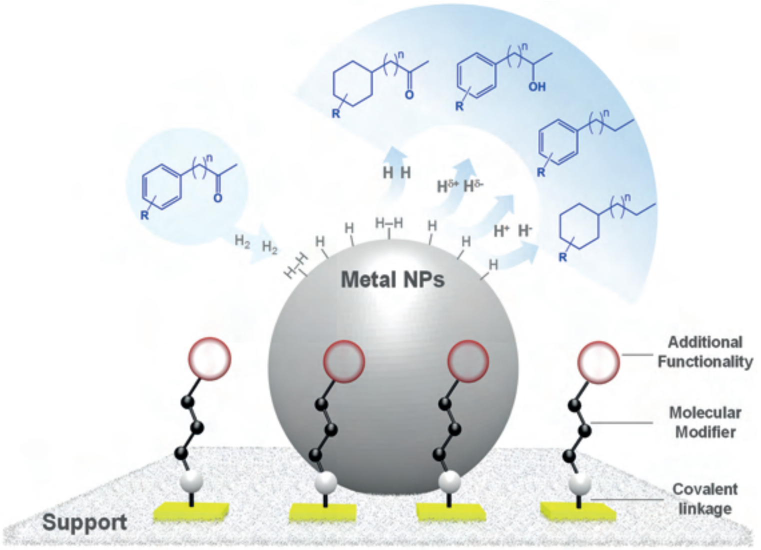

Figure 1. Schematic representation of the concept of nanoparticles on molecularly modified surfaces (NPs@MMS) for controlled hydrogenation and hydrogenolysis

Adaptivity to intermittent energy supply: activity switch

A key control parameter in catalysis is the reaction temperature as it directly impacts on the activation energy and hence on activity and selectivity. Traditional thermal energy transfer is rather sluggish as it involves heat transfer throughout the complete reactor environment (solvent, reactor parts, etc.). In contrast, magnetic induction heating offers the possibility to transfer thermal energy in an extremely localized, rapid, and energy efficient manner. In catalysis, the rapid heating and cooling of magnetically heated NPs is of great interest to address the challenges associated to the use of fluctuating renewable energy sources. The development of catalytic systems capable of reaching high temperatures under magnetic induction activation proves particularly difficult, however, and the benefits of magnetic induction are until now only accessible using complex and specifically designed materials. To tackle this challenge, we developed a simple and versatile strategy to bestow commercial heterogeneous catalysts with magnetic heating capabilities (Figure 2).[3] As a case study, $Cu_2Cr_2O_5$ was decorated with ferromagnetic iron carbide NPs (ICNPs) possessing excellent induction heating performance. Analysis of the materials revealed that the nanosized heating devices could be decorated on $Cu_2Cr_2O_5$ in a stable and robust manner without affecting the intrinsic catalytic properties. The new materials could be applied to a continuously operated liquid-phase hydrogenation reaction of a model substrate under magnetically induced heating, showing outstanding stability and tolerance to intermittent electricity supply. The catalytic system reacted in real time to the energy supply, switching the reaction on and off as an immediate response to the applied magnetic field. This strategy should be transferrable readily to a wide range of heterogeneous catalysts and transformations, thus paving the way toward the development of catalytic systems that can be readily adapted to the use of fluctuating renewable energy.

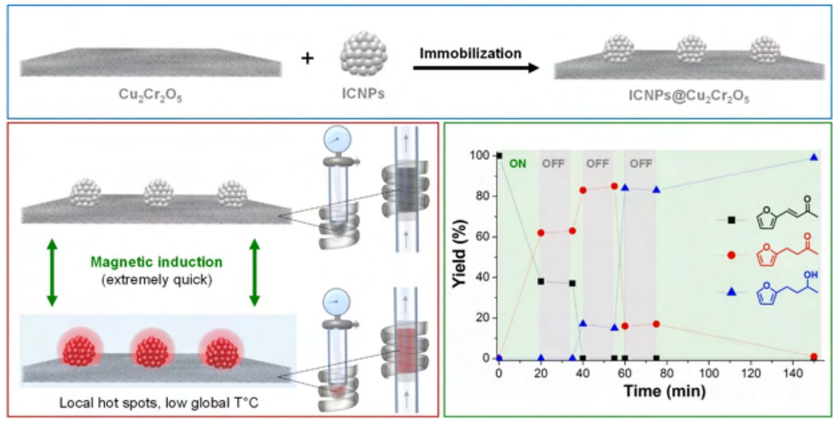

Figure 2. Illustration of the approach followed to develop of magnetically-responsive catalytic system adaptive to intermittent energy supply.[3]

In addition, we recently demonstrated the possibility to coat the surface of ICNPs directly with a catalytically active metal (Cu in this case). The resulting multifunctional Cu@ICNPs catalytic system was found highly active and selective for the hydrodeoxygenation of aromatic aldehydes to aromatic alkanes under mild observable conditions (3 bar H_2, 105 °C) when heated by magnetic induction.[4] Interestingly, the catalyst's adaptivity to intermittent power supply was demonstrated by stopping and re-starting the alternating current magnetic field regularly. A wide range of substrates with various functionalities could be readily hydrodeoxygenated, including biomass-derived furfural, hydroxymethylfurfural, vanillin and syringaldehyde. In contrast, no significant hydrodeoxygenation activity could be observed when using conventional heating, even at 200 °C. This approach is simple and flexible, and can pave the way toward the development of other magnetically responsive adaptive catalytic systems capable of promoting challenging transformations under mild conditions through magnetic induction heating.

Adaptivity in product formation: selectivity switch

In this case, we combined defined metal NPs with CO_2-responsive support materials to rationally design a hydrogenation catalyst capable of adapting its reactivity to the source of H_2. The aim was to develop a catalyst that is able to "recognize" whether the feed gas is composed of pure H_2 (e.g. from water electrolysis) or a mixture of H_2 with CO_2 (e.g. from biomass reforming).[5] Introducing CO_2 into the feed gas would allow to "switch" the product formation by reversible selectivity control. Based on previous experience, we deposited ruthenium NPs on an amine-functionalized support in collaboration with the group of Prof. P. Jessop at Queen's University in Kingston, Canada. The amine groups of the support were chosen due to their interaction with CO_2 to form carbamates. Spectroscopic investigations revealed that the presence of the ruthenium NPs led to hydrogenation of CO_2 generating formate species on the surface. The molecular changes at the surface were found to be fully reversible, as the ammonium formate decomposes back to H_2 and

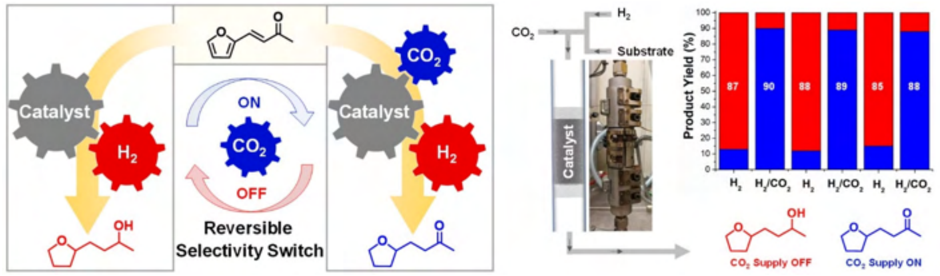

Figure 3. Selective hydrogenation reaction using a CO_2-responsive adaptive catalytic system to switch between two different products from the same substrate.[5] Concept exemplified here for the hydrogenation of biomass-derived furfuralacetone.

CO_2 regenerating the initial amine structure when the CO_2 supply was stopped. The catalytic performance of the materials in the amine state and the formate state differed drastically. Depending only on the gas supply, the catalyst operates in two different modes producing selectively two different products from the same starting material under otherwise identical conditions. In particular, when the hydrogenation was performed under a gas stream of pure H_2, biomass-derived furfuralacetone was completely hydrogenated to give the corresponding saturated alcohol. However, when a mixture of H_2 and CO_2 was used, a sharp change in selectivity was observed, where the furan ring and the double bond were still hydro-genated while the ketone was conserved. This adaptive change in selectivity applied to a range of furan derivatives of different structures. Notably, the two modes of operation could be alternated by switching on or off the CO_2 supply to the gas stream almost in real time (Figure 3).

These proofs of concept of adaptive catalytic systems for hydrogenation reactions open many new opportunities to develop other adaptive catalytic systems and enable flexible production schemes on basis of renewable feedstock and energy supply.

Publications resulting from this research area (2020–2022)

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A number of joint publications evidences collaborations within the CEC [2d, 2e, 2i, 3, 4] and as part of the Joint Workspace with MPI für Kohlenforschung [2e, 2g].

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The transition to renewable energies our societies engage is expected to involve a significant shift towards electricity as a major energy vector. This shift will strongly impact our ways to produce materials and goods. Electrifying the chemical sector will involve a large implementation of electrosynthesis, the art to make or break chemical bonds by the direct use of electrons or holes. In our team, we investigate how *organometallic electrocatalysis* can foster electrosynthetic conversions. In particular, we address this question in the frame of reactions creating added-value from readily available building blocks, such as protons and carbon dioxide (Figure 1).[1] To this end, our team explores three main synthetic manifolds: the conversion of carbon dioxide into chemical primers of fuels, the selective hydrogenation of organic compounds and the construction of added-value chemicals by combination of organics backbones with abundant building blocks. We present here current achievements of the team, with a special focus on the first two directions.

However, only very few studies have precisely investigated the influence of the nature of the metal center itself on the electrochemical activation of CO_2. Here, we took a systematic approach by incrementing the metal across the 3d row while keeping the same ligand framework.[3] To be able to primarily address metal-centered processes, our design relies on a PNP pincer-type ligand, having no redox activity in the electrochemical window under consideration but offering good stabilization of low-valent states. Metal centers were varied in the series of Mn, Fe, Co, Ni, Cu, Zn. Interestingly, within the series of complexes, we found that metal-centered reductions are only observed for Fe, Co and Ni analogues, whereas Mn, Cu and Zn complexes produce ligand-centered processes or degradation (Figure 2a). Reduction of the Ni complex to the d^{10} Ni(0) state leads to interaction with CO_2, likely in an Aresta-type Ni-η^2-CO_2 complex. However, electron transfer to CO_2 is insufficient for electrocatalytic activity. In the case of the Co counterpart, the d^9 Co(0) forms a CO_2-adduct that can undergo further electron uptake into a Co(I) metallacarboxylate, amenable to turnover.

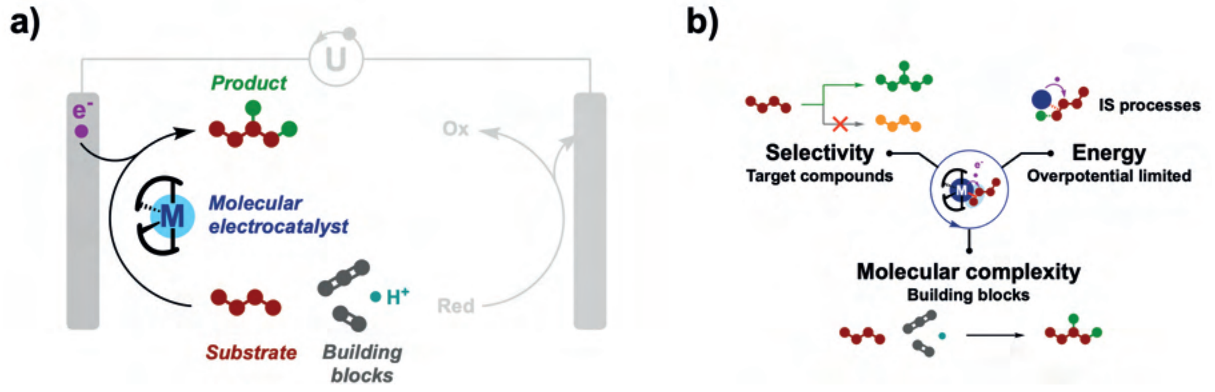

Figure 1. Organometallic electrocatalysis approach to generate molecular complexity from organic primers and abundant building blocks: a) general scheme; b) challenges addressed. (adapted from ref[1])

CO_2 electroreduction

Electrocatalytic CO_2 reduction by molecular complexes is being thoroughly investigated. A comprehensive survey of the literature performed by the team reveals that the product distribution (CO or HCOOH) obtained with transition metal complexes as electrocatalysts depends empirically on the d-period.[2]

These results, together with few previous reports, highlight that an unsaturated coordination sphere of 4 to 5 ligands and a configuration comprised between d^7 to d^9 in the reduced state of +I or 0 foster electrochemical CO_2 activation for complexes bearing redox-innocent ligands (Figure 2b).

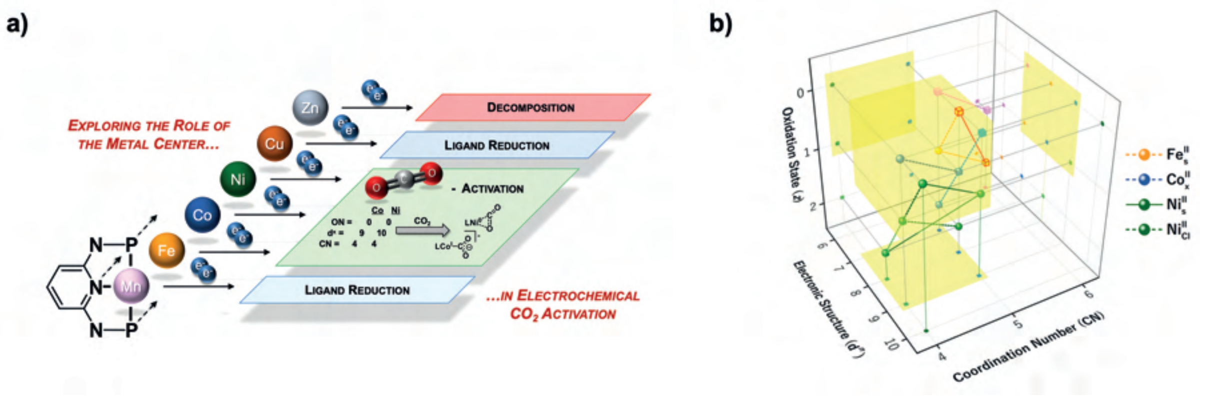

Figure 2. a) Reduction behaviour upon variation of the 3d metal center within the same redox innnocent ligand framework. b) Electronic and geometric properties favoring electrochemical CO_2 activation (yellow area) for complexes based on redox innocent ligands. (adapted from ref[3])

In addition, we have also investigated ligand exchange equilibria, in relation with the redox changes of the complexes under consideration. Indeed, chloride ligands classically encountered in the pre-catalyst due to the preparation from chloride metal salt precursors are prone to exchange with the solvent, the more so as reduction of the metal center takes place. Inspired from Laviron's works, we could summarize these exchanges along reduction pathways in so-called *cube schemes*. We found that this effect is particularly marked upon reduction of the metal complexes, although the oxidized metal centers have high affinity for chloride versus solvent (acetonitrile here), which underlines the importance of taking into account spectator ligands in the formulation of the species entering catalysis.

From chemical to electrochemical catalysis

To switch from chemical reductions to electrochemical ones, inspiration can be taken from the breadth of catalysts already developed for the chemical routes. Mn-based complexes based on a P^RNP^R pincer ligand system constitute a particularly well studied class of complexes achieving reduction/reductive functionalization of CO_2 and other organics substrates. Under chemical hydrogenation conditions, these complexes shuttle via synergistic activation of H_2 on an *in situ* generated amido [N=Mn] precatalyst into a Mn(I) hydride key intermediate [HN-MnH]. These key intermediates are generated usually at high temperature and 1-30 bar of pressure of hydrogen. Electrochemical generation of these intermediates would enable transposing such catalysis to mild conditions that do not require hydrogen pressures and can operate at room temperature. In this endeavour, we investigated here the electroreductive behaviour of a series of $[Mn(P^RNP^R)(CO)_2L]^q$ pincer complexes by experimental and theoretical approaches. We found that the complexes generally undergo two consecutive one-electron reductions or a two-electron one. The nature of the P-substituents has only minor effect on the reduction potentials, whereas the type of the fifth ligand (L) drastically influences the reductive behaviour. Interestingly, two-fold reduction of the cationic complex $[Mn(P^RN^HP^R)(CO)_2(S)]^+$ (S = solvent or empty coordination site) into a putative Mn(-I) species is affected by the addition of a proton source (PhOH) and namely produces a reoxidation wave at a potential of $E_{p,a} = -0.53\ V_{Fc}$ (Figure 3a). For comparison, the synthetically isolated $[Mn(P^RN^HP^R)(CO)_2(H)]$ hydride complex displays an oxidation wave at a close potential ($E_{p,a} = -0.47\ V_{Fc}$). We thus propose that the $[Mn(P^RN^HP^R)(CO)_2(S)]^+$ complex produces upon two-fold reduction in the presence of acid the corresponding Mn(I) hydride. Theoretical calculations further support that the evolution of the hydride is favored at applied negative potentials (Figure 3b) and indicate a closely matching oxidation potential ($E^0 = -0.46\ V_{Fc}$). The electrochemical generation of this Mn hydride species opens opportunities for the utilization of this class of popular $[Mn(P^RNP^R)(CO)_2(L)]^q$ complexes in electrocatalytic applications, as for instance CO_2 reduction.

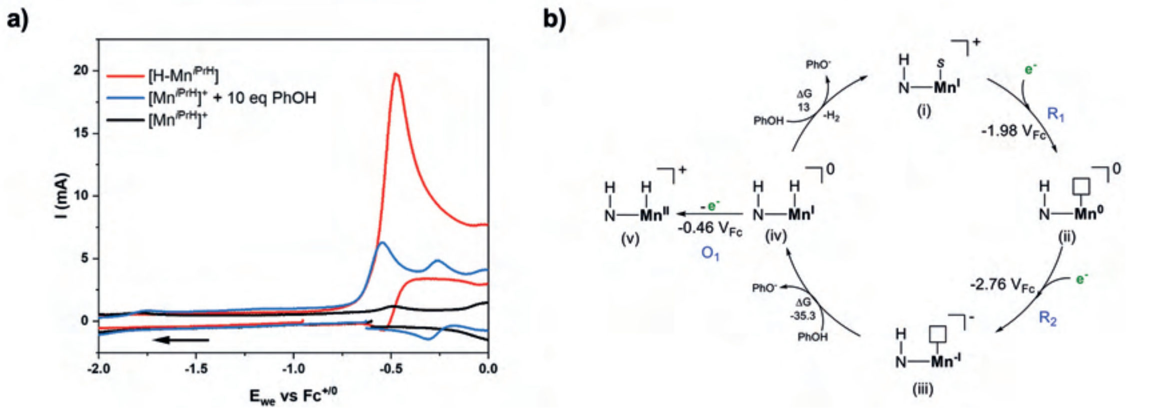

Figure 3. a) Cyclic voltammograms of $[Mn(P^RNP^R)(CO)_2(S)]^+$ in the presence and absence of phenol and of $[Mn(P^RNP^R)(CO)_2(H)]$. b) Computational proposal for the reduction-protonation sequence of $[Mn(P^RNP^R)(CO)_2(S)]^+$.

In the course of these studies, we found that the Mn(I) amido pre-catalyst $[Mn(P^RNP^R)(CO)_2]$, undergoes reactivity with the CO_2 substrate. The resulting complex was isolated, fully characterized and the molecular structure obtained by X-ray diffraction namely evidences a 4-membered Mn-O-C-N metallacycle (Figure 4).

This complex displays very good stability in atmospheric conditions compared to the amido precursor and a hindered reactivity towards proton sources. We thus suggest that this species may be an off-cycle intermediate in hydrogenation of CO_2 catalysed by $[Mn(P^RNP^R)(CO)_2]$.

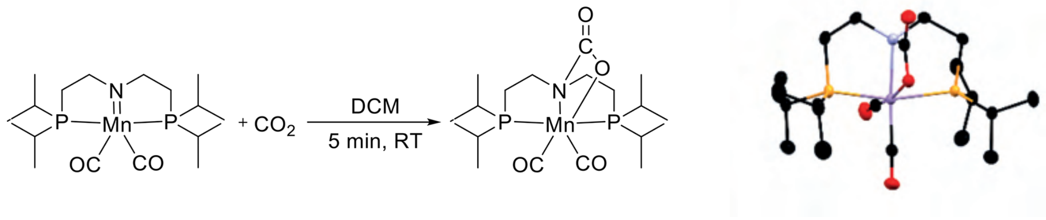

Figure 4. Synthesis and molecular structure of $[Mn(P^RNP^R)(CO)_2(CO_2)]$.

Organics hydrogenation

In our endeavour to address selective organic hydrogenations by electrocatalysis, we investigated the partial hydrogenation of alkynes to olefins. In the chemical value chain, olefins are indeed among the most important precursors for base and fine chemicals (as for instance in polymer chemistry), and are widely obtained from their parent alkynes using hydrogen gas. A major challenge in this transformation is to avoid the over-hydrogenation of the starting alkyne that results in alkane compounds of lower added-value.

We have showed here that the production of olefins from alkynes can be electro-chemically catalyzed by a simple molecular nickel $[Ni(bpy)_3]^{2+}$complex at ambient temperature and pressure, using benzoic acid as the proton source (Figure 5a).[4] Moreover, this system is applicable to various internal alkynes and exhibits little to no undesirable over-hydrogenation to alkanes.

We have further investigated in details the mechanism. We found that a $[Ni(bpy)(PhCOO)_2]$ catalytic species forms in situ. Direct use of this isolated complex as electrocatalyst results in higher performance than with the $[Ni(bpy)_3]^{2+}$ one, including a high faradaic efficiency (>99%). Organometallic syntheses have allowed to isolate and highlight the role of important nickelacyclopropene and vinyl intermediates. On the basis of electrochemical, *in-situ* spectroscopic and kinetic studies but also DFT calculations, the ECEC mechanism proved to be the most favorable pathway. Nickelacyclopropene was found to be the on-cycle resting state. Furthermore, the first protonation of this complex was shown to be the rate-determining step. The observed *cis*-selectivity is be governed by the protonation of a nickel(I) vinyl intermediate. We could further discard the involvement of metal hydrides as catalytically competent species for alkyne hydrogenation under our conditions. While most hydrogenation reactions are assumed or proven to shuttle via metal hydrides, our findings highlight an original pathway in catalytic hydrogenations.

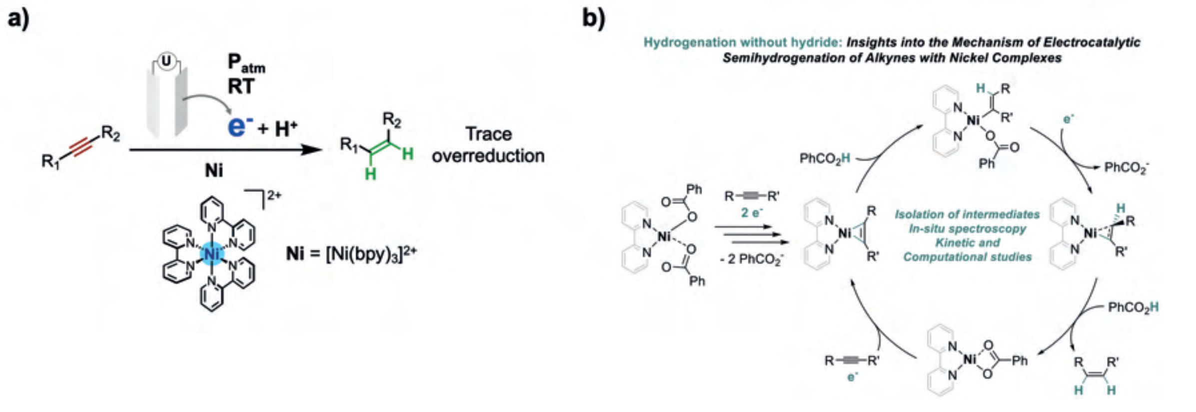

Figure 5. Alkyne semihydrogenation using a) $[Ni(bpy)_3]^{2+}$ molecular electrocatalyst (adapted from ref[4]) and b) the more efficient $[Ni(bpy)(PhCOO)_2]$ catalyst for mechanistic investigations.

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Research Area: Multiphase Catalysis

Objectives

Finding new and efficient ways to form carbon-carbon bonds from carbon monoxide and carbon dioxide is of great importance on the path to developing green processes of a sustainable future. The multiphase catalysis group focuses on the development of new reaction systems and processes and on understanding catalysts in different dimensions. These dimensions are the molecular level, the phase level, and the system level, which are decisive to develop stable, active and selective catalysts. Especially for energy conversion processes the long-term stability of catalysts are of enormous importance.

Investigating methods of stabilizing catalysts requires an in-depth understanding of the dynamic behavior of the catalyst on the molecular level in complex reaction systems which are employed in continuously operated processes. Methods for a long-term stability of molecular catalyst systems are investigated by recycling the catalyst and separation of reaction products[2]. Such recycling and separation techniques imply the existence of phase boundaries such as a liquid/liquid, liquid/gas or liquid/solid interface. A thorough understanding of the mixing and interfacial behavior is crucial for the development of the catalyst system and its eventual separation. Thus, an essential part of the work in the multiphase catalysis group is the combination of different research fields starting from the catalyst development, the understanding of catalyst recycling techniques and finally scaling up the system to a continuous process to investigate the dynamics of systems in long-term experiments by operando spectroscopy, as depicted in Figure 1.

Activities

The development of new processes to produce bulk chemicals based on sustainable alternatives is one of the key aspects of the multiphase research group (Figure 2). Examples for processes under development are the synthesis of formic acid with a multiphase approach for catalyst recycling, the synthesis of isocyanates via a dehydrogenation of amides for the production of monomers for polymerization, or the conversion of biomass sugars to platform chemicals[3,4,5].

An innovative approach was developed in a homogeneously catalyzed reaction system to mimic the C–C bond formation of Fischer-Tropsch reaction but with an enhanced selectivity for specific olefin, aldehyde or alcohol products. The three-step reaction cycle consists

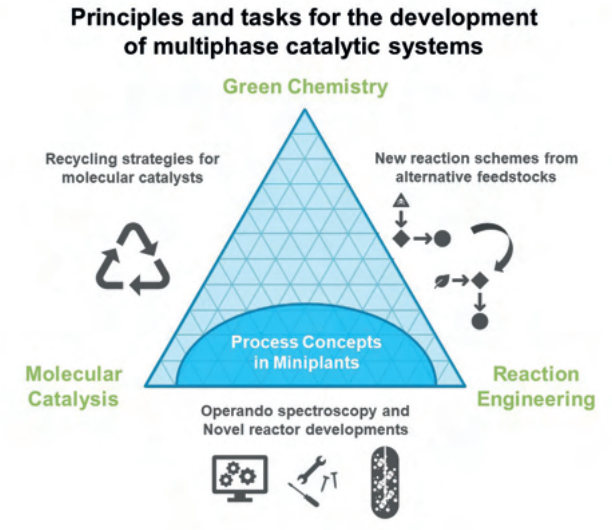


Figure 1. Different stages, tasks and tools in the development of multiphase catalytic systems.

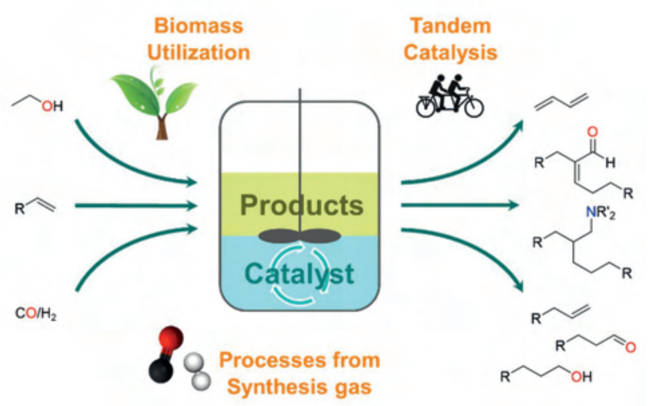


Figure 2. Reactions studied by the Multiphase Catalysis group.

of the hydroformylation of linear olefins, the hydrogenation of the resulting aldehydes to alcohols and a dehydration to retrieve the olefin with an increased carbon chain length. For these steps, highly selective homogeneous catalysts are used, resulting in less waste and higher selectivity for the final product[6,7,8].

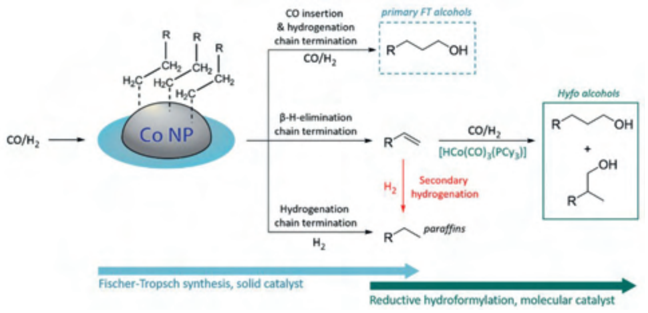
In the last years in conjunction of an EU funded project called "REDIFUEL" new ways for synthesizing e-fuels were developed[9]. The REDIFEL project aimed at developing a new process for the production of synthetic diesel fuels from bio-synthesis gas. In this context we investigated the conversion of C_5 to C_{10} olefin mixtures from a Fischer-Tropsch plant to alcohols as fuel additives. Rhodium in combination with tertiary amines were barely investigated for this reaction in the past and it was possible to develop very reactive catalytic systems showing a high catalytic activity and selectivity at the same time. In contrast to commonly applied phosphorus ligands, tertiary amines are much more stable which was highlighted in several different concepts presented to recycle the rhodium/tertiary amine catalysts developed in this group[10,11,12].

Another innovative example for the application of tandem catalysis has been developed together with project partners ITQ/CSIC: The combination of the heterogeneously catalyzed Fischer-Tropsch synthesis with the homogeneously catalyzed hydroformylation to produce alcohols directly from synthesis gas (Figure 3)[13]. In this approach, a cobalt-based Fischer-Tropsch catalyst, showing a high selectivity towards olefins, is used together with a homogeneous molecular cobalt catalyst. This system is able to directly convert the in situ generated olefins from the Fischer-Tropsch reaction to alcohols via the reductive hydroformylation reaction. The combination of these two catalysts in this "multi" tandem approach allows to circumvent drawbacks like high levels of the side product CO_2 or low chain growth probability, usually accompanied with other approaches aimed at producing alcohols from synthesis gas. At the same time an unrivaled alcohol selectivity above 70% with high CO-conversions are possible due to the interception of in situ olefins before secondary hydrogenation to paraffins occurs. The resulting paraffin/alcohol mixtures from bio-synthesis gas would be directly applicable as bio-synthetic diesel fuels.

The development of these new processes requires the investigation into new separation techniques for operating continuous miniplants. As such, the previously described conversion of FT-olefins to the corresponding alcohol mixtures was carried out continuously for more than 100 h on stream to test for the long-term catalyst stability.[14]

One of the operado spectroscopy tools to investigate the reaction system during catalysis and recycling is a borescope implemented in a miniplant set up. With borescope measurements, the interface of multiphase reaction-system can be investigated in detail. Using the apparatus allows the analysis of the interfacial area during the reaction by an in situ photo optical sensor in a pressurized reactor. Changes from a biphasic to a monophasic system or changes of the catalyst solubility are visualized even in closed stainless-steel reactors. As the reaction proceeds, the change of the interfacial area by the formation of the reaction product and the conversion of the substrate is visualized and these observations can be correlated with other effects during the reaction. With this knowledge it is possible to understand the macroscopically observed information in depth and to optimize a chemical process.

Figure 3. Combination of Fischer-Tropsch synthesi and Reductive Hydroformylation for the direct conversion of synthesis gas.



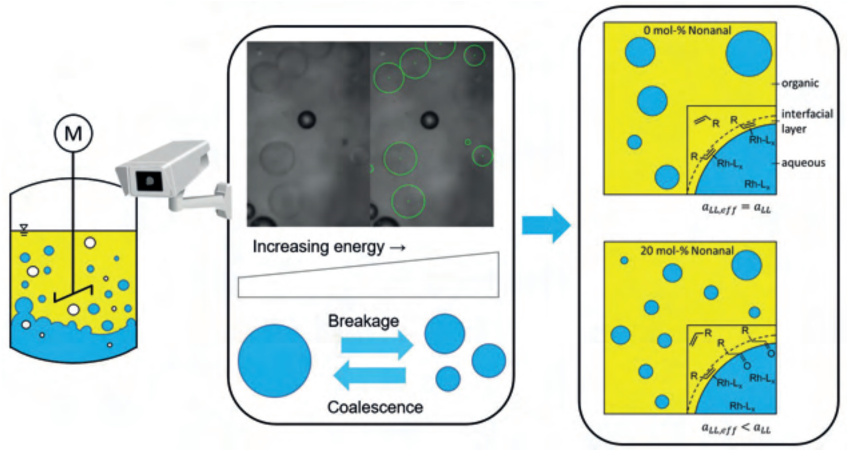


Figure 4. Overview of a borescope measurement, with the photo optical sensor pictures of the reaction mixture and the bubbles/droplets are taken. A mathematical model can distinguish between gas bubbles and liquid droplets and calculate the liquid-liquid interfacial area.

Studying the multiphase hydroformylation, it was possible to explain the high reactivity by very low water solubility of the long chain olefin substrates using the borescope. Herein it was found, that the reactivity is not depending on the solubility of the alkene substrates. The photo optical measurements showed a strong influence by the amphiphilic product of hydroformylation, nonanal. With the reaction progress and an increasing nonanal amount in solution a 2-fold increase of the liquid-liquid interface was observed. By varying the catalyst concentration, an accumulation of the catalyst at the interface seems to be unlikely. Rather, the amphiphilic product, nonanal, is situated at the interface, thus, increasing it but also reducing the effectively available interfacial area for the Rh-catalyst (Figure 4)[15,16].

In coming projects of the multiphase catalysis group, the borescope measurement technique will be used for the investigation of other liquid-liquid-gas catalytic systems. The effect of adding for example a mass transfer agent as well as the effect of the interfacial area in tandem or cascade reactions with a biochemical approach will be studied using this technique.

Knowledge of catalytic mechanisms is of importance, both in the development of new catalysts and in the improvement of existing ones. In particular, deactivation pathways of catalysts are rarely object of scientific interest. However, this is valuable knowledge for the development of more robust and stable catalyst systems and an important criterion for the scalability of catalytic processes. Operando studies are a useful technique to study catalyst deactivation and fill this gap of knowledge. In such studies, spectroscopic methods are used to connect reaction kinetics to spectroscopic data of catalyst species obtained under reaction conditions[1,17].

A semi-batch miniplant for operando studies with an infrared spectrometer, a benchtop NMR spectrometer for ^1H and ^{31}P NMR measurements and a GC-FID has been implemented in our group. The setup has been designed in a flexible manner, allowing the group to use different reaction vessels from Schlenk-equipment to 300 ml pressurized reactors.

The setup has been successfully applied in mechanistic investigations on the reductive hydroformylation with a Rh/amine catalytic system. IR-spectra provided evidence to the presence of a $[Rh(CO)_4]^-$ anion as main species in the reaction. In another approach, the setup was used to investigate the oxidation of phosphine ligands as a deactivation pathway in Pd-catalyzed reactions. Data deconvolution of the IR-spectra was used to subtract overlapping peaks of the two main components, triphenylphosphine and triphenylphosphine oxide, leaving the spectra of Pd-species. By these means the main Pd-species present could be identified[8].

In the future, the setup will be connected to catalyst recycling units, such as a distillation column. This will allow for investigations on the long-time stability of the catalyst.

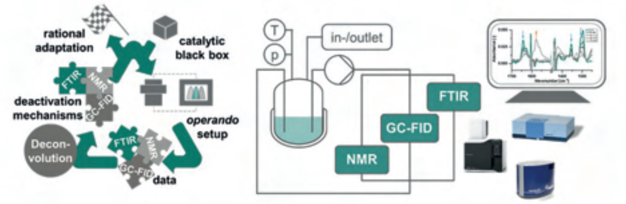


Figure 5. Strategy applied in this group for operando studies (left) and operando setup as implemented (right).

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DEPARTMENT OF HETEROGENEOUS REACTIONS

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General

The period is characterized by the extremely fruitful evolution of the institute through the activities of the two other departments allowing the execution of the final phase of the department of heterogeneous reaction; its dismantling that was planned originally for the year 2016. The pandemic and its consequences as well as the finalisation of the building phase led to decision to leave the founding director in function until April 2022. Organisation and scientific activities were aligned accordingly.

The organisational measures foresaw to conclude the "Aufbauplanung" of the Institute with leaving behind a team of service groups that should provide critical competencies and infrastructures considered essential for the work of the institute. This was decided together with dedicated resource planning for these groups during the foundation of the institute by the Section and the Senate of the MPG as being a key structural element of the new institute. *"The collaborative style of operation of the new MPI is emphasized by a substantial collection of central facilities required by the departments. It should be avoided to let them develop into specialized but isolated centres of excellence; the joint use of basic functions of energy conversion chemistry should create a synergistic atmosphere." (Founding Concept, June 2010)* and *"Servicegruppen sind ein zentraler Bestandteil des Institutskonzeptes. Indem die Abteilungen gemeinsame Funktionen auch gemeinsam betreiben, entstehen Synergie und kritische Kompetenz. Zudem wird die Duplizierung von Infrastruktur minimiert. Aus heutiger Sicht sind die Servicegruppen essentiell, um die Mission des Institutes zu erfüllen. Die Arbeitsfähigkeit der Servicegruppen wird zudem als wichtiges Argument für die Attraktivität des Institutes für weitere Mitglieder der Leitungsebene gesehen."* (Gründungskozept MPI CEC Juni 2011).

This led to the transfer of former group activities of the Department into central service units designated as "scientific infrastructure" in the organisational diagram of the Institute. They are now overseen by the Managing Director. The idea is that these groups perform independent research in their respective field of competence and act as service and knowledge providers for other research units of the institute.

The period of the report further saw a significant increase in the visibility of the topic "chemical energy conversion" as a vital and critical element of the energy transition. A review by the director[1] on the topic tries to define the term "chemical battery" as functional description of the family of chemical reactions designated as chemical energy conversion. It may serve as distinction to the many other chemical energy conversion activities, where not so much the storage of energy is the key motivation but the energy- or resource-efficient production of molecules. The scientific results of the MPI CEC and related intense activities in advising decision makers in politics and economy through its directors contributed notably to this evolution at least in the German National context.

Electrocatalysis

The department was highly engaged in contributing to the conceptual understanding[2] of the material science of the OER reaction determining the overall performance of water splitting. The individual reports of the groups reflect this effort. Here a summary of the overarching insight shall be given. The starting point of the research strategy was the question if OER is a catalytic reaction with an electrical stimulus ("electrocatalysis") or an electrochemical reaction with its own foundational concept of direct electron transfer processes. This differentiation has severe consequences for the design of electrode materials that are in the first case catalytic surfaces hosting all elementary steps of the OER reactants or if they are only sources and sinks of charge carriers into the surrounding homogenous reaction medium retaining maximum chemical inertness ("nobility").

We began with the study of Ir oxide in the PEM process[3] as we had already substantial activities in the past years in understanding reactivity and photoemission spectroscopy of this material. In a substantial effort based upon a proven operando study of the material dynamics of IrO_2 upon stepwise increase of the polarisation potential it was shown that the charge associated with the "pseudo-capacity" of the electrode is associated with the conversion of the prevailing Ir-oxihydroxide surface into a defective oxide hosting deprotonated singly-coordinated oxygen species. The applied potential finally oxidises these sites into oxyl radicals that react with OH^- and form the oxygen molecule. The potential required to form these active sites depends on the disposition of the material prior to polarisation and shows no sharp "onset potential". Deeper analysis with theoretical models and comparison to the analogy of the Deacon reaction allowed concluding that the electrode kinetics can be well described by the standard Langmuir Hinshelwood mechanism of interface reactions and does not require a special "electrochemical" concept.

The resulting material concept[4] of an OER electrode is a bifunctional system requiring a base material with high electron-conducting properties (metal) and likewise a hydrophilic termination layer allowing sufficient chemical dynamics so that terminal oxygen species can exist with little activation barrier. The idea of a dynamical self-organisation of a metallic precursor base[5] was found a suitable strategy against the complicated control of autogenous formation of reactive terminations, as found in cases of NiO or Ir oxide. Layered double hydroxides are a suitable structural motif. The combination of hydrophilic adaptive surface structures with conductivities allowing currents of several Amperes per cm^2 with low Ohmic losses is a demanding design challenge that is intensified by the base requirement of electro-chemical stability[6] in the electrolyte environment. Dissolution and complexation of the flexible surface are facile mechanisms of degradation, even when re-deposition limits the macroscopic loss of material. In alkaline electrolytes complexation[7] and formation of insulating co-precipitates are limiting factors[8] in choosing base materials and promoting additives for stable OER performance when avoiding precious metals.

A different approach is to avoid metals and their stability problems in electrolytes and turn to synthetic carbon with or without metallic additives at their surfaces. This class of materials allows wide flexibility in structural design and choice of active sites. The quinone-hydroquinone couple serves as metal-free alternative to the singly coordinated oxyl found on metal oxides in OER catalysis. This concept was verified[9] with remarkable performance. Carbon allowed further to use dynamical NMR techniques to highlight the important nature of the hydrophilicity for the function of a water-splitting electrode. Both the structure-modifying effect of water molecules and the need for low-pk functional groups to facilitate the dissociative adsorption of the reactant water were studied quantitatively. The standard paradigm that $^{-}$OH groups on a redox-active surface are sufficient for reactive hydrophilic contact was challenged at least for functional groups on carbon. [10]

Translational CEC

The MPI is highly active in participating and coordinating translational projects of chemical energy conversion. There fundamental chemical science is translated within cooperative project with industry in technological concepts and demonstrators as pre-requisites for true technological application. This is very notably the case in the Kopernikus project Power2X (Department Leitner) but also in Carbon2Chem, in PrometH2eus (plasma chemistry for novel electrode materials) and in TransHyDE where the departments Schlögl and DeBeer are engaged. Such projects exemplify the profile of the MPI that by its mission is not attempting technological or "practical" contributions to the energy transition but rather is exploring avenues and providing toolboxes for others to create science-based novel technologies.

Examples for the role of science in these activities can be found in the Carbon2Chem project that moved in its second phase during the reporting period. A technology study of the potential for hydrogen ex methane pyrolysis[11] showed that this approach for the realization of a Mt-facility to convert CO_2 from steelmaking is no alternative to massive import, as local electricity will also not suffice for the amount of hydrogen required. The core process of methanol synthesis was benchmarked[12] for the project and the controversial issue of possible insufficient stability of Cu/ZnO systems for CO_2-only reduction was resolved[13] and traced back to the dual role of Zn as component of brass in reducing feed and as defective ZnO in water-rich feeds. The creation and operation of a laboratory twin (in Oberhausen) of the pilot plant (in Duisburg) and extensive on-line quantifications of detrimental trace gas impurities that initially escaped the gas-cleaning and conditioning facility were only made possible through extensive method developments (including the CI-MS-TOF methodology) and their implementations in the pilot plant environments.

In TransHyDE the department hosts a substantial part of the coordination and communication team for a project with over 90 partners. Such a critical managing function can only be performed within the stable framework of an institution that does not depend on the resources of the project. A key project for the future global transport of renewable hydrogen is the use of ammonia and hence the energy-efficient reforming of ammonia back to hydrogen through "cracking". Here the department coordinates a large activity that tackles this challenge from a fundamental viewpoint (identification of the kinetic bottlenecks) and simultaneously from a catalyst development effort. The reason for this parallel approach is the critical need for a solution in order to supply the translating partners with useful materials that perform with lower energy consumption than the state-of-the art methane reforming catalysts suggested by industry today.

A technology study[14] paved the way for selecting the strategy. The work flow for rapid identification of possible lead structures is using the methodology of digital catalysis[15] in order to prepare the results for later in-depth structure-function analysis using tools of machine learning and artificial intelligence. The work on ammonia reforming connects directly to the related issue of ammonia synthesis using the Haber-Bosch process that is studied in Carbon2Chem where the roles of promoters and poisons[16] on the energy required clearly relate to both reactions that are interconnected by an equilibrium that is effected, however by different kinetic pathways for the forward and backward reactions.

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Electron Microscopy & XPS

The electron microscopy group was set up at the MPI CEC in 2020 with the installation of a new transmission electron microscope (TEM). Directly connected to a glovebox, this unique setup allows for the investigation of inert transferred samples using standard TEM sample holders. This electron microscope is not only used by TEM experts but also by scientists of other research groups, employing the ChemiTEM workflows [1] which guide the users step by step in a standardised way through TEM experiments and data analysis using an app-based interface. We developed these workflows, as well as the aforementioned prototype of a TEM directly connected to a glovebox, in collaboration with the Fritz Haber Institute of the Max Planck Society (FHI) and Thermo Fisher Scientific.

In the beginning of 2022, the electron microscopy and surface analytics groups were joined, forming the electron microscopy & XPS group, which enabled new synergies by combining the different available electron spectroscopy techniques such as electron energy-loss spectrometry (EELS), X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) with the imaging and diffraction capabilities on the micro- and nanoscale of electron microscopes.

The main focus of the electron microscopy & XPS group lies in the investigation of surfaces and particles and their chemical, structural, and electronic properties. Next to our own research, e.g., in inert transfer microscopy, sample preparation, XPS data analysis, and EELS, we aid other workgroups with our expertise, also in close collaboration with our colleagues at the MPI KOFO. Especially our inert transfer capabilities allow for the careful characterisation of catalyst materials without contact to air. Furthermore, the electron microscopy & XPS group participates in collaboration projects such as the NFDI consortium FAIRmat and the cluster of excellence UniSysCat.

Inert sample transfer as key for catalytic sample investigation

Electron microscopy is needed to investigate catalysts in different stages of their lifetime in order to obtain information on their morphology, microstructure and local chemical composition up to oxidation states and the variation of those through the catalyst particles. Since the catalyst particles might be affected by contact to air, they are usually prepared for TEM investigation inside a glovebox using an inert transfer sample holder for the microscope. However, the construction of these holders limits the analytic capabilities, tilting of the sample is very limited and it is not possible to provide a low background for energy dispersive X-ray spectroscopy (EDX). We use the prototype of a highly modified TEM to which a glovebox system is directly connected. This allows us to circumvent most of the aforementioned issues. The samples can be prepared in the standard sample holders inside the glovebox and are directly inserted into the TEM. This excludes any external influence and allows for low background measurements and even to perform electron tomography.

One application for this system is the investigation of $Cu/ZnO/Al_2O_3$ based methanol synthesis catalysts from the Catalytic Technology group. Since this catalyst contains reduced copper particles, contact to air may lead to unwanted oxidation and change the catalyst material. Therefore, it is important to exclude the influence of air from the transfer of the sample from the reactor to the TEM. Using our unique TEM – glovebox interface, we were able to investigate spent catalyst samples after different treatments which were first transferred inertly from the reactor to the glovebox, and then to the TEM. Since we are using the regular sample holders, EDX, EELS and high resolution TEM could be used to characterise the differences between differently treated samples (Fig. 1).

Inert transfer via a glovebox also makes the oxidation states of functional groups in protein catalysts accessible. In collaboration with the department of inorganic spectroscopy, a workflow for inert preparation and EELS measurements has been developed that is capable of measuring EELS of sufficient quality for oxidation state determination on the Fe $L_{2,3}$-edge and the O K-edge on proteins with functional Fe sites. The stability of the sample in the electron beam is a challenge, so integration over a certain region is needed to obtain sufficient data quality. This limits the resolution, however, the investigated areas after integration can be up to ~20 nm small, which still exceeds the capabilities of X-ray measurements.

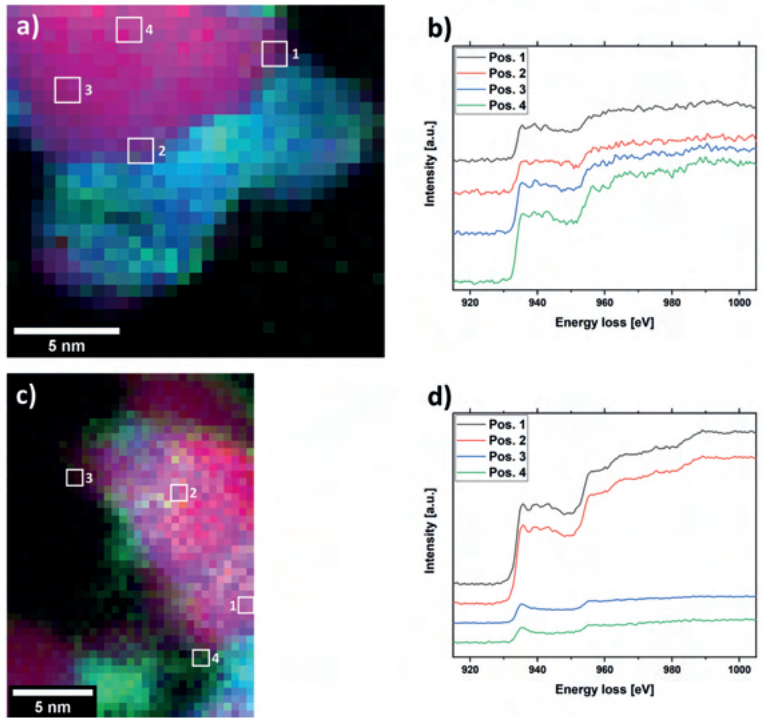

Figure 1. a) Inertly transferred methanol synthesis catalyst. The bulk and the surface consist of Cu-metal as can be seen from EELS measurements in b). c) Catalyst treated with diluted O_2. d) EELS measurements show that the bulk consists of Cu-metal, while there is a surface layer consisting of Cu_2O. Colour code in a) and c): red – Cu, green – O, blue - Zn.

Carbon contamination and its prevention in electron microscopy

One challenge we face in TEM experiments is the formation of amorphous carbon contamination accumulating on the specimens' surface. This contamination is caused by organic molecules that get reduced by the electron beam. These carbonaceous molecules can originate from the sample itself (e.g., as ligands or solvent residues) or from the equipment utilized (e.g., sample holders). We focus on improving the measurement quality of samples which contain a high amount of carbon. To achieve this goal, both, a clean microscope environment and clean samples are of utmost importance.

Therefore, a solid understanding of how contamination affects the microscope environment is a crucial step to enhance the overall cleanliness of the vacuum environment close to the specimen. As many catalyst samples at our institute are synthesized in solution, outgassing of the solvents in the microscope and the time the solvent residues remain in the direct sample environment is of significant relevance for our TEM measurements. We performed experiments to gain insight in the quantitative and qualitative composition of the residual solvents by mass spectroscopic measurements inside a decommissioned TEM octagon, i.e., the region close to the sample and the objective lens system. In addition, using this setup, the efficiency of plasma cleaning as an established cleaning procedure in electron microscopy [2] could be assessed for different contaminants.

Regarding sample cleanliness, there are several mitigation strategies which can reduce the amount of carbon contamination. [3] However, these methods often rely on harsh treatments, which may change the properties of the sample. We have developed a setup dedicated to cleaning the samples before TEM investigations, which allows for a relatively mild sample-specific pre-treatment in order to remove volatile organic components by various vacuum and temperature settings based on the samples' properties. After testing with samples from the department of molecular catalysis, these pre-treatment steps have shown to be efficient and result in much less contamination compared to samples dried at ambient pressure (Fig. 2).

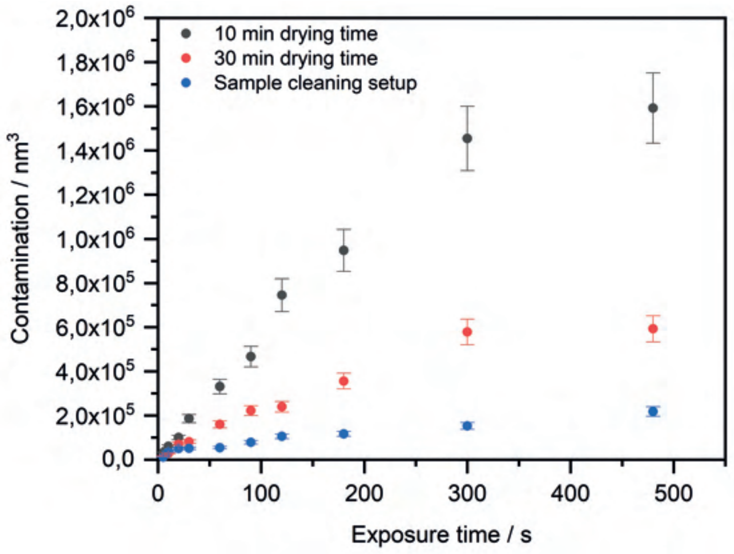

Figure 2. Contamination after exposing a TEM grid prepared with 1 µl of THF to the electron beam for a certain time. The different amount of contamination after sample pre-treatment in the dedicated sample cleaning setup or at ambient pressure can be seen.

Near-ambient pressure X-ray photoelectron spectroscopy

Near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) is a powerful tool to perform in-situ investigations of the electronic structure of catalysts in reactive environments, in order to understand the underlying physics and dynamics of surface properties related to the catalytic performance. Together with the department of inorganic spectroscopy, we are using X-ray spectro (micro)scopic methods to probe the electronic structure of iron-based ammonia synthesis and decomposition catalysts. In a series of operando NAP-XPS and scanning transmission X-ray microscopy (STXM) experiments, we could show that the near-surface composition of such catalysts critically influences the adsorption of different nitrogen species, which in turn determines their catalytic activity.

We have found that the presence of a gas phase in NAP-XPS experiments significantly influences the photoemission signal due to inelastic scattering of the outgoing photoelectrons, which can result in additional and often unwanted features in the measured spectrum. In order to model this effect, we developed a comprehensive quantitative description of the elastic and inelastic scattering of photoelectrons traveling through the solid and gas phase in NAP-XPS. [4] Equations were derived to model the resulting signal, which can be used to simulate or remove the inelastic scattering signal from measured spectra. For a more in-depth analysis of the scattering processes, Monte Carlo simulations of photoelectrons traversing the near-ambient pressure gas phase were performed, which led to new insights into the influence of the geometrical configuration of the sample and the spectrometer. The work was supplemented with a software tool using the developed algorithms, which can be used by other NAP-XPS researchers to model their data and to remove the gas phase inelastic scattering signal background, ultimately leading to a quantification that is more accurate.

Due to the ever-evolving complexity of XPS experiments, data sets are becoming harder to analyse manually. In order to extract the most knowledge from the data as possible, we are developing modern data science and machine learning methods. A recent project focused on using convolutional neural networks for the automated

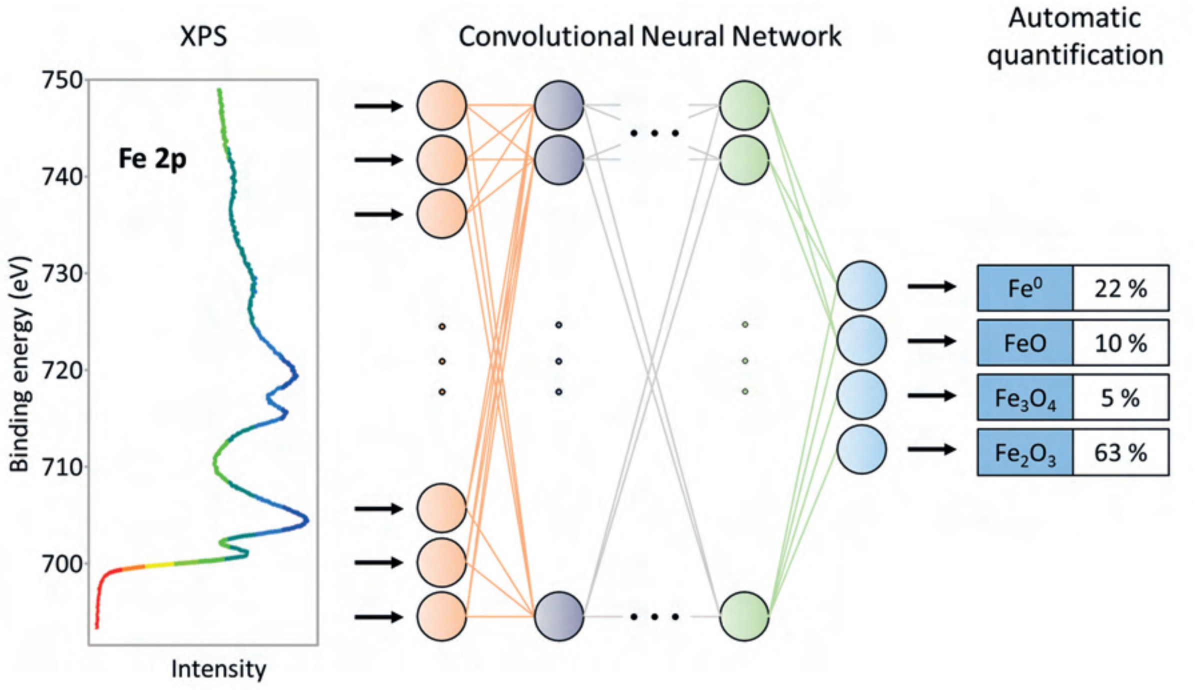

Figure 3. Illustration of the convolutional neural network approach for automated quantification of core-level XP spectra.

analysis of complex transition metal XP spectra (Fig. 3). This entails the simulation of synthetic training data sets and designing neural networks that lead to direct insights about the electronic structure and morphology of the sample surface. We could show that using neural networks can lead to a dramatic acceleration of the analysis process, while still retaining the required accuracy and depth of analysis.

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Carbon Synthesis and Applications (2020 – 2022)

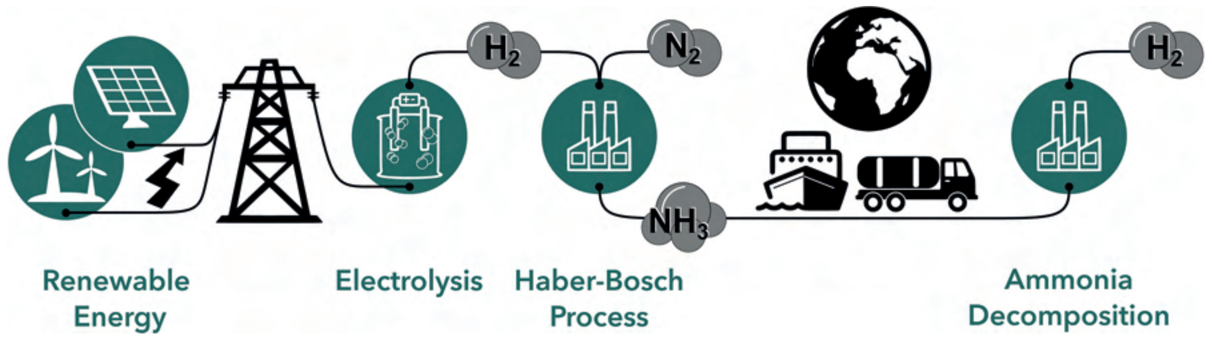

Figure 1. Process chain of a future hydrogen-based energy supply. In this concept, hydrogen production takes place through renewable energies in windy or sunny regions by means of electrolysis. The hydrogen produced is converted into ammonia, via the well-known Haber-Bosch process, which is technically easier to transport over long distances. At the desired destination, the ammonia is converted back into hydrogen through a catalytic ammonia decomposition step.

The aim of our research is the knowledge-based development of advanced carbon-based catalysts for application in different energy related processes, for example, electrocatalytic water splitting or ammonia decomposition. In the process chain (Figure 1) that enables our future energy supply, based on hydrogen (H_2) as chemical energy carrier, numerous catalysts are in use. The process chain comprises the generation of renewable energies (in sun and wind-rich regions), the use of electricity in electrolysers for the production of hydrogen, its conversion in the Haber-Bosch process with nitrogen (N_2) into ammonia (NH_3) on site, global transport and the recovery of the hydrogen by ammonia decomposition at the desired destination. Different material property requirements are demanded of the catalysts for the various applications. We focus on composite materials of catalytic active metal oxides and carbon support materials that combine the individual positive material properties. In addition, we are preparing and investigating metal-based electrodes to gain fundamental understandings of electrocatalysis. Including the investigation of reaction mechanism by formed intermediates through in situ experiments.

The carbon support materials are synthesized by bottom-up or top-down methods. Through the generation of specific functional groups, a homogeneous distribution of metal species can be achieved and an anchoring and thus stabilization of the metal species is made possible. Systematic studies are performed to determine the structure-property-correlations. The non-linear interaction of materials properties, such as conductivity, porosity, hydrophilicity or particle size complicates the knowledge-based synthesis of materials. Nevertheless, over the last three years we have contributed to a better understanding of electrodes and have also started to explore carbon-based catalysts in the field of ammonia decomposition.

Carbon-based Electrode Materials

For a global application, the material solution for the electrodes must be sustainable, scalable, and relatively inexpensive compared to the current precious metal-based electrodes. A key requirement to sustainable and green energy systems is that all harmful or rare resources utilized in the process must be part of a closed material cycle. A basic idea we have been investigation for the last few years is the use of a carbon-based sacrificial electrode. A continuous hydrogen production takes place at the cathode through catalytic water splitting during the oxygen evolution reaction (OER), while intentionally allowing the decomposition of the electrode into CO_2 analogous to the process of natural biomass decomposition (Figure 2). This strategy of a sacrificial electrode could provide a scalable and low-cost material solution for hydrogen production from renewable energy sources when produced from biomass. We have demonstrated the theoretical and technical feasibility of using carbon to produce hydrogen.[1] Not only under standard laboratory conditions but with free-standing electrodes in different

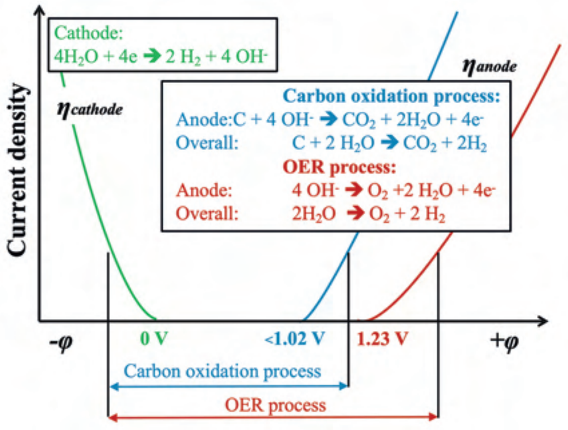

Figure 2. Electrochemical polarization curves of water splitting when use of carbon as sacrificial electrode. The insets are the related reaction equations of both OER and carbon oxidation.

electrolytes, high and dynamically applied potentials to simulate the connection to e.g. a photovoltaic system. In addition. We have also investigated to what extend the performance, in terms of hydrogen production, can be improved by chemical modifications.[2] Introduction of metal species highly improved both oxygen evolution and carbon oxidation activity. By an increase of the annealing temperature and the annealing time of the carbon samples, their electrocatalytic performance increases. The reason is that the high temperature and the long-time lead to a decrease of the amorphous entities, edges and defects, which are the sites that being oxidized first. By adjusting the balance between the reciprocal water oxidation and carbon oxidation, an optimized hydrogen production can be reached. The sources of carbon-containing precursors are infinite from plants and food waste. It turned out that not only metal species in the carbon materials themselves have a major influence, but also iron impurities in the electrolyte contribute very strongly to the performance (activity and stability).[3] These findings were further correlated with specific carbon functional groups. That could be investigated by our former developed non-linear thermogravimetric investigation by direct speciation separation of oxygen functional groups.[4] The concept of sacrificial electrodes provides an industrially scalable and sustainable option to obtain hydrogen from water and also a substitution of the low-efficiency carbon-based fuel (like coal) combustion process.

We were also able to show that nitrogen-containing materials exhibit a significant shift towards catalytic OER (Figure 3). The work was supported by the fundamental studies of nitrogen model catalysts in order to determine the influence of the individual functional N species.[5] Specifically, dynamic evolution of active sites and key adsorbed intermediate products including O^2 (ads), superoxide anion $O^{2-}*$, and OOH* could be monitored with in situ spectroscopy. We propose that the formation of *OOH species from $O^{2-}*$ ($O^{2-}* + H_2O \rightarrow OOH^* + OH^-$) is a possible rate-determining step (RDS) during the oxygen reduction reaction (ORR) process, whereas the generation of O^2 from OOH* species is most likely the RDS during the OER process.

Electrode Materials

Cobalt oxide (assigned as CoO_x) is an efficient OER nanocatalyst, which has been extensively studied as a replacement to noble metal-based catalysts.[6] The recent observations and understandings for the interfacial state, adsorbed intermediate products, and rate-determining steps on CoO_x, however, have remained elusive because of the dynamic transformation of different Co ions and the transient nature of the intermediates formed during the OER process. We have intensively worked with CoO_x species and proposed that under the chosen experimental conditions, the redox process between Co(III) and Co(IV) species does not follow a proton-coupled electron transfer mechanism that is thought to be common prior to the OER, but it involves a proton-decoupled electron transfer, clarified by isotope labeling experiments and in situ electrostatic modulation. The interfacial state of CoO_x is negatively charged prior to the formation of Co(IV)=O species. The Co(IV)=O species are demonstrated to directly regulate the OER performance.

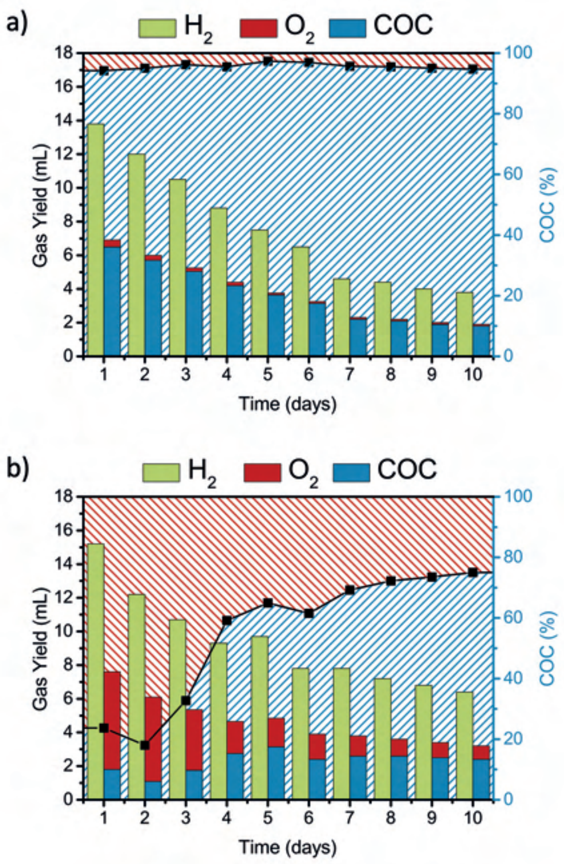

Figure 3. Daily gas collection in a two-electrode "Hofmann" cell: Hydrogen at the cathode; oxygen and the carbon oxidation contribution (COC) at the anode for (a) hydrothermally derived carbon (HTC) and (b) nitrogen modified HTC. Red-shaded areas demonstrate the hydrogen production from water oxidation (catalytic process), whereas blue-shaded areas represent the hydrogen production from carbon oxidation.

Moreover, we could experimentally monitor the dynamic evolution behaviors of Co(IV)=O, Co(O)O⁻, OOH*, and $O^{2-}*$ intermediates during the OER with in situ time-resolved infrared spectroscopy (Figure 4), and the following elementary step $OOH^* + OH^- \rightarrow OO^-* + H_2O$ is likely to be the unexpected RDS in the OER process.

Prometheus

The lates BMBF (Ministry of Education and Research) funded project (PrometH_2eus) deals with targeted surface modification by means of a synthesis downstream plasma treatment. Both our own preliminary work and results from recent studies show that Ni-based materials can be treated by plasma process to produce non-equilibrium phases with improved electrocatalytic performance. In addition, it has been shown that the stability of these materials can be increased in application. Plasma treatment therefore provides a cost-effective and scalable opportunity to optimize materials in a process-independent manner, and therefore represents an important additional component in materials synthesis. Plasma treatment also offers the advantage of being relatively easy and cost-effective to integrate into existing large-scale processes, for example roll-to-roll processes. The complex plasma system has been installed and started up. The first systematic investigations in which the plasma parameters were varied and electrocatalytic measurements were fulfilled were carried out. There is a lively exchange with the other project partners, so that first publishable results are expected soon.

Ammonia Decomposition

The AmmoRef project, which is part of the TransHyDE BMBF funded project (see separate project description), is the most extensive project to date in the working group dealing with the reforming of ammonia (recovery of pure hydrogen). To date, there is no technology for reforming ammonia that can be used on a large industrial scale. Therefore, the technological fundamentals are researched and developed in this association to ensure an environmentally friendly, economical and safe solution for future energy supply. In an initial literature study, the challenges to identify catalyst materials from literature studies with potential for application in large-scale industrial processes were explored.[7] On the one hand, the requirements on the catalyst are quite demanding. Of central importance are the conditions for the primary reaction that have to be met by the catalyst. Likewise, the catalytic performance, i.e., an ideally quantitative conversion, and a high lifetime are critical as well as the consideration of requirements on the product properties in terms of pressure or by-products for potential follow-up processes, in this case synthesis gas applications. On the other hand, the evaluation of the multitude of literature studies poses difficulties due to significant varieties in catalytic testing protocols.

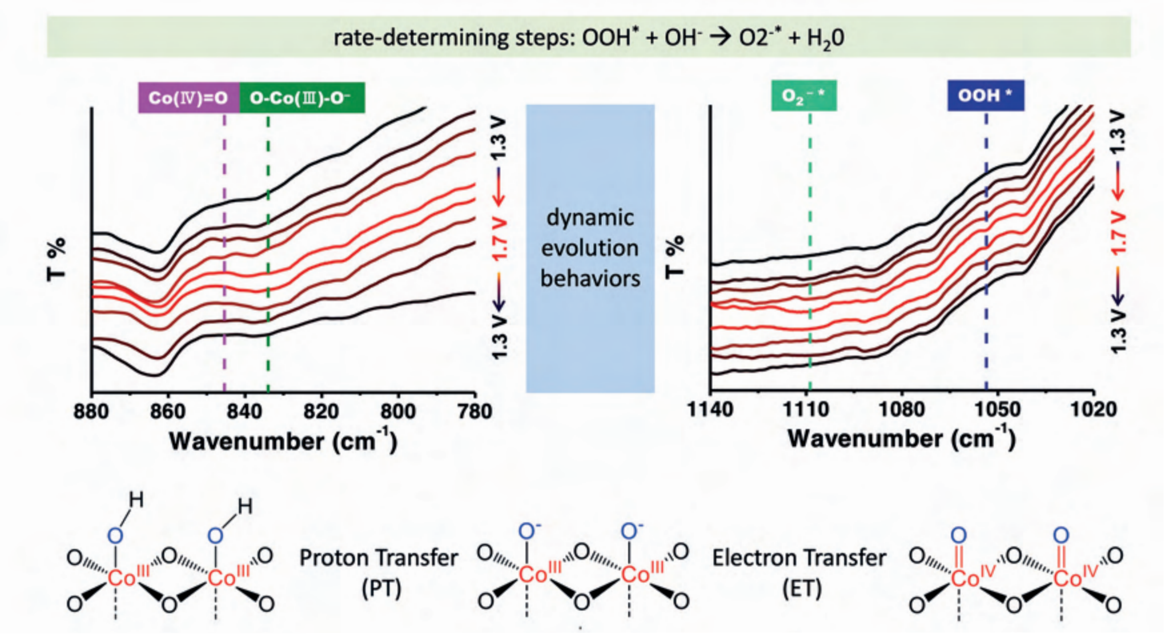

Figure 4. In situ ATR-IR spectra monitoring and identification of the involved intermediate products during the OER process of active Co-oxo species (left) and oxygen species (right). And a schematic drawing of the possible oxidation process of Co(III) to Co(IV) involving a proton transfer (PT)-decoupled electron transfer (ET) mechanism. Were two octahedral structures bridged with O atoms were used as an ideal model because Co(III) typically lies in the octahedral site. Using two octahedral structures are shown to roughly describe the possible interfacial state of CoO_x.

In the research group, the focus is on the synthesis of carbon-based catalysts to gain highly active, stable and cost-effective catalysts without precious metals through a knowledge-based approach. Systematic studies are carried out to investigate the influence of material properties on the catalytic activity. The influence of real structures is also investigated by different synthesis methods, only scalable methods are used in the choice of synthesis methods to ensure a later industrial realization.

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Electronic Structure

Main Research fields

We focus our research on operando investigations of the electronic structure of catalysts and electrode surfaces used in heterogeneous catalytic reactions and electrochemical processes like the 2-propanol oxidation reaction over Cobalt oxide catalysts and the oxygen evolution reaction (OER) over Ir and the CO_2 reduction reaction (CO2RR) over Cu, respectively. The development of electrochemical cells enabling operando X-ray absorption spectroscopy and X-ray photoelectron spectroscopy in the soft X-ray range is an essential part of our work.

IrO_x in OER

The oxygen evolution reaction (OER) has an important role in many alternative-energy schemes because it supplies the protons and electrons required for converting renewable electricity into chemical fuels. Electrocatalysts accelerate the reaction by facilitating the required electron transfer, as well as the formation and rupture of chemical bonds. This involvement in fundamentally different processes results in complex electrochemical kinetics that can be challenging to understand and control, and that typically depends exponentially on overpotential. Such behavior emerges when the applied bias drives the reaction in line with the phenomenological Butler-Volmer theory, which focuses on electron transfer, enabling the use of Tafel analysis to gain mechanistic insights under quasi-equilibrium. However, the charging of the catalyst surfaces under bias also affects bond formation and rupture, the effect of which on the electrocatalytic rate is not accounted for by the phenomenological Tafel analysis and is often unkown. We have performed pulse voltammetry and operando X-ray absorption spectroscopy measurements on Iridium oxide and have shown that the applied bias does not act directly on the reaction coordinate, but affects the electrochemically generated current through charge accumulation in the catalyst. We have demonstrated that the activation free energy decreases linearly with the amount of oxidative charge stored. We have shown that this relationship underlies electrocatalytic performance and can be evaluated using measurement and computation. [1]

We explored the effects of chemical bond making/breaking steps on the oxygen evolution reaction rate of Iridium oxide electrocatalysts using pulse voltammetry to compare potential, charge and performance.

CuO_x in CO2RR

Copper can uniquely perform the electrocatalytic reduction of CO_2 into valuable hydrocarbons and alcohols [2] suffering from low current density, high overpotential, low selectivity and electrode deactivation over time hindering its industrial application. Thus, revealing the nature of the active/stable centers of copper during the electrochemical reduction of CO_2 is fundamental to design more efficient catalysts. Typically, element specific X-ray spectroscopy was used for that purpose being technically challenging to perform these measurements in presence of liquids. This technical limitation forced the use of *ex situ* characterizations and bulk sensitive methods and, thereby, prompted many different interpretations of the active/stable copper oxidation state during the CO_2RR. In order to overcome this issue and provide an unambiguous description of the electronic structure of copper during the electrocatalytic reduction of CO_2 to valuable hydrocarbons, we enabled the detection of surface sensitive photoelectrons (i.e. TEY-XAS and/or XPS) using a 2D membrane (graphene) transparent window, enabling surface sensitive spectroscopies during electrochemical reactions [3]. Furthermore, using this approach, we performed for the first time *in situ* electrochemical scanning electron microscopy (ECSEM), even with back-scattered electrons, under reaction conditions. In addition, a bulk sensitive measurements in total fluorescence yield mode (TFY) [4,5] were accomplished linking the changes in the surface of the catalyst with its bulk.

It was found that the copper electrode/electrolyte electrified interface is ruled by the formation of reduced copper (Cu^0), being thermodynamically stable and active during the cathodic reduction of CO_2 to hydrocarbons.

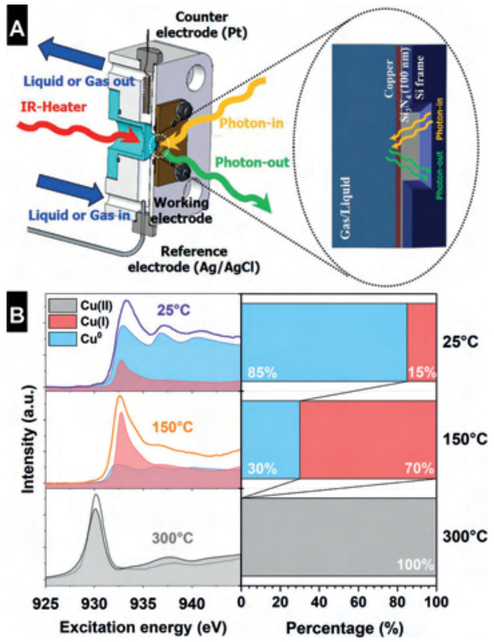

Figure 1. (A) Schematic drawing of the in situ cell, which allows for the thermal oxidation of the copper electrode in the presence of gases, using an IR-laser heater, or as the electrochemical cell when the gas is exchanged by a liquid electrolyte. The electrochemical cell contains a PVD Cu working electrode (deposited on the Si_3N_4 membrane), a Pt wire counter electrode, and an Ag/AgCl reference electrode. The detection method for X-ray absorption spectroscopy is also shown schematically in the membrane zoom: PIPO measurements in TFY. (B) Cu L_3 absorption edge measured in the XAS–TFY mode of the in situ oxidized 50 nm thick PVD copper at three different temperatures in air and the linear combination of relevant copper reference samples that resemble the collected spectra. Furthermore, the estimated percentage of each component is shown on the right side.

The reduction of copper electrode takes place also in the catalyst bulk indicating that the stable copper phase is the same in surface and near-surface. This finding is in good agreement with the expected thermodynamics equilibrium under such conditions in the respective Pourbaix diagram. These results imply that the reported active copper oxides can be only stabilized due to kinetics and they are not stable at high cathodic potentials required to perform the CO_2RR.

Instrumentation

It has been realized that a simple vacuum tank backfill approach to do ambient pressure X-ray photoelectron spectroscopy does cover many but not all aspects of such experiments and offers disadvantages, for example its poor sample amount to gas volume ratio and limited flexibility. Small volume reaction cells with a well-defined gas-solid interaction zone and gas contact time are required. Here we describe a versatile reaction cell platform that can easily be adapted to the needs of the scientific task. In Figure 2 a sketch of the reaction cell (A) and its main components (B) is presented.

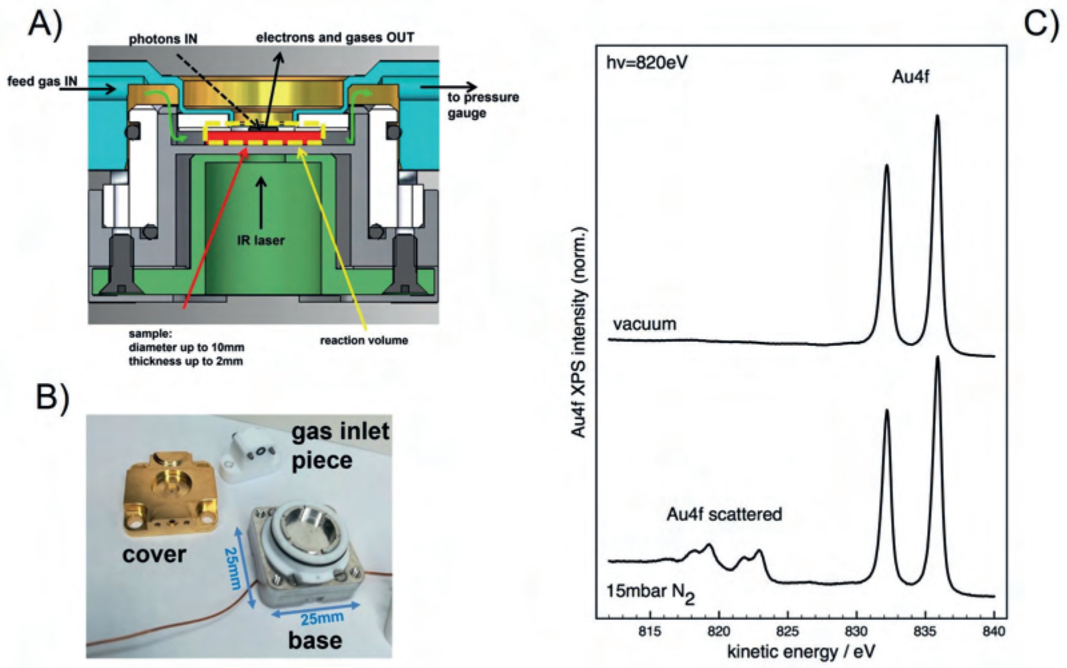

Figure 2. A) is a sectional view of the gas-solid reaction cell with indication of gas in/out flows and the sample compartment, B) pictures the main components of the reaction cell with the base holding the sample, the cover lid to close the cell compartment, and the gas inlet pieces organizing the gas flow into the cell. C) shows Au4f core level peaks in vacuum (top) and 15mbar of N_2, (bottom) with the inelastically scattered Au 4f photoelectrons ("Au4f scattered"). The photon energy was 820eV.

The cell allows dosing gases with calibrated mass flow controllers into a small reaction volume of a few µl above the sample surface as shown in Figure 2A. The sample can be heated with a NIR laser from the rear and the temperature is measured with a thermocouple. The cell can hold all standard sample formulations from single crystals, foils, wafers to pressed powders. The pressure of the gas can be measured in various ways, either directly with pressure gauges at the inlet/outlet of the feed gases or indirectly for example via the applied gas flow after calibration of the scattering of the released photoelectrons. The reaction cell consists of a few, easy to manufacture parts that are displayed in figure 2 B. A base unit holds the sample and is closed with a cover lid. Gas inlet pieces are attached to the cover to organize the gas inlet and outlet. Sample exchange is simply done by detaching the cover from the base. This few easy to manufacture components create a handy, reliable unit that allows using individual gas-solid reaction environments for each experiment. XP spectra of the Au4f core levels of a gold foil measured in vacuum and in 15mbar N_2, respectively, are compared in Figure 2C. It becomes obvious that high-quality, high-resolution spectra can be obtained. Additional peaks at lower kinetic energy compared to the main Au4f peaks are observed. They are resulting of distinct, inelastic scattering of primary photoelectrons in the gas phase [6]. This substantiates the presence of a high local gas density, i.e. pressure in the vicinity of the sample surface.

Due to the modular, standardized instrumentation concept of the AP-XPS spectrometers operated by the Fritz-Haber-Institut at BESSY II, the new reaction cell platform can be mounted to all spectrometers operated at the CAT@EMIL, BElChem, and ISISS beamlines without any modification to the instruments, i.e. it is a retrofit/add-on to existing set-ups [7]. The exchangeable cover of the reaction cell can be designed in various ways. It can either come with an aperture of various sizes in the metal cover. This introduces an additional aperture differentially pumped by the surrounding vacuum tank to the AP-XPS system without modifying the integrity of the instrument by e.g. replacing the entrance aperture/front cone of the spectrometer lens system. The latter approach has been followed before at other AP-XPS set-ups [8]. Or the cover can be equipped with an X-ray transparent SiN_x membrane that holds for example a hole array. In both cases high pressure XPS spectra can be obtained. Instead of a hole array also SiN_x membranes with a single center hole can be used. A hole of a diameter of 50µm allows a cell pressure of 1000mbar without that any modifications to the existing pumping scheme or change of the spectrometer entrance aperture is required. Another use case is to mount a cover with a closed SiN_x membrane. In that case, soft X-ray absorption spectra (NEXAFS) both in total electron yield and fluorescence yield mode can be recorded at varying pressures up to 1000mbar.

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Catalytic Technology

The focus of the catalytic technology group is on investigating heterogeneously catalyzed reactions within the scope of energy conversion and storage. Here, catalysts will play a major role for future energy-effective and sustainable technologies, especially heterogeneous catalysts that are nowadays the mostly applied catalysts for large-scale processes. A deeper understanding of the working catalyst can help to improve available catalysts or provide suggestions for the development of alternative catalysts. Increasing the overall efficiency of a process by more effective catalysts reduces the utilized resources for both, materials and energy and thus can enable the feasibility of future process chains (Fig. 1).

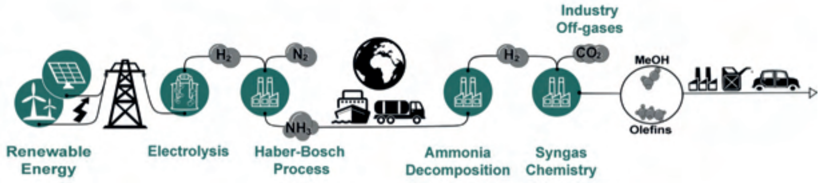

Figure 1. Scheme of a future process chain for energy generation, transportation and storage.

On the background of a changing energy supply from fossil to renewable resources like e.g. wind and solar, hydrogen generation by water electrolysis is a key step for energy storage and overcoming the fluctuations of natural energy resources. As the energy density of hydrogen is low compared to fossil fuels its conversion to substances with a high hydrogen content combined with an easy transportation and storage capability, like e.g. ammonia or methanol, is suggested as more efficient for energy storage [1]. The combination with exhaust gases from industry by implementation of carbon capture and usage (CCU) technologies will offer the advantage of an additional reduction of CO_2 emissions [2].

Ammonia synthesis

Besides its application as fertilizer ammonia represents a promising energy carrier to store and transport hydrogen produced from renewable energy. Although ammonia synthesis is applied since more than a century the active phase of the Fe-based catalyst under industrially relevant conditions and the role of the several promoters is still not sufficiently understood. The detailed investigation of a series of differently promoted iron-based catalysts reveal that promoters not only affect surface area and mesoporosity or act as binder for the wuestite grains (Fig. 2) [3]. They furthermore strongly influence the reduction by impeding the disproportionation of the wuestite precursors resulting in an increased catalytic performance.

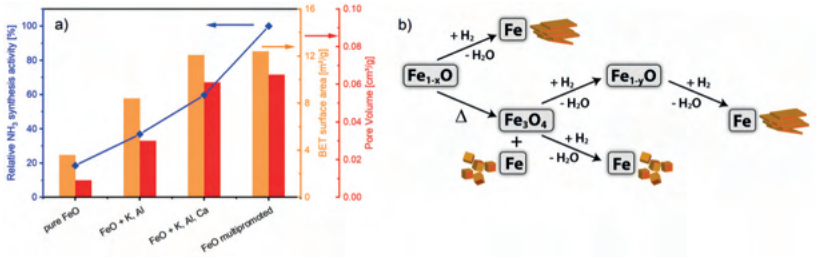

Figure 2. a) Relative NH_3 synthesis activity at 400 °C and 90 bar of differently promoted Fe-based catalysts compared to their BET surface area and pore volume after catalytic testing. b) Possible reduction pathways with disproportionation of $Fe_{1-x}O$. [3]

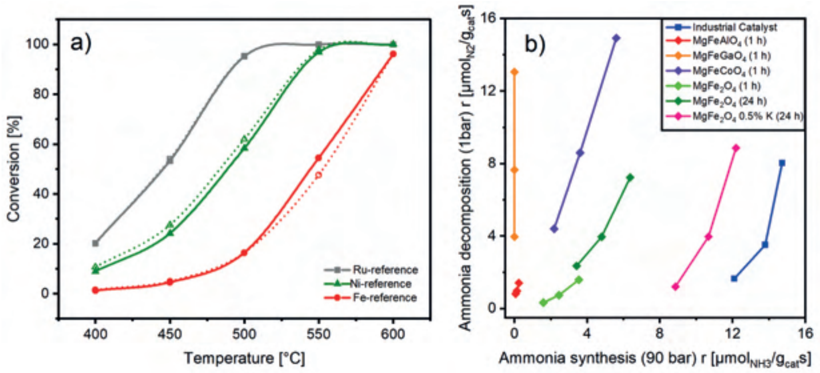

Figure 3. a) Activity of different industrial catalysts in ammonia decomposition. b) Influence of different promoters on the activity of magnesioferrite-derived catalyst in ammonia synthesis and decomposition [4].

Industrially applied catalysts are nowadays still prepared by high-temperature melting, which hampers laboratory studies. To overcome this a systematic series of $MgFe_2O_4$-based model catalysts synthesized from a layered double hydroxide precursor prepared by the group of M. Behrens at the University of Kiel as well as in the inorganic chemistry department at the FHI in Berlin are applied for further fundamental studies [4]. These catalysts provide even with only Mg and K as promoters a significant activity and a high stability in ammonia synthesis. By varying the catalyst composition and adding further promoters the catalyst's structure can be modified and the impact of this modification on the activity is investigated. Furthermore, these alternative catalysts provide the perspective to avoid the high temperature melting process of the iron oxide precursor by low-temperature self-organization of layered iron-oxihydroxide precursor with a mineral spacer to obtain a high surface area. By this energy-effective synthesis it is now possible to investigate the interplay of morphology and promoter chemistry in the formation of the active iron species.

Ammonia decomposition

Using ammonia as hydrogen carrier for energy storage and transportation requires its decomposition to release the hydrogen for further energy or chemical applications. For this reaction up to now no industrial process is available. Here, identifying possible catalyst systems for an energy-efficient decomposition and defining suitable process designs are crucial steps to enable the use of ammonia as future energy carrier. Despite no systematic catalyst development has taken place so far, available industrial catalysts already show reasonable activities for ammonia decomposition (Fig. 3a). Considering the strong influence of promoters a successful catalyst development and optimization seems promising (Fig 3b). Catalyst development in the BMBF-funded project AmmoRef is therefore supported by catalyst screening as well as kinetic investigations. Newly designed test facilities are used enabling fast screening of numerous catalysts following standardized test protocols, ensuring comparability of the results obtained, to break down the variety of possible catalysts to those applicable in an industrial process.

Methanol synthesis

Besides ammonia methanol is a potential hydrogen carrier in a future energy and carbon economy. Furthermore, already today methanol is one of the most important industrial bulk chemicals, which is produced from a synthesis gas mixture containing CO, CO_2 and H_2 applying a $Cu/ZnO/Al_2O_3$ catalyst. The syngas is derived nowadays from fossil resources and rich in CO. For a future sustainable and environmentally friendly application its production from carbon-containing exhaust gases with H_2 derived from renewable energies seems to be a promising route to reduce CO_2 emissions from industry and minimizing the use of fossil resources. Although a considerable effort is invested to find a new catalyst for these changed boundary conditions, the industrially applied Cu-based catalyst is still clearly superior to the newly developed ones also in CO_2 hydrogenation to methanol [5]. Therefore, for a fast implementation of industrial-scale CO_2 hydrogenation the use of the actual industrial catalyst is unavoidable, but requires a deeper understanding under the altered conditions. Dynamic changes of synthesis conditions caused by the incorporation of renewable resources within this process chain were found to have no restraining influence on the catalyst lifetime [2]. This supports the idea of applying methanol synthesis from CO_2 in a renewable network for energy storage and/or production of chemicals. Furthermore, the impact of trace components like oxygen in the feed gas on the stability of the catalyst is investigated to determine the required gas cleaning for applying unusual feed gases for methanol synthesis like steel mill exhaust gases. The increase of the activation energy while oxygen impurities are present in the feed gas indicate that oxygen affects the active sites and, moreover, oxygen accelerates the deactivation as it induces sintering of the Cu particles (Fig. 4). Further studies are focusing on finding operation parameters in CO_2 hydrogenation to methanol where reasonable lifetimes of the Cu-based industrial catalyst can be achieved enabling its application in the envisaged renewable network.

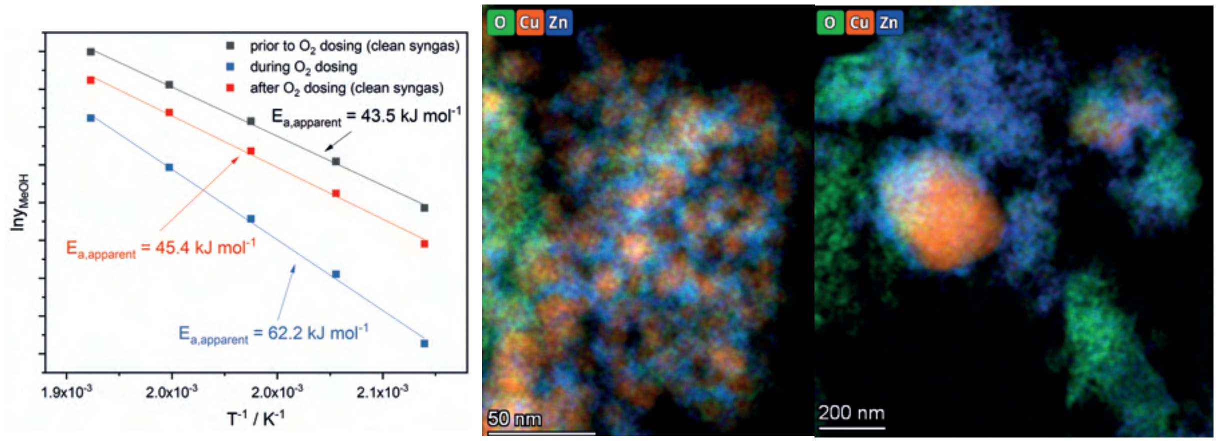

Figure 4. a) Apparent activation energies for the methanol formation from a CO_2-rich synthesis gas with and without oxygen in the feed gas. TEM images of a Cu/ZnO-based methanol synthesis without (b) and with (c) oxygen in the feed gas.

Analysis of exhaust gases from steel mill plants

One important aspect for applying conventional heterogeneously catalyzed reactions in a renewable network in combination with exhaust gases from industry is the altered gas composition. Here, not only the main components for the reaction have to be taken into account. Also, the different minor and trace components have to be considered and may require adjustments for the gas treatment compared to the nowadays applied processes. In the Catalytic Technology group the capability of those gases as chemical feedstock for methanol and/or ammonia synthesis in a circular economy is investigated. An extensive study is performed to gain a deeper understanding of the time-depending composition of steel mill exhaust gases with respect to both, the main and trace components. The composition of the three metallurgical gases (blast furnace gas, basic oxygen furnace gas and coke oven gas) depends on the process conditions as well as the raw materials used. Therefore, a detailed analysis of these gases over long periods is required for the further process design including gas cleaning and their usage in a chemical reaction. To address this, a high-end gas analysis is operated directly on-site at the steel mill monitoring the raw as well as purified gases. The main components like nitrogen, hydrogen, oxygen, carbon oxides and methane are analyzed by gas chromatography. Trace components like metals, sulfur-, nitrogen, and chlorine-containing compounds, polycyclic aromatic hydrocarbons, and BTEX-aromatics are analyzed by a new generation PTR-QiTOF-MS for high performance analysis. Besides the analysis of the real gases also method optimization plays an important role to adapt this technique to complex gas mixtures. In particular, the contribution of instrument artefacts and memory effects was investigated extensively. As they may contribute in the same range to the mass spectra as the trace components in the real gases a detailed knowledge on their involvement is mandatory to ensure a correct interpretation [6].

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Summary

The aim of our research is the investigation of dynamic energy conversion phenomena at electrified interfaces, with main focus on water electrolysis (i.e. oxygen evolution reaction (OER) and hydrogen evolution reaction (HER)) as well as fuel cell reactions (particular focus on oxygen reduction reaction (ORR)). The in-depth investigation of such complex phenomena requires a multidisciplinary approach. Therefore, we employ methodologies that will address scientific challenges from various relevant perspectives. This kind of multifaceted approach can give more complete and in-depth knowledge on the underlying electrocatalytic mechanisms. For this reason, a variety of different metal-based, metal oxide-based or composite-based catalytic systems (flat samples, nanostructured samples, polycrystalline materials, single crystals etc.) are evaluated under transient and steady state conditions using advanced analytics including: Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) coupled to electrochemical Quartz Crystal Microbalance (eQCM), elevated temperature Rotating Disc Electrode (RDE), Kelvin probe (KP), in-situ and operando X-ray Absorption Spectroscopy (XAS)[1] (**Fig. 1**) [1]. Gathered information on complex behavior of electrified interfaces during electrocatalytic performance (e.g. intrinsic rate of dissolution, transient mass changes, effect of impurities on rate of electrocatalytic reaction, adsorption energies etc.) will give us an advanced view on electrocatalytic processes and supply valuable information about the properties essential to identify electrocatalysts with superior performance.

Advanced protocols for electrocatalyst benchmarking

Activity and stability benchmarking is important for electrocatalysts design for the OER. In our group, besides classical kinetic tools like rotating disc electrode (RDE), several electrochemically-coupled flow cells (EFC) coupled to ICP-OES were developed, allowing dynamic and stationary time resolved monitoring of catalyst dissolution[2]. Relevant information from such benchmarking protocols can then be illustrated in a single "spider" graph as shown in **Fig. 2**.

Hydrogen Evolution Reaction (HER) Investigation

Although most of the spotlight for understanding and optimizing water electrolysis falls on the more sluggish oxygen evolution reaction (OER), understanding of hydrogen evolution reaction is still not yet complete. On the example of HER in alkaline media (**Fig. 3**), we have shown that in-depth analysis of the preexponential frequency factor and its relation to activation energy and electrocatalytic reaction rate will be essential[3].

Such an approach can improve our mechanistic understanding of electrocatalytic activity and have a great impact on the design and fine-tuning of state of the art electrocatalysts.

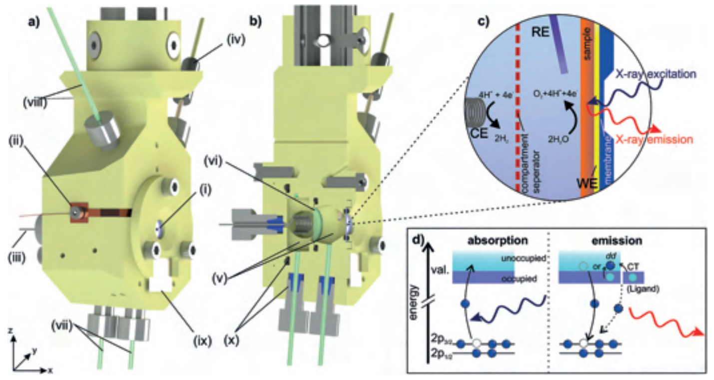

Figure 1. Sketch of the flow cell, designed for soft X-ray photon-in–photon-out spectroelectrochemical experiments, and working principle.

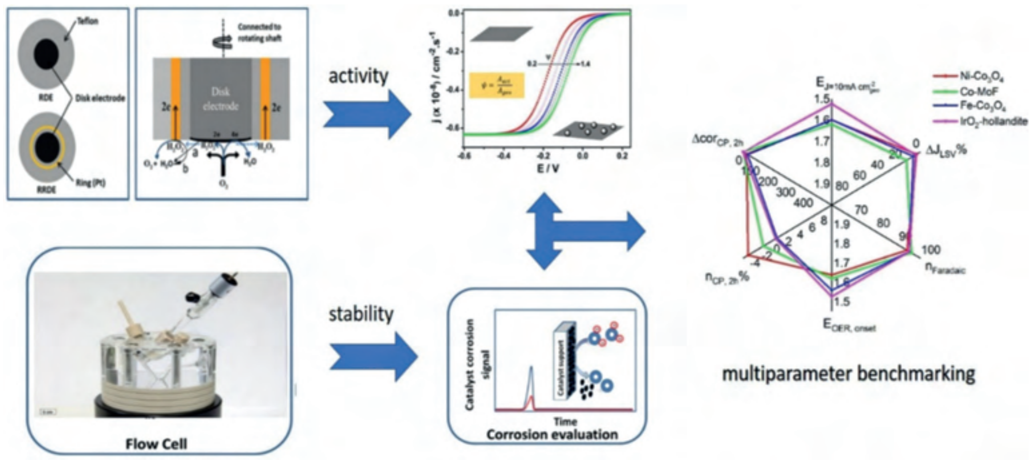

Figure 2. Evaluation of OER catalyst performance, including in-operando dissolution, by a combination of different techniques like ICP-OES, RDE etc., including "spider" graph for catalyst benchmarking.

Next, we focused our efforts on understanding how the structure of catalyst materials both in acidic (Ir-based electrocatalysts) and alkaline (Ni-based electrocatalysts) environment, can affect the activity and stability of such catalysts.

Structure/activity relations

Next we investigated two stoichiometrically identical Co_2FeO_4 catalysts with indistinguishable X-ray diffraction patterns, however, with drastically different OER kinetics. The enhanced activity and stability measured with our specially designed high surface area EFC coupled to an ICP-OES was attributed to local nanoscale inhomogeneities as seen by TEM, due to a Co^{2+}-rich phase linking the spinel domains of the Co_2FeO_4 electrocatalyst. Understanding of subtle local differences in the structure of chemically similar electrocatalysts is necessary to make a structure/activity relation[4].

Mixed oxides

Additionally, we have studied the effect of Ni on the activity and stability of an IrNi mixed oxide catalyst. Catalyst characterization by XPS and XAS indicated that the surface of Ni-doped IrOx catalyst contains an IrO_x-rich phase and it confirmed the presence of Ir^{3+} and Ir^{4+}, while EXAFS analysis confirmed IrO_6 distortion compared to rutile IrO_2, with longer Ir–O bond distances in the first coordination shell and more disordered intermetallic bond distances in the second coordination shell (Ir–Ir and/or Ir–Ni)[5]. Activity and stability towards OER was thus linked to the formation of a IrO_x-rich phase due to doping with Ni, showcasing the effectiveness of the approach on lowering the iridium concentration, while keeping the activity and stability of the system.

Intermetallics as OER catalysts

We then moved on to the investigation of the Al_2Pt intermetallic compound as an electrocatalyst for OER. It was shown that the intermetallic compound with higher concentration of the main group element provides the basic bulk stability of the system and modifies the electronic structure of Platinum. Such a modification is This modification enables its conversion into a partly oxidized hydrated gel phase that optimally reacts with water in a porous structurethat is prevented from crystallization via mixing with non-dense hydrated alumina passivation layer, which acts as a mineral spacer that allows the diffusion of reactants and products and inhibits dissolution.[6].

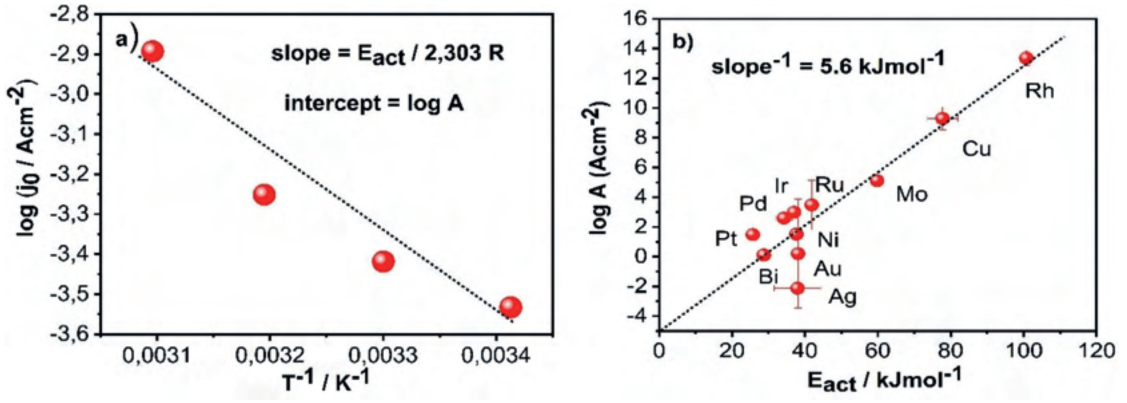

Figure 3. a) Example of Arrhenius plot for electrocatalytic HER on Ir in 0.1 M KOH. b) Relation between activation energy and preexponential frequency factor for HER in 0.1 M KOH.

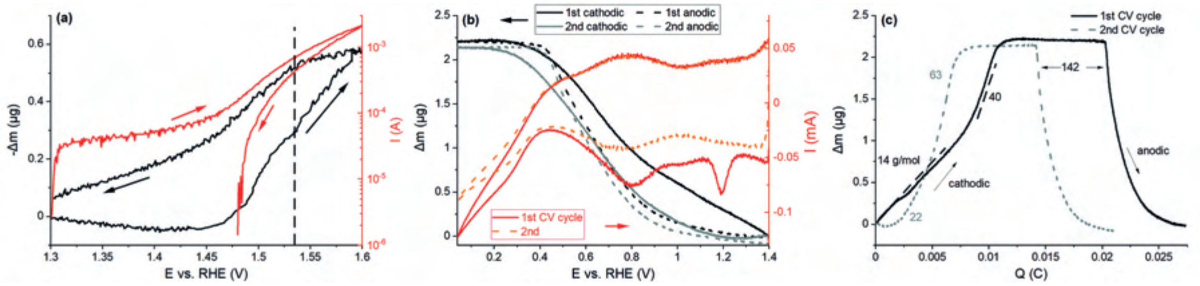

Figure 4. a-c) Mass variation (left *y*-axis, black line) and current response in the logarithmic scale (right *y*-axis, red line) against the potential during OER sweeping (1.3–1.6 V, RHE, 5 mV s^{-1}, first full cycle).

Catalyst regeneration

Recently we demonstrated the dynamic nature of the IrO_x structures and the manner in which OER conditions regulate their hydration degree. During potentiodynamic conditions, a logt dependent charge growth is accompanied by deactivation (**Fig. 4**), due to the deprotonation-induced dehydration of μ_2-$OH(H_2O)_x$ and subsurface species during OER[7]. Activity is however fully restored upon electrochemical reduction with an accompanied mild dissolution. On the other hand, potentiostatic conditions irreversibly deactivate IrO_x, due to accelerated logt dependent growth of μ_2-O species, with simultaneous decrease of μ_1-O species.

Finally, understanding the still elusive effect of electrolyte impurities on the activity and stability of Ni-based electrocatalysts for the alkaline water electrolysis is important for a better mechanistic understanding of the reaction and the design of new electrocatalysts[8]. Thus, we are accelerating our efforts in gaining a fundamental understanding of the manner in which impurities in the electrolyte can affect catalyst performance. Our results suggest a interplay between the Ni catalyst surface and the electrolyte impurities which enhances the activity and decreases the catalyst dissolution rate.

Impurities effect on electrocatalysis

Thus, in our latest work, we investigated the effect of surface functionalization on the destabilization and reinforcement of NiFe-based electrocatalysts for OER in alkaline environment[9]. Dissolution of thermodynamically unstable hydrated Fe from the electric double layer results in catalyst deactivation, which however was controlled through the addition of the nonpolar heterocyclic compound Tetraphenylporphyrin (TPP). Dissolution is thus suppressed while at the same time catalyst lifetime was prolonged via Fe redeposition. This work improved our mechanistic understanding of Fe containing Ni-based electrolcatalysts and paves the way for the design of stable electrocatalysts for the alkaline water electrolysis.

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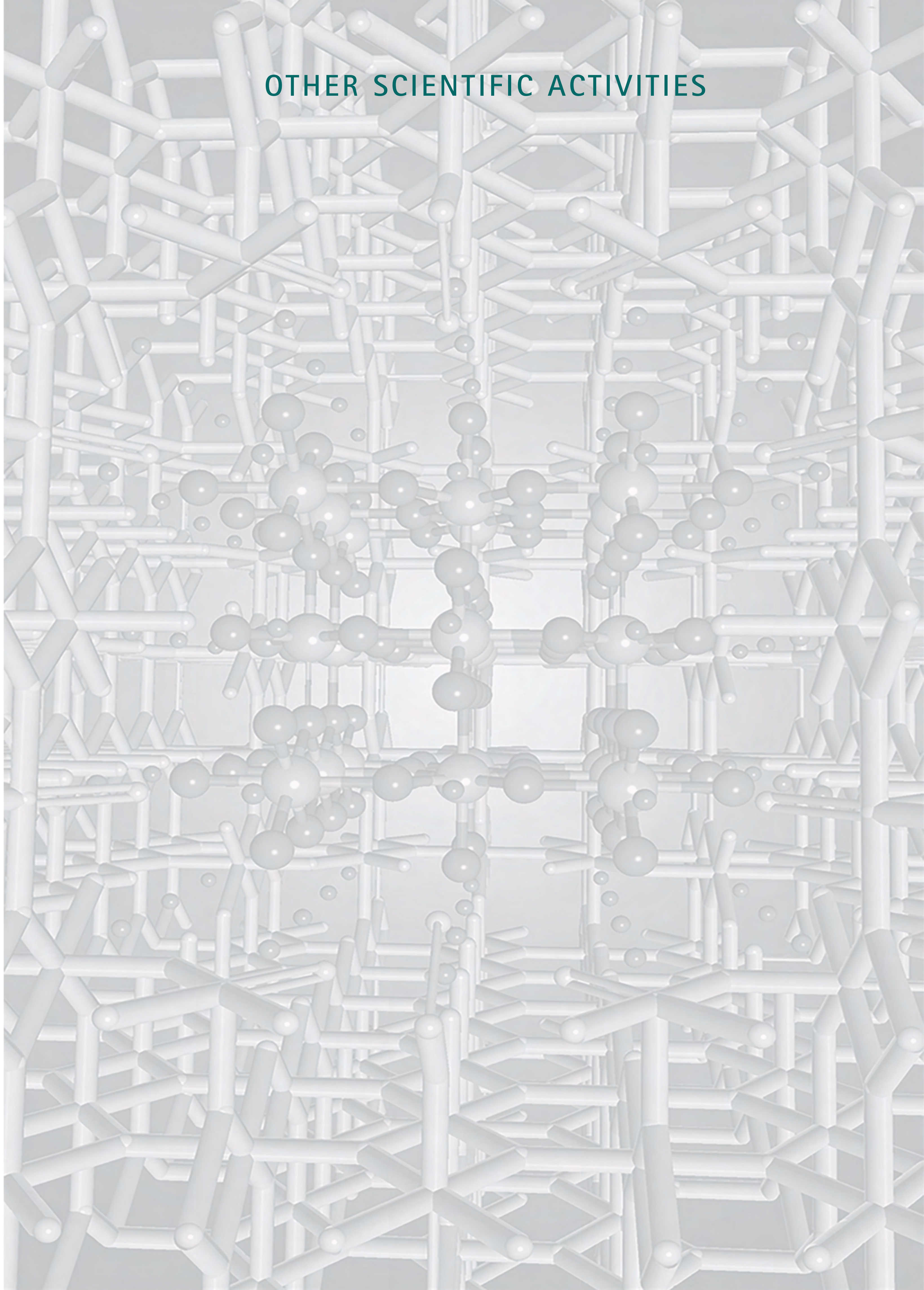

OTHER SCIENTIFIC ACTIVITIES

Prof. Dr. Wolfgang Lubitz

Dr. rer. nat. Freie Universität Berlin (1977)
Habilitation Freie Universität Berlin (1982)
Research Fellow University of California, San Diego (1983-1984)
Assoc. Professor Organic Chemistry, Freie Universität Berlin (1986-1989)
Assoc. Professor Experimental Physics, Universität Stuttgart (1989-1991)
Full Professor Physical Chemistry, Technische Universität Berlin (1991-2001)
Honorary Professor Heinrich-Heine-Universität, Dusseldorf (since 2000)
Director MPI CEC and Scientific Member of the MPG (2000-2017)
Director Emeritus (since 08/2017)

The Department of *Biophysical Chemistry* was formally closed 2017 after the official retirement of Prof. Wolfgang Lubitz who continued to work in the institute as "director emeritus" during the past ~ 6 years to finalize his projects, in particular the work on the energy-converting (metallo) proteins hydrogenase and wateroxidase. These complex enzymes are of great importance since they catalyze in a highly efficient way hydrogen production and consumption in Nature and light-induced water splitting, respectively. A detailed knowledge of their function in biology is of great importance for the bioinspired development of synthetic catalysts required for designing and improving processes for the transformation of our society from fossil to renewable energies. The significant progress in the understanding of wateroxidase and the hydrogenases achieved together with former group members and several external collaborators during the last years has been described in the previous and in this scientific report and is documented in about 40 publications in scientific journals and book chapters.

Photosynthesis and Light-induced Water Splitting

Photosynthesis is of central importance for all life on earth. In this process the sun's energy is stored in organic compounds (carbohydrates) via reduction of CO_2 from air. The reducing equivalents are coming from "biological hydrogen", NADP(H), that is provided by the light-induced oxidation of water in the so-called photosystem II (PSII). The process takes place on a unique protein-bound μ-oxo bridged tetranuclear Mn/Ca cluster (Mn_4CaO_5) whose structure was determined by x-ray crystallography in Japan (Shen and Kamiya, Nature, 2011). The water oxidizing unit exists with very little variation in all species performing oxygenic photosynthesis (plants, algae, cyanobacteria). Light driven water oxidation is a highly complicated multi-electron/multi-proton process, which requires photo-induced charge separation and electron transport in the reaction center, storage of oxidizing equivalents, coordinated proton release, substrate water binding, O-O bond formation and dioxygen release at the catalytic center. During the catalytic cycle the Mn_4CaO_5 cluster passes through five intermediate states, S_0 to S_4, in the so-called Kok cycle (Fig. 1) during which 4 electrons and 4 protons are released, 2 waters are bound and finally O_2 is ejected as waste product.

Since all S states can be trapped in PSII (except for the elusive S_4 state) and since they all exist in paramagnetic forms, cw/pulse EPR and related techniques (ENDOR, EDNMR) are the methods of choice to detect, follow and characterize the intermediates of the Kok-cycle, and determine their electronic structure, the distribution of the valence electrons in the complex (i.e. spin and oxidation states of the Mn ions) that are the basis for the chemical reaction. In conjunction with quantum chemical calculations performed in cooperation with Dr. D. Pantazis in the group of Prof. F. Neese (MPI Kohlenforschung, Mülheim/Ruhr) this approach provided detailed insight into the mechanism of biological water oxidation (see Fig. 1) that we have described in a recent publication [1].

One of the open questions in water oxidation is the identification of the two substrate water molecules binding to the Mn/Ca cluster. Exchange kinetics have been determined by Messinger et al. using MIMS (membrane inlet mass spectrometry). This experiment showed 2 different water molecules entering the catalytic cycle at different positions; the exchange kinetics depends on the species, temperature, pH value, the S state and the presence of Ca or Sr in the cluster. The fast water W_f exchange is 2 orders faster than that of the slow one, W_s (~1 s^{-1}). MIMS showed that 2 waters are indeed bound by the cluster at different times and positions in the cycle and are converted to O_2 (Cox, Messinger BBA, 2013) but not exactly where they are bound. This information is, however, available from EPR techniques. The experiment requires labeling of water with a magnetic oxygen isotope ($H_2{}^{17}O$) and a technique that can resolve the ^{17}O hyperfine coupling with the paramagnetic Mn ions in the different S states in PSII. A few years ago (Rapatskiy et al, JACS, 2012; Lohmiller et al. JACS, 2017) we could show that this can be done with high field (94 GHz) ELDOR-detected NMR (^{17}O EDNMR) which shows a much higher sensitivity (factor 30) than ^{17}O ENDOR. Three different types of water molecules bound to Mn were determined in this way – both for S_2 and S_0. By comparison with modified PSII and model systems a proposal for the assignment of the substrate water (O5, Fig. 1) was made. However, no kinetic data were available from this approach and a comparison with the MIMS data was lacking due to the limited time resolution of the experiment (incubation time ≥10 s). We have therefore set up a home-build microliter rapid freeze quench (RFQ) system with a time resolution in the ms range (Fig. 2). This allowed performance of time resolved ^{17}O EDNMR experiments on the S_2 state (both on Ca-PSII and Sr-PSII samples) and made a direct comparison with the MIMS data possible (Fig. 3) [2]. These measurements finally showed that the oxygen O5 in the Mn_4CaO_5 cluster (Fig. 1) can be assigned with confidence to the slowly exchanging substrate water W_s detected in MIMS. We are currently improving the instrument and the sample preparation to perform experiments also in the other S states. A challenge is the detection of the incoming second water (O6 or Ox) by ^{17}O EDNMR on the S_3 state – and, naturally, time resolved detection of the fast exchanging water W_f.

Our results on the water oxidizing system in PSII have been described in 3 recent reviews [1, 3, 4] and in the

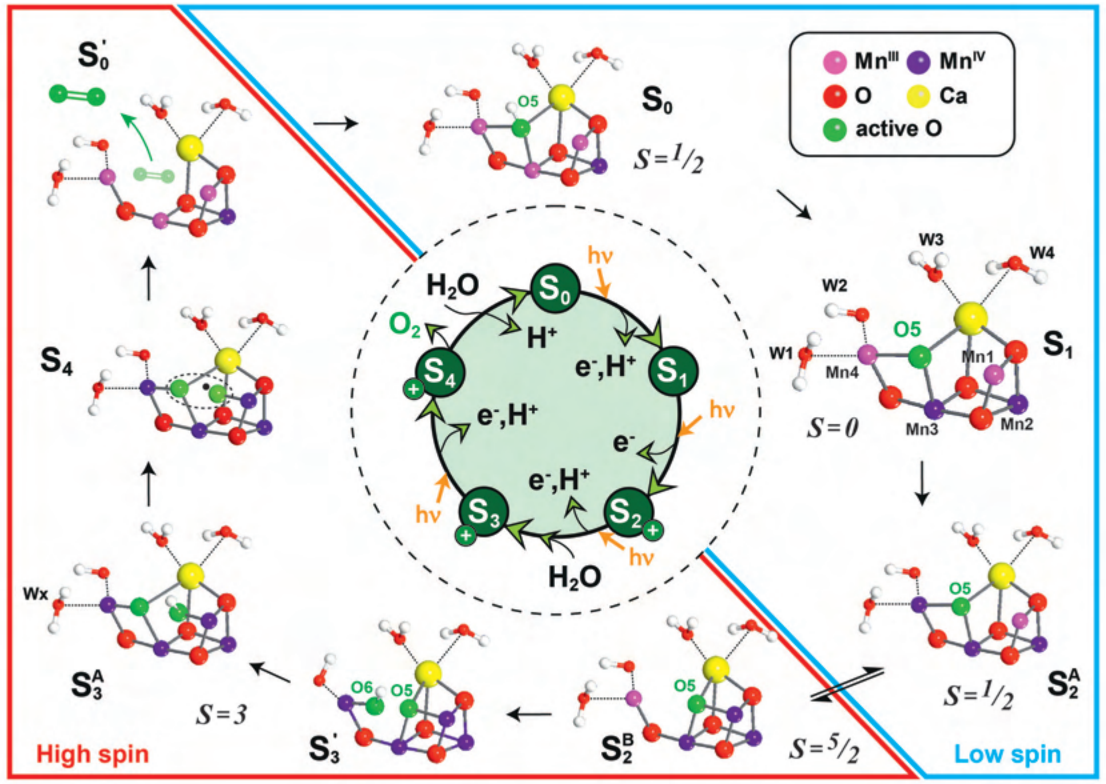

Figure 1. Proposed water oxidation cycle in oxygenic photosynthesis (Kok cycle) detailing the five basic S states, S_0 to S_4, binding of the two substrate water molecules, and the light-driven release of electrons and protons (inner circle). In the outer circle the changes of the Mn_4CaO_5 cluster related to the different S states are given (S_1 structure based on Umena et al. Nature, 2011); structural isomers are given as well as the spin state *S* of the cluster, the oxidation states of the individual Mn ions (Mn^{III}, Mn^{IV}), the binding of substrate waters (oxygen O5, O6, green) and formation of the O-O bond and O_2 release. Here, only the most likely oxyl-oxo (radical) coupling mechanism is shown, which was originally proposed by P. Siegbahn (Acc. Chem. Res. 2009); for further details, see [1].

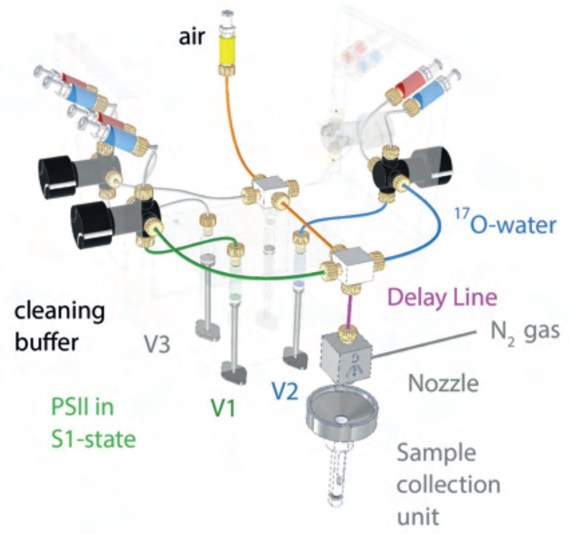

Figure 2. Experimental set-up of the rapid freeze quench (RFQ) system (based on a Biologic QFM 400) for mixing $H_2{}^{17}O$ (blue) with PSII (green) to study water binding kinetics to the Mn cluster. Specifications: 100 ms deadtime (for PSII), 15μl sample volume, time resolution determined by delay line (magenta), sample collection on a cold brass surface followed by packing into an EPR tube (for X-, Q-, or W-band) (Rapatskiy, unpublished).

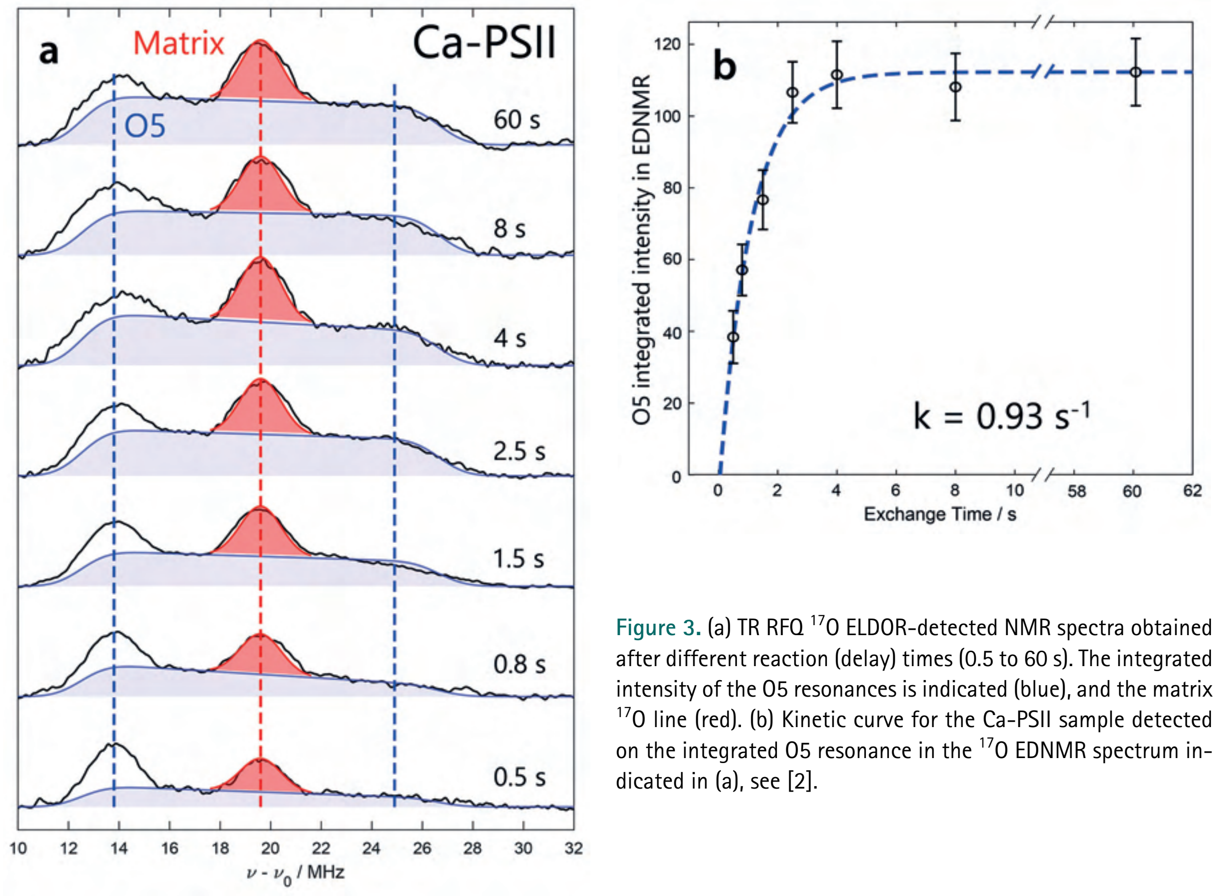

Figure 3. (a) TR RFQ ^{17}O ELDOR-detected NMR spectra obtained after different reaction (delay) times (0.5 to 60 s). The integrated intensity of the O5 resonances is indicated (blue), and the matrix ^{17}O line (red). (b) Kinetic curve for the Ca-PSII sample detected on the integrated O5 resonance in the ^{17}O EDNMR spectrum indicated in (a), see [2].

monograph "Chemical Energy Storage" (R. Schlögl, editor; De Gruyter, 2022) [5]. The work has also been presented in a large number of plenary and award lectures during the last 5 years (Bunsenvorlesung, Marburg, 2017; Ernst Reuter Lecture, FU Berlin, 2018; Luigi Sacconi Foundation Lecture, Florence, Italy, 2018; Harden McConnell Lecture in Stanford and Caltech, CA, USA, 2019; Ernst-Abbe-Kolloquium Jena 2020; Nobel Symposium, Stockholm, Sweden, 2022).

Hydrogenases - Hydrogen Production and Consumption in Nature

The two classes of catalytic hydrogenases in Nature, [NiFe] and [FeFe] hydrogenase, have been studied over the years in our group. The work on [NiFe] hydrogenases has been terminated several years ago (for reviews see Shafaat et al. BBA, 2013; Lubitz et al. Chem. Rev. 2014), whereas research on [FeFe] hydrogenases has continued.

[FeFe] hydrogenases are the champions of reversible hydrogen conversion in many bacteria, archaea, and algae. Furthermore, these enzymes are amenable to artificial maturation (Berggren et al. Nature 2013; Esselborn et al. Nat. Chem. Biol. 2013), which allowed the preparation of high amounts of the enzyme in very good quality and of many modifications of the active site, establishing the field of (semi)synthetic hydrogenases (Siebel et al. Biochemistry 2015; Birrell et al. Joule, 2017).

The work done in collaboration with the former group leaders James Birrell, Hideaki Ogata and Edward Reijerse is described in detail in the report by Dr. Birrell. Thus, only a brief summary of the highlights of this work is given here:

- A controversy in the literature about the structure of key intermediates of [FeFe] hydrogenase in the catalytic cycle (binding of hydride and positions of CO and CN$^-$ ligands) was settled by a careful evaluation of results from FTIR, NRVS [6] and EPR [7] supported by DFT calculations.
- Our previous time resolved IR experiments (TRIR) on [FeFe] hydrogenase using a laser-induced potential jump (Sanchez et al. JACS 2019) in cooperation with Prof. B. Dyer (Emory Univ, Atlanta, USA) have been continued [8, 9] showing that all proposed intermediates in the catalytic cycle are kinetically competent. This important work fully supported the catalytic cycle established by our group for [FeFe] hydrogenases [10].
- A critical review on the mechanism of [FeFe] hydrogenases was published detailing the structural and spectroscopic evidence for the conclusions made on the catalytic intermediates; a discussion of other "views" has also been presented in this work [10].
- The highly active oxygen sensitive [FeFe] hydrogenase from *Desulfovibrio desulfuricans* has been used for constructing a redox polymer-based high-current density H_2-oxidation bioanode in cooperation with Prof. W. Schuhmann (Ruhr University Bochum) for a biofuel cell [11]. The bioanode showed very high current density and still functions at O_2 levels of 5%. The constructed membrane-free dual gas diffusion H_2/O_2 biofuel cell exhibited a very high power density. These excellent results were based on our earlier joint work with the Schuhmann group on the protection of hydrogenases against oxygen by using tailor-made redox polymers (Plumeré et al. Nature Chem. 2014, Oughli et al. ACIE, 2015).
- The first artificial maturation of a bifurcating [FeFe] hydrogenases (from *Thermotoga maritima*) has been reported followed by an in-depth biochemical and spectroscopic characterization [12]. The work was chosen for the cover of the journal (J. Biol. Inorg. Chem.) for the entire year 2020.
- Subsequently, the structure of this bifurcating hydrogenase has been determined using cryoEM in cooperation with Dr. J. Blaza (University of York, UK) and a proposal could be made for the mechanism of the bifurcation, [13]. This is considered an important contribution to the little understood problem of electron bifurcation in hydrogenase systems.

The results on hydrogenases obtained during the period of the report have been summarized in two book chapters [5, 14] and in one recent review article [10].

Other systems

During the report period a number of further projects were performed in cooperation with external groups. In all these projects specialized magnetic resonance experiments (pulse EPR, ENDOR, EDNMR) at different frequencies were used that are available in the Mülheim EPR laboratory with the aim to solve difficult problems on catalytic and energy-converting systems. A selection of these projects are briefly introduced below.

In photosynthesis the triplet states of the photosystems were further characterized in cooperation with Profs. D. Carbonera and M. Di Valentin from Padua (Italy) using pulse Q-band EPR/ENDOR techniques. This has led to detection of the hyperfine structure and spin distribution of the primary donor triplets ^{3}P700 in PSI and ^{3}P680 in PSII supplementing our earlier data obtained for the primary donors in bacterial photosynthesis. In the two photosystems the triplet exciton is not delocalized over a dimer but localized on a monomeric chlorophyll that could be identified in this work [15].

Time resolved W-band EPR was used to characterize the light-induced charge separation and decay kinetics of the radical species in PSI obtained from an unusual desert microalga (*Chlorella ohadii*) that is able to perform photosynthesis under extreme high light conditions. This and further experiments - as the structure determination by cryoEM (at EMBL, Heidelberg) - contributed to understanding the adaptation mechanism by which *C. ohadii* minimizes photodamage [16]. The work was done together with Prof. R. Nechushtai (Hebrew University Jerusalem) in the framework of a DIP project.

Earlier EPR work performed in collaboration with Prof. K. Möbius (FU Berlin), Prof. G. Ventoroli (Bologna, Italy) and A. Savitsky (now TU Dortmund) on the effect of a specific (glassy) sugar matrix (trehalose) on the structure and function of embedded photosynthetic proteins (bacterial reaction centers, PSI and PSII) were summarized in an extensive review article. Furthermore, the question of the remarkable bioprotection of the protein by the trehalose in the fully dehydrated (anhydrobiotic) state could be clarified and a mechanism proposed [17].

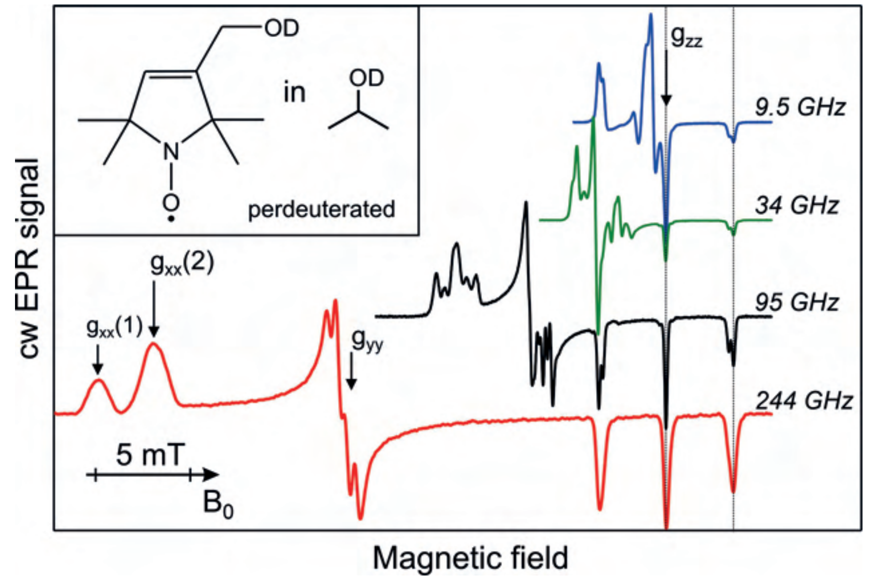

Figure 4. Multifrequency cw EPR spectra of a deuterated pyrroline-type nitroxide in fully deuterated iso-propanol at T=90K (spectra aligned at the g_{zz} field value) demonstrating the improved spectral resolution with increasing external magnetic field, which allows a precise determination of the g values and nitrogen hyperfine structure. Two subfractions of the nitroxide radical are detected that are further analyzed by pulse EPR and ENDOR experiments. These are explained by different microenvironments (H-bond situation) [18].

In many proteins and enzymes hydrogen bonding is playing an important role in adjusting and fine-tuning the physical properties of embedded cofactors. How massive the influence is on the function of chlorophylls and quinones in light-induced charge separation and electron transfer in photosynthetic reaction centers has been shown in several of our earlier papers, in which EPR spectroscopy was use as a probe for the generated radical ions, for reviews see (Lubitz & Feher, Appl. Magn. Reson., 1999; Lubitz et al. Acc. Chem. Res. 2002). In a recent paper we have investigated the effect of H-bonds on nitroxide radicals as neutral paramagnetic model systems using multifrequency EPR/ENDOR supported by DFT calculations, see Fig. 4 [18].

EPR experiments have also played a central role in the elucidation of the various paramagnetic species in carnitine metabolism in the human gut and in setting up a catalytic cycle for carnitine monooxygenase, a project performed with Profs. D. Jahn and J. Moser (Braunschweig) [19].

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Prof. Dr. Frank Neese

The Joint Workspace (JWS) was founded in 2018 concomitant with the move of Prof. Frank Neese from the MPI CEC to the neighboring MPI für Kohlenforschung (MPI KoFo). Its purpose is to intensify the collaboration between scientists at the two institutes. The JWS consists of spectroscopy laboratories located in the MPI CEC as well as the high-pressure laboratory at the MPI KoFo that is headed by Dr. Nils Theyssen. In addition to high pressure experiments, the JWS's scientific activities cover the entire range between experimental and theoretical spectroscopy. During the reporting time, the activities in the spectroscopy laboratories included the Mössbauer & MCD Molecular Paramagnetism and Bioinorganic Spectroscopy MPI-CEC group of Dr Eckhard Bill (deceased October 2022) and Dr. Daniel SantaLucia, the EPR and Raman MPI-KoFo group of P.D. Dr. Maurice van Gastel, the Reactivity MPI-KoFo group of Dr. Shengfa Ye (left the campus in November 2020), the Molecular Magnetism MPI-KoFo group of Prof. Dr. Michael Atanasov and the Advanced Experimental and Theoretical spectroscopy MPI-KoFo group of Dr. Dimitrios Manganas. The capabilities of the JWS laboratories include optical and vibrational spectroscopies (IR, multi-wavelength Raman, UV/VIS, and fluorescence) as well as an extensive array of magnetic techniques including (Mössbauer, MCD, EPR and SQUID magnetometry) that are operated by van Gastel's and SantaLucia's groups and provide service and scientific support between all the departments across the two MPI Institutes. These experimental efforts are aided by Atanasov's and the Manganas' theoretical spectroscopy groups, which provide assistance in predicting and interpreting the experimental data with advanced quantum chemical calculations. In the sections below, a short report is provided of a select number of projects that have been performed under the umbrella of the joint workspace by the involved scientists.

Joint Workspace of the Mülheim Chemistry Campus

Prof. Dr. Frank Neese, Dr. Eckhard Bill, Dr. Daniel SantaLucia

EPR (VTVH) Mössbauer, UV-Vis-NIR MCD Spectroscopies and SQUID Magnetometry Lab

The Joint Workspace includes labs capable of conducting multi-frequency cw-EPR, both zero-field and VTVH Mössbauer, and UV-Vis-NIR MCD spectroscopy as well as SQUID magnetometry. In the period under review (2020 – Nov. 2022), these labs provided fruitful collaborations between research groups in the KoFo and the CEC; we want to emphasize especially the bridge between theoretical and experimental studies provided by these instruments.

In particular, we refer to the collaborative effort between Prof. Dr. Frank Neese, Dr. Eckhard Bill, and Dr. Shengfa Ye.[1] The electronic structure of an intermediate spin ($S = 1$) Fe(II) tetraphenylporphyrin (TPP) complex used for CO_2 reduction catalysis was thoroughly investigated with a combined spectroscopic and theoretical approach. The electronic structure of the ground state had been debated in the literature as either $^3A_{2g}$ or ^3E_g. The electronic structure of the complex was probed with VTVH Mössbauer and THz EPR spectroscopies as well as SQUID magnetometry. An effective Hamiltonian approach was found to be necessary for adequately modeling the electronic structure of the complex and reproducing the observed spectroscopic properties. It was concluded that the ground state is, accidentally, nearly triply-degenerate, with the separation of the $^3A_{2g}$ and ^3E_g states on the same order of magnitude as the spin-orbit coupling constant for Fe(II). Ab initio calculations the investigation found that the ground state is, in actuality, multiconfigurational with ~88% $^3A_{2g}$ and ~12% ^3E_g character. This near-degeneracy of the ground state is hypothesized to be of crucial importance for the complex's CO_2-reduction capability, as the near-degeneracy of the ground state could act as an electron reservoir for the doubly-reduced complex, facilitating binding to CO_2 in the first step of the catalytic cycle by allowing the electron-density at the Fe-center to remain more or less constant.

Lately, we have focused on a number of upgrades to our continuous wave (cw) X-band EPR instrument. We have recently purchased a new microwave bridge and console that will allow us to extend our capabilities to X- and Q-band cw-EPR measurements. Furthermore, we have also recently purchased a He re-liquefier (the so-called Stinger system). We currently estimate that this instrument alone is responsible for roughly 50% of the liquid He costs associated with our labs; once the He re-liquefier is installed, this will dramatically decrease. In previous years, we had already upgraded our VTVH and UV-Vis-NIR MCD spectrometers with closed-cycle magnet cryostat systems, as well as replaced our old magnetometer with a new SQUID magnetometer featuring a closed-cycle 'evercool' liquid helium dewar. We anticipate that the combined effects of our closed-cycle instruments and with our new He re-liquefier for the EPR will substantially reduce costs associated with liquid He usage. This will allow us to do any experiments at liquid He temperatures, which is often necessary for detailed probes into electronic structure, in essence allowing for our labs to continue to do cutting-edge experimental studies.

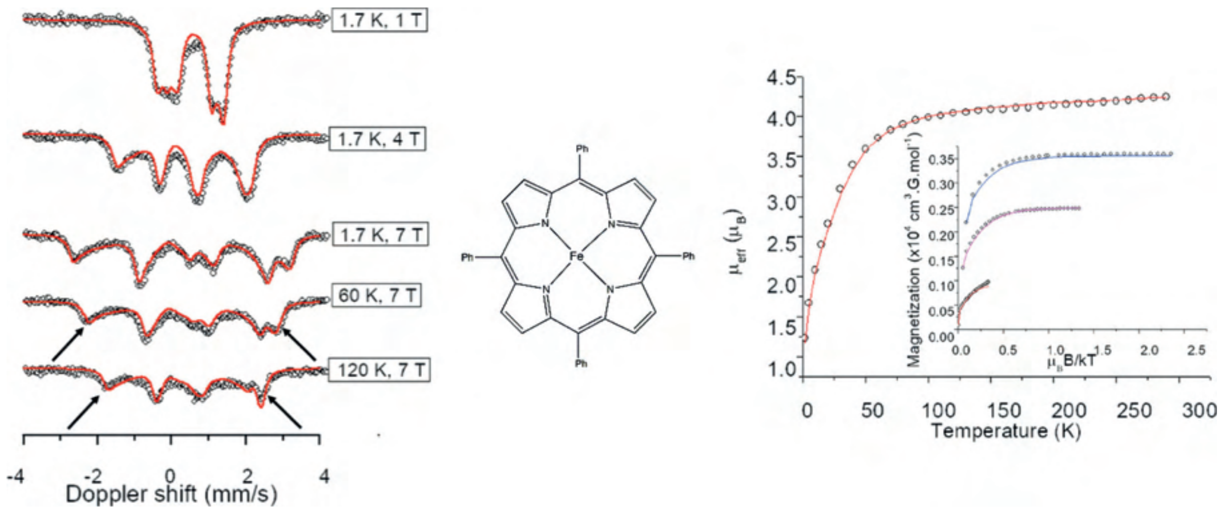

Figure 1. VTVH Mössbauer spectra (left) and dc susceptibility/reduced magnetization (right) for the intermediate spin ($S = 1$) Fe(II) TPP complex (center). Effective Hamiltonian fits to the data are shown in red for the VTVH Mössbauer data (left), red for the dc susceptibility data (right), and red, magneta, and blue for the reduced magnetization data at fields of 1, 4, and 7 Tesla, respectively (right).

PD. Dr. Maurice van Gastel, Anchisar Libuda

Raman and EPR Spectroscopy

Research in the van Gastel's group focuses on the understanding of general processes in catalysis by spectroscopic investigation of the electronic structure of reaction intermediates using primarily resonance Raman (rRaman), Electron Paramagnetic Resonance spectroscopies (EPR) and quantum chemistry. For this purpose, we have realized our instrumentation development efforts by setting up a Raman Lab equipped with multiwavelength Raman lasers. Presently, we are building up a hybrid magnetic Raman / magnetic FTIR spectrometer.

A characteristic research example reflecting our activities within the period under review refers to a collaborative project between the departments of Prof. Neese (PD. Dr. M. van Gastel, Dr. A. Haack) and Prof. Fürstner (Dr. J. Hillenbrand). In here, we combined spectroscopic and theoretical methods to study triphenyl- and dimethyl-phenyl siloxy molybdenum and tungsten alkylidyne catalysts for alkyne metathesis. Using NMR, X-ray, UV-VIS, Resonance Raman spectroscopy and DFT calculations, we investigated the influence of different ligand systems and metal centers on the geometric and electronic structure and thermochemistry of different intermediates, in particular the starting alkylidyne and the derived metallacyclobutadiene and metallatetrahedrane. This included a mechanistic and kinetic study on the formation and isomerization of metallacyclobutadienes and metallatetrahedranes. Upon changing from monodentate to tripodal siloxy ligands, we found that a higher steric strain is imposed, which modulates the relative energies of the different intermediates. Additionally, intramolecular dispersion interactions between bound substrate and ligand can be operative. Tungsten as the central metal leads to stronger M-C σ-bonds, which overstabilize the reaction intermediates and preclude effective turnover. Furthermore, kinetic modeling strongly suggests that metallatetrahedranes are off-cycle intermediates based on the high barriers for direct formation but low barriers for isomerization from metallacyclobutadienes. We infer from our findings that effective catalysis can only be achieved when factors that (over)stabilize intermediates, such as strong M-C bonds or large dispersion interactions, are prevented by appropriate catalyst design.

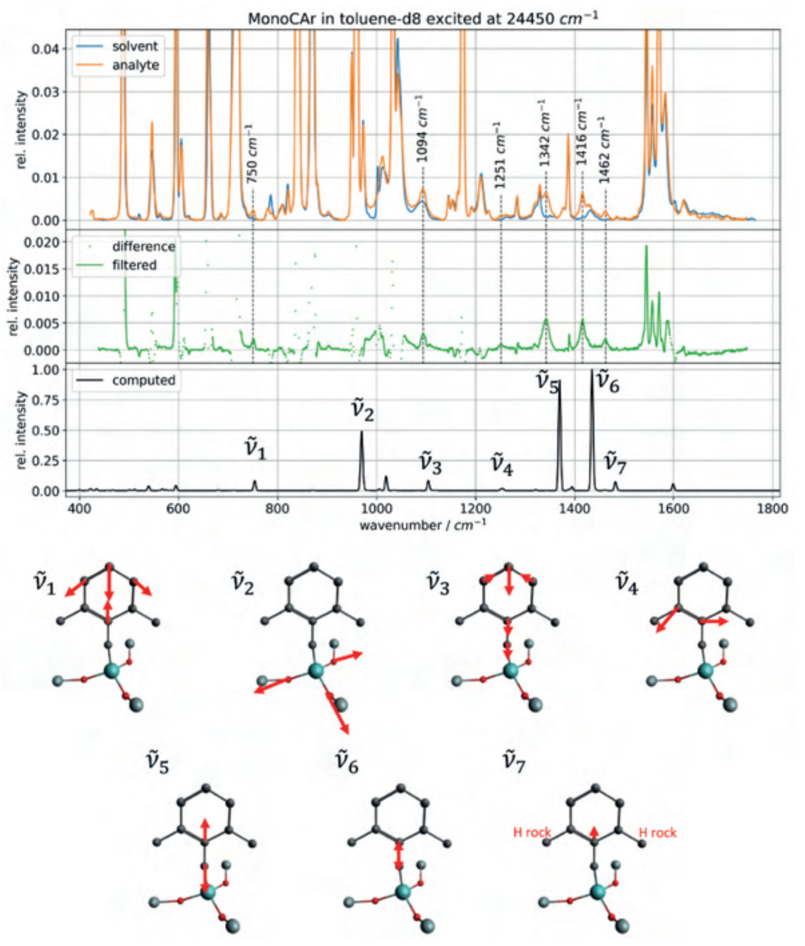

Figure 2. Example Resonance-Raman spectra and assignment of band of the **1-CAr** complex (3 mM in toluene-d_8) at 100 K. An excitation laser with a photon energy of 24450 cm^{-1} was used at a power of 45 mW.[2]

Prof. Dr. Mihail Atanasov

Molecular Magnetism Group

The Molecular magnetism group is faced with studies on the electronic structure and magnetic properties of complexes with open d- and f-shells. Single molecular (single ion magnets), SMM(SIM) are paramagnetic molecules(ions) with strongly anisotropic and long-living magnetic moments. They are induced by external static or oscillating magnetic fields. Such molecules are of potential interest in molecular devices for storing and reading information at a molecular level. The manipulations of such moments by microwave electromagnetic ration (EPR) are of potential use in molecular spintronic for use in quantum processors (q-bits). We applied state-of-art theoretical methods in order to identify suitable candidates for SMM(SIM)s and/or to analyze and interpret experimental magnetic data on new molecular magnetic materials. We also envisaged development of new theoretical and computational protocols for the prediction of their magnetic properties. Our aim was the exploration of the relationship between the electronic and geometric structure of SMM/SIM and their spectroscopic and magnetic properties. The existence of long living anisotropic magnetic moments is widely prohibited by interactions between the magnetic moments with the environment. The leading mechanism are spin-vibrational (spin-phonon) interactions. Understanding factors that contribute to this phenomenon is essential for designing next generation spintronics technology, including single-molecule magnets and spin-based qubits, wherein long-lifetime magnetic ground states are desired. We reported spectroscopic and magnetic characterization of the isoelectronic and isostructural series of homoleptic zero-valent transition metals triad M(CNDipp)$_6$ (M = V, Nb, Ta; CNDipp = 2,6-diisopropylphenyl isocyanide), and have shown experimentally and theoretically the significant increase in spin relaxation rate upon going from V to Nb to Ta.[3] Correlated electronic calculation and first principle spin-phonon computation support the role of spin-orbit coupling in modulating spin-phonon relaxation. Our results provide experimental evidence that increasing magnetic anisotropy through spin-orbit coupling interactions leads to increased spin-vibronic relaxation, which is detrimental to long spin lifetime in paramagnetic molecules.

We used a combination of inelastic neutron scattering (INS), Raman, and far-IR magneto-spectroscopies (FIRMS) to comprehensively probe the magnetic excitations and spin-phonon coupling in Co(AsPh$_3$)$_2$I$_2$ (Figure 3, left)).[4] With applied field, the magnetic zero-field splitting (ZFS) peak (2*D*) shifts to higher energies in each spectroscopy as exemplified by the FIRMS spectrum (Figure 3. right). INS placed the ZFS mode at 54 cm^{-1}, as revealed by both variable-temperature and variable-magnetic-field data, giving results that agree well with those from both far-IR and Raman studies. Both far-IR magneto-spectra (FIRMS) and Raman magneto-spectra also reveal the presence of multiple spin-phonon couplings in the form of avoided crossings with neighboring phonons (Figure 3, right). The results constitute a rare case in which the spin-phonon couplings are observed with both Raman-active (*g* modes) and far-IR-active (*u* modes) phonon modes. These couplings are fit using a simple, yet expanded avoided crossing model with coupling constants of ~1-2 cm^{-1}. The combined spectroscopies accurately determine the magnetic excited level and the interaction of the magnetic excitation with phonon modes. Density functional theory (DFT) phonon calculations compare well with INS, allowing for the assignment of the modes and their symmetries. Electronic calculations elucidate the nature of ZFS in the complex.

Within our joint workspace (JWS) activities at CEC we extended our studies to paramagnetic molecules with more than one magnetic center. Theoretical studies of the magnetic and spectroscopic properties have been restricted to applications of Density Functional Theory. A mixed valence binuclear Fe$^{2.5+}$-Fe$^{2.5+}$ (Robin-Day Class III) transition metal complex, [Fe$^{2.5+}$μTe$_2$Fe$^{2.5+}$]$^{1-}$, composed of two FeN$_2$Te$_2$ pseudo-tetrahedral units with μ-bridging Te^{2-} ligands was reported to exist in an unprecedented S = 3/2 ground state (Nature Chemistry, https://doi.org/10.1038/s41557-021-00853-5). For this and the homologous complexes containing Se^{2-} and S^{2-}, the Anderson-Hasegawa double exchange spin-Hamiltonian was broadly used to interpret the corresponding structural, spectroscopic and magnetic data. First principles multireference ab initio calculations have been used to simulate magnetic and spectroscopic EPR data; analysis of the results affords a rationale for the stabilization of the S = 3/2 ground state of the Fe$_2$ pair. Complete Active Space Self-Consistent Field (CASSCF) calculations and dynamical correlation accounted for by means of *N*-Electron Valence Perturbation Theory to Second Order (NEVPT2) reproduce well the *g*-factors determined from simulations of X-band EPR spectra.[5] A crucial technical tool to achieve these results is: i) use of a localized orbital formulation of the many-particle problem at the scalar-relativistic CASSCF step; ii) choice of state averaging over states of a given spin (at the CASCI/NEVPT2 step); and iii) accounting for spin-orbit coupling within the non-relativistic Born-Oppenheimer (BO) many-particle basis using Quasi-Degenerate Perturbation Theory (QDPT). The inclusion of the S = 5/2 spin manifold reproduced the observed increase in the magnetic susceptibility (c*T*) in the high temperature range (*T* > 100 K), which is explained by thermal population of the S = 5/2 excited state at energy 160 cm^{-1} above the S = 3/2 ground state. Theoretical values of c*T* from experimentally reported data points in the temperature range from 3 to 30 K were further computed and analyzed using a model which takes spin-phonon coupling into account. The model considerations and the computational protocols of this study are generally applicable to *any mixed valence dimer*. The work can potentially stimulate further experimental and theoretical work on bi- and oligonuclear transition metal complexes of importance to bioinorganic chemistry and life sciences. The computational protocol described in this work can be equally applied to larger magnetic nuclearity complexes, such as the Mn4CaO5 clusters of the oxygene evolving complex of natural photosynthesis and also to the iron-molybdenum cofactor (FeMoco), a Fe^{2+}Fe$^{2.5+}_4$Fe$^{3+}_2$Mo^{3+}S$_9$C complex, facilitating formation of ammonia from atmospheric N$_2$ in a well-known, but yet not completely understood biological nitrogen fixation process. Both topics are intensively under investigation within groups of our two institutes, the Max-Planck institute of chemical energy conversion and the Max-Planck institute für Kohlenforschung.

For more activities of the molecular magnetism group within the period under review, please see the following references.[3, 6-10]

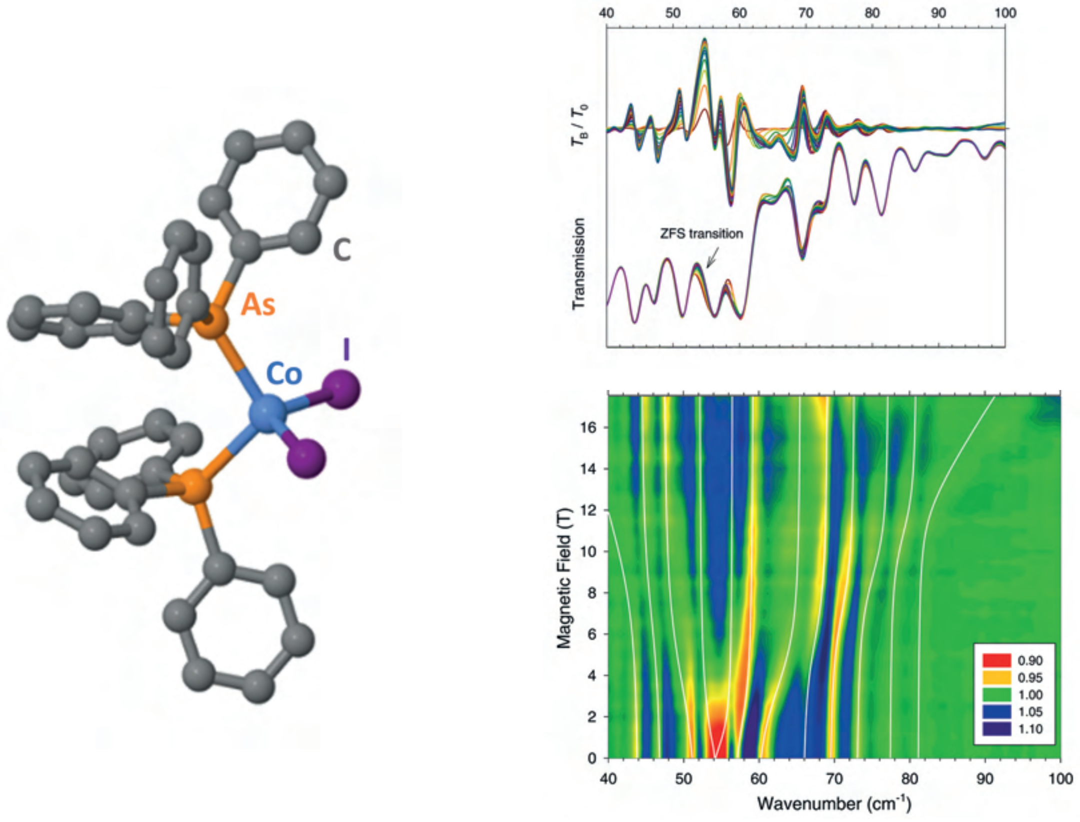

Figure 3. (Left) Molecular structure of Co(AsPh$_3$)$_2$I$_2$ (1). Atom labels: Co (blue), As (orange), C (gray) and I (purple), while H atoms are omitted for clarity; (Right), (Top-A) FIRMS spectra. (Top-B) FIRMS spectra normalized to the zero field spectrum of 1. (Bottom) Contour plot of normalized transmission data (by average across all fields) of 1. White lines indicate fittings from Eq. 2.

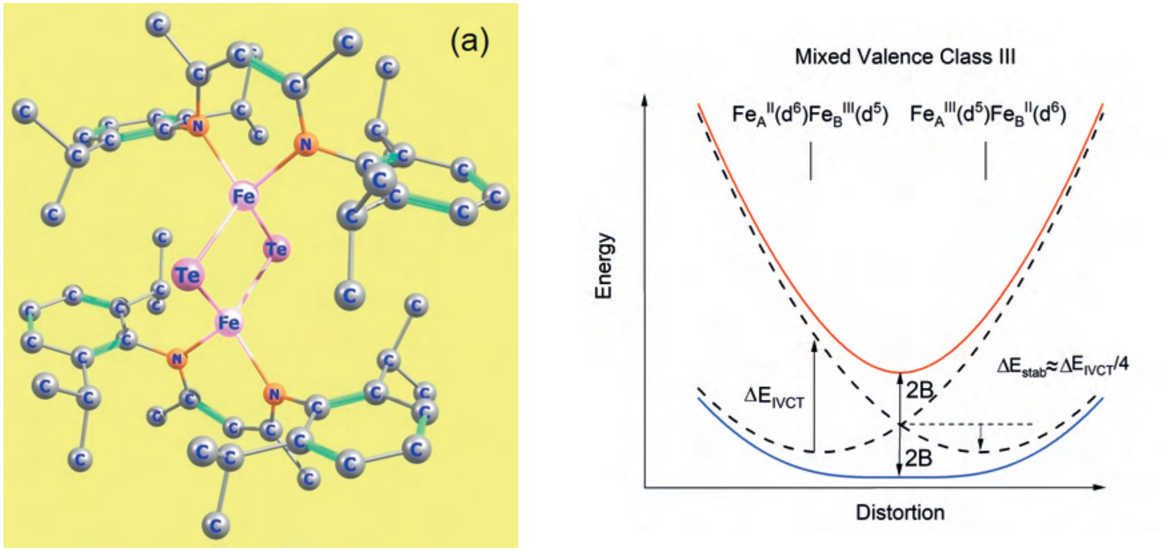

Figure 4. (Left) Experimental X-ray structure of the mixed valence complex Fe$^{2.5+}$-μTe$_2$-Fe$^{2.5+}$(3) (Right) Configuration energy diagram (schematic) for 3' in the limit of a complete delocalization of the extra electron over the two iron sites (Fe$^{2.5+}$μTe$_2$Fe$^{2.5+}$, Class III).

Dr. Dimitrios Manganas

Advanced Experimental and Theoretical Spectroscopy Group

Research in the Manganas group focuses on the development and application of advanced theoretical spectroscopic methodologies that are applicable in a wide range of chemical systems. Our long-term focus is to employ in house developed wavefunction based methods in an effort to evaluate unique spectroscopic signatures of transition metal complexes and materials in both equilibrium and under operando conditions. This requires to use methods that do not belong in the standard arsenal of quantum chemistry. The group is mutually working in close interaction with the other Joint Work Space groups as well as with the X-ray spectroscopy groups across the Inorganic Chemistry Department. The theory development activities are performed in close collaboration with the development groups of the Molecular Theory and Spectroscopy Department of the neighbor MPI-Kofo institute.

During the 2020-2022 period the group was focused in developing computational protocols that are able to unravel the complex intensity mechanism of X-ray magnetic circular dichroism (XMCD) spectroscopy employing the complete active space configuration interaction in conjunction with N-electron valence second order perturbation theory (CASCI/NEVPT2).[11] It was shown that the intensity and the sign of the XMCD bands involves a many particle state mixing mechanism between states of same and different multiplicities that are mixing through spin-orbit coupling interactions. These interpretations were evaluated critically against the generally accepted spin-summation rules highlighting the limitations of the later. In a similar concept a general and efficient protocol for computing intensities of absorption (ABS), CD, MCD/XMCD spectroscopies was developed that goes beyond the electric dipole approximation on the basis of the exact light-mater operator.[12] In this concept the protocol is able to probe a large variety of otherwise electric-dipole or spin-forbidden transitions providing access to the relevant spectra of a wide range of chemical systems.

In a parallel activity the group was also involved in developing a 2-shell abinitio ligand field theory (AILFT) which was incorporated into an abinitio variant of a multiplets program (called orca_lft) that is a portable and standalone program of the ORCA family of programs. Among others orca_lft contains an internally build NEVPT2 database of the 1-electron ligand field matrix and the respective Slater Condon LFT parameters across the elements of the periodic table and it is able to treat a wide range of X-ray spectroscopic problems. As a first application orca_lft was employed to interpret the Kb mainline X-ray emission (XES) spectra on a series of Nitrogenase-Related Mo model complexes.[13]

Entering the field of solids, the group was involved in collaborative scheme between the MTS department and the FAccTs company in an effort to develop a general embedded cluster protocol called Ionic-Crystal QM/MM which is able to treat embedded clusters of variety complexity in terms of involved centers, total charge and coordination environment. In parallel a utility program was developed called orca_crystalprep that is able to generate Ionic-Crystal QM/MM embedded cluster inputs that are ready to run starting from a crystallographic ".cif" file, thus diminishing considerably the construction complexity of the embedded cluster models. As a first application of the embedded cluster protocol a library of inorganic solids where employed to compute NMR chemical shieldings at the density functional theory (DFT) level of theory over a range of chosen DFT functionals.[14] It was shown in particular that double-hybrid functionals provide robust and efficient predictions that can be used to aid the interpretation of routinely solid-state NMR measurements.

In a final activity the group was involved a collaborative project together with the group of professor Dr. Wolfgang Schnick in LMU Munich aiming the understanding of the photoluminescence properties of phosphors with potential application in the field of narrow band light emitting materials (LEDs). In this concept a Time Dependent DFT (TD-DFT) protocol in conjunction with excited state dynamics (ESD) was developed that is able to interpret the photoluminescent spectra of a family of narrow band Eu doped phosphors. On these basis simple and general descriptors were developed that are able to correlate the energy position of the 1st excited state and the covalency of the involved emitting 5d orbital with the color and bandwidth of the emission spectrum of a given phosphor.[15]

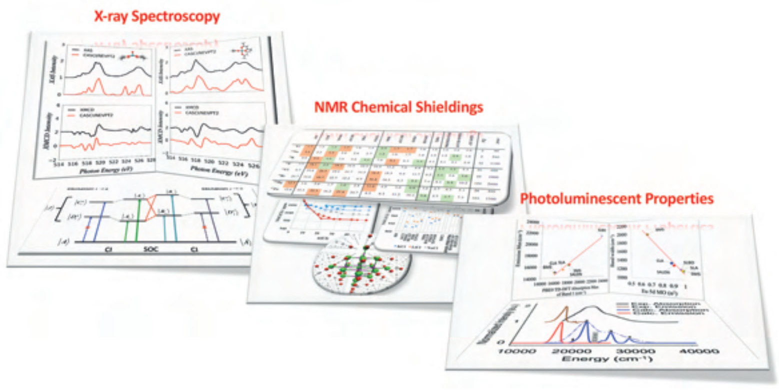

Figure 5. An illustration showing various computational protocols that have been developed to compute a wide variety of spectroscopic properties of molecules and solids.

Prof. Dr. Walter Leitner Molecular Catalysis

and Dr. Nils Theyssen, MPI KoFo Technical Laboratories

In the reporting period, the focus of joint research was on two different projects. Activities were continued with regard to the synthesis of the iron silicate *Ferripyrophilite* under very mild conditions. Based on our findings, this material can be generated from iron powder, a mesoporous silica source such as SBA-15 and water at 100 °C in a simple glass flask under air. Due to its ultrathin two-dimensional (2D) nanosheet morphology and the associated high specific surface area, the remarkable temperature stability (up to 800 °C) and the numerous hydroxyl groups, which are chemically easy to functionalize, this material continues to enjoy our attention.[16] The present research activities investigate the influence of palladium and platinum nanoparticles sorbed on the SBA-15 starting material on the subsequent formation of the iron silicate. The motivation for this arises, on the one hand, from the fact that, in retrospect, the phase transformation into an iron silicate was found precisely with such materials. On the other hand, the structure obtained in the presence of the noble metals exhibits improved homogeneity and an even higher content of structurally incorporated iron atoms. Compared to *Ferripyrophilite* with the molecular formula $Fe_2[Si_4O_{10}](OH)_2$, the presence of the noble metal nanoparticles resulted in the composition $Fe_3[Si_4O_{10}](OH)_5$. In this structure, all octahedral centers of the TOT layered silicate are occupied by iron atoms (in the case of the *Ferripyrophilite* this is only 2/3). The obtained materials are currently further tested as catalysts in a variety of transformations including ammonia synthesis.

In the second study, done in cooperation with the group of Dr. Alexis Bordet, the special properties of supercritical carbon dioxide were again used profitably in the synthesis of organic molecules. In combination with Rh nanoparticles immobilized on molecularly modified silica as catalyst, the hydrogenation of fluorinated arenes with polar functionalities was achieved. This methodology enables a versatile pathway for the production of substituted fluorocyclohexane derivatives, which are used as building blocks for pesticides, pharmaceuticals and semiconductors. In contrast to direct alkane fluorination methods, this approach can be done in a single step, thus having a much higher atom economy and avoids the usage of hazardous chemicals. In comparison with the former existing protocols in which non-polar organic solvents like *n*-hexane or *n*-heptane were used,[17-18] the transformation in supercritical carbon dioxide shows a much better tolerance for polar functionalities.[19]

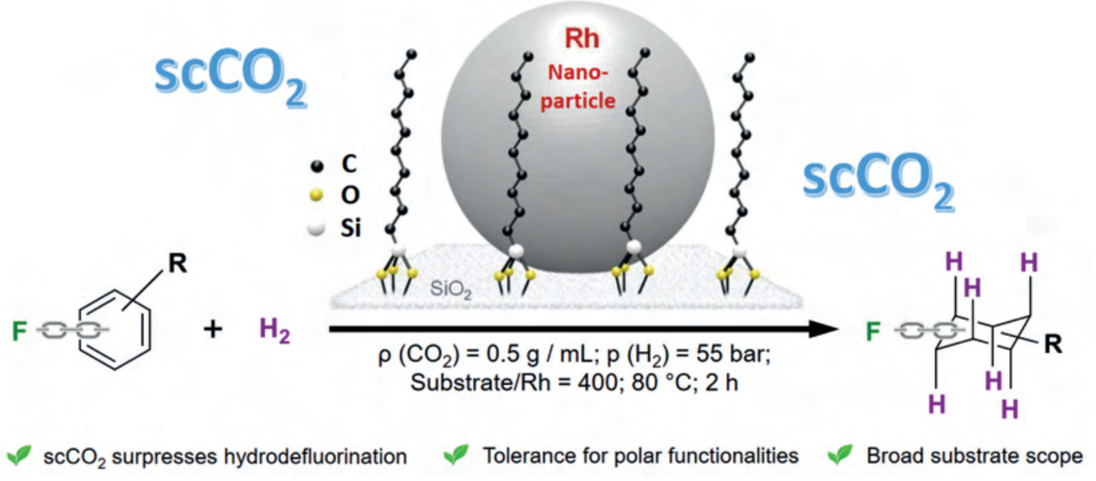

Figure 6. Hydrogenation of fluorinated arenes in supercritical carbon dioxide.

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The EPR Research Group at MPI CEC

The EPR Research Group at MPI CEC, led by Alexander Schnegg, develops and applies advanced electron paramagnetic resonance (EPR) methods to study paramagnetic states in materials and molecules relevant for the next generation of sustainable chemical energy conversion and storage. For research within the group and the user community at the Mülheim campus, the EPR group operates a unique array of 5 advanced pulse/continuous wave multi-frequency (MF-EPR, 3 GHz to 20 THz) EPR spectrometers. Currently, four scientists, one PhD student and one research technician are working in the group. Research work in the reporting period has led to the development of novel EPR methods and their application to problems in catalysis research and inorganic chemistry. This progress is reflected by 28 publications in high profile journals including Nature Chemistry, JACS, Angewandte Chemie, Chemical Science and ACS Catalysis. The following major research directions and projects are outlined.

Research Directions and Highlight

Catalysts frequently adopt paramagnetic states and catalytic reactions follow radical mechanisms. Our group applies EPR methods, for the assignment, quantification and characterization of these paramagnetic states. Current research focuses on radical formation in catalytic reactions.[1, 2] Furthermore, transition metal (TM)[3-7] and main group[1] active sites are characterized via their electron spin coupling parameters. In cases where spin transition energies are not accessible to commercially available EPR spectrometers or where paramagnetic states are short lived during catalytic reactions, new spectroscopic tools are developed.

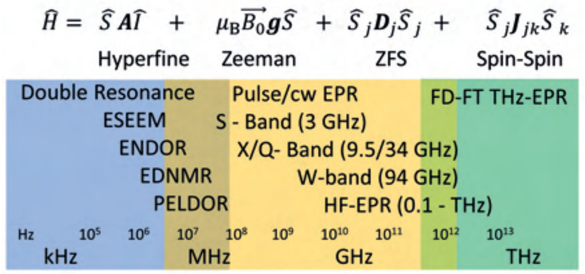

Figure 1. Electron spin coupling and EPR spectrometer ranges. Electron Spin Hamiltonian (SH) and EPR methods ruler indicating the EPR methods available at MPI CEC, ordered towards their respective excitation frequency ranges.

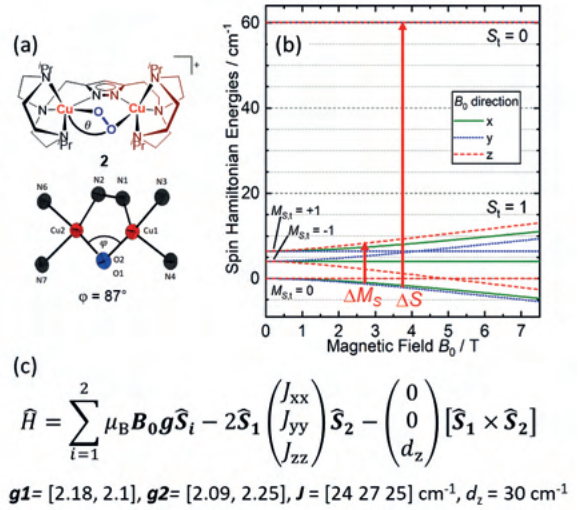

Figure 2. THz-EPR assigns anti-symmetric exchange and singlet triplet mixing in biomimetic Cu_2 peroxo complexes. (a) Molecular structure and core structure of $Cu(II)_2$ (S =1) peroxo complex **2**, synthesized in the Meyer group (U Göttingen).[3] (b) Spin energy level diagram of 2 vs magnetic field, B_0, calculated with the SH given below. Solid red arrows indicate ΔM_S (left) and nominally forbidden ΔS (right) transitions probed by THz-EPR (Note 60 cm^{-1} corresponds to ~ 2 THz). (c) SH of the coupled Cu ions including symmetric and anti-symmetric exchange interactions with SH parameters obtained from best fits to the experimental spectra published in Ref 3.

In the last years, the EPR group pioneered the development of very high frequency (VHF, ≥ 95 GHz) EPR spectrometers for the assignment of very large zero field splittings (ZFS) in TM compounds.[3, 5, 7-9] Figure 1 depicts a scheme indicating the excitation energy range of EPR spectrometers currently available in the EPR group at MPI CEC. The latter include commercial S-, X- and Q-band spectrometers, a laboratory built pulse/cw W-band spectrometer, which is among the leading instruments in its class, a novel ultra-wide band VHF-ERP spectrometer (0-12 T, ν_{mw} = 80, 160, 240, 320, 480 and 960 GHz) and instrument time at a unique synchrotron based frequency domain THz-EPR spectrometer (0 -12 T, 100 GHz – 20 THz) at BESSY II (Berlin, Germany). Recently VHF-EPR in field and frequency domain has been employed to high spin TM complexes, for the assignment of oxidation states,[7, 10] the influence of the coordination geometry on the electronic structure,[9] the (non)innocence of ligands,[7] multi configurational character of the electronic ground state[5] as well as the relation to other spectroscopic properties like chemical shifts.[8] Particularly important, VHF-EPR could be successfully applied to integer spin states with very large ZFS (> 500 GHz). *E.g.* in the catalytically relevant Fe(II)[5, 8] and Fe(IV)[7] states, which are EPR silent in commercial spectrometers. A further important achievement was the extension to multi-nuclear TM clusters for the independent determination of their ZFS and exchange couplings. Very recently, THz-EPR was employed to study triplet to singlet intersystem crossing in biomimetic Cu_2 complexes. Figure 2 depicts the spin energy level diagram and the observed THz-EPR transitions of the Cu_2 peroxo complex **2**. The latter is one out of a series of $Cu(II)_2$ peroxo complexes, mimicking the initial state in type III Cu proteins immediately after dioxygen binding. Simulations of THz-EPR spectra of **2** allowed for a precise determination of the surprisingly large ZFS in **2** and its structural congeners. More importantly, antisymmetric exchange (d_z in Figure 2) was identified as the source of the large ZFS and mixing between singlet and triplet states. The latter renders nominally forbidden transitions from the triplet ground state to excited singlet states (ΔS) allowed and accessible to THz-EPR. These findings are of great relevance for the understanding of oxygen activation at Cu and Fe sites, with potential implications for the design of future green chemistry catalyst. The applied THz-EPR approach is not limited to the present case. As we have recently shown it is applicable to other exchange coupled TM coordination compounds[11, 12] and may in the future provide new insight in the spin couplings of a large variety of multi nuclear clusters or TM-radical complexes, hardly accessible by other techniques.

A further focus in the group are dedicated *in situ* EPR[14] set-ups to monitor paramagnetic states during catalytic action. Our EPR facilities allow for light excitation in the EPR cavity, automated temperature cycling, liquid flow, freeze quench and spectro-electrochemical (SEC) EPR. Liquid phase EPR (including flow experiments) is applied within CRC 247 for the identification of radical reaction pathways during liquid phase alcohol oxidation reactions.[2] SEC EPR is used in CRCs 247 and 1048 for the identification of paramagnetic Co and Fe active sites, respectively. A combination of *in situ* liquid solution EPR and advanced MF-EPR was recently employed for the EPR characterization and determination of the activation energy of the Bismuth radical equilibrium complex (REC) **I**[1, 13] (see Figure 3). Homolysis of **I** leads to an organic radical (**II**) and a Bi(II) complex (**III**). The latter enables mild and selective activation of amines and alcohols.[1] X-band EPR allowed for the assignment of the formed radical (**II**) and equally important the determination of the activation energy of the homolytic cleavage,[1] via quantification of the radical amount as a function of temperature. While **II** can be detected at room temperature, **II** escapes EPR detection in solution due to its fast spin relaxation. For a full characterization of **III**, our partners at MPI KOFO embarked for the synthesis of stable analogues of complex **III**. The latter gave characteristic X-band EPR signals. However, due to the very large HF splittings, simultaneous simulations of X-, Q-band and W-band EPR spectra had to be employed (see Figure 3 (c)). Extracted EPR parameters and complementary quantum chemical calculations finally allowed for a detailed characterization of the elusive Bi(II) complex.[13] This example highlights the power of studies combining *in situ* liquid phase and advanced MF-EPR at cryogenic temperatures for the assignment and characterization of paramagnetic states determining catalytic processes.

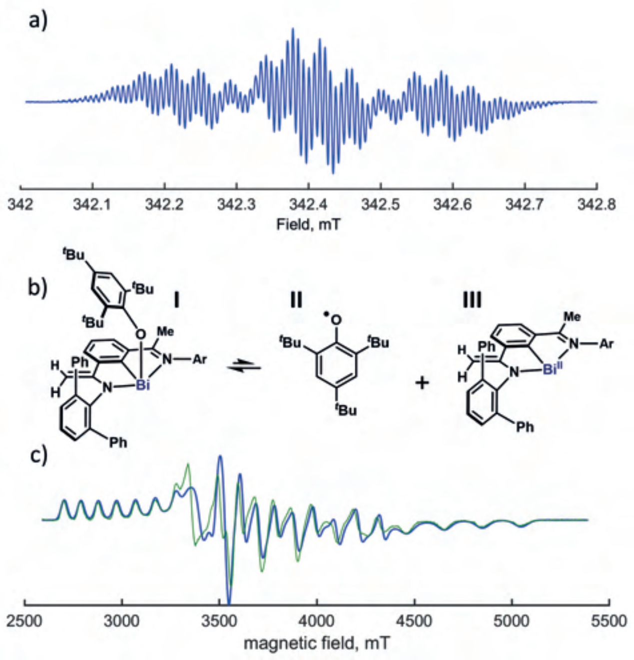

Figure 3. Multifrequency EPR characterization of paramagnetic states involved in Bi catalysis a) X-band EPR spectrum of radical II formed after dissociation of I at 25 ° C, synthesized in the Cornella group (MPI KOFO).[1] b) Structures of Bi REC complex **I** and its dissociation products **II** and **III**. C) W-band EPR of the synthetically obtained analogue of Bi(II) complex **III** (blue experimental, green simulation with g = (1.589, 1.719, 2.119) A_{209Bi}= (4106 MHz, 2377 MHz, 3003 MHz)).[13] In the present case, a combination of W-band (95 GHz) and the large accessible field range (0 - 6 T) of the W-band spectrometer at MPI CEC are essential to fully resolve the spectrum.

Collaborations and Research Networks

At the **Mülheim Chemistry Campus** we closely collaborate with researchers at the Joint Workspace of MPI CEC and MPI KOFO. Thereby, advanced EPR methods are complemented with magnetic characterisation techniques like SQUID magnetometry, MCD and Mössbauer spectroscopy and applied for magneto structural correlations in TM complexes.[3, 5, 6, 10] These tools are employed in collaborations with partners at MPI CEC in particular with the groups of Prof DeBeer,[4] Dr Cutsail, Prof Wiegand, Dr Kaeffer, Prof Muhler (Ruhr University Bochum (RUB) and Max Planck Fellow at MPI CEC)[2] and at MPI KOFO with the groups of Prof Ritter,[15] Dr Cornella[13] and Prof Neese.[4, 5]

The Joint lab EPR4Energy of MPI CEC and Helmholtz-Zentrum Berlin für Materialien und Energie (HZB) has been initiated by Dr Schnegg and Prof Lips (HZB). EPR4Energy enables access to synchrotron based THz-EPR at BESSY II (30 % of the user time of the THz-EPR spectrometer at HZB's synchrotron)[3, 5, 7, 8, 9, 12] and the operation of a novel VHF-ERP spectrometer (0- 12 T, ν_{mw} = 80-960 GHz) owned by MPI CEC. Joint research at the THz-EPR facility lead to successful projects with partners from the inorganic chemistry community in particular Prof Plass (U Jena),[12] Prof Meyer (U Göttingen),[3] Prof Gade (U Heidelberg),[8] Prof Bendix (U Copenhagen),[11] Prof Ye (State Key Lab, Dalian, China)[5, 10] and Prof Telser (Roosevelt U, USA).[7] A Schnegg, in addition, serves as principal investigator (PI) in the BMBF network project "EPR on a Chip" (2018 – 2023, coordinator Prof Lips HZB), which develops miniaturized yet sensitive EPR detection schemes for future applications in catalysis research.[16]

Collaborations with University groups have been established with the working group of Profs Enders (U Heidelberg), Krewald and Kramm (U Darmstadt)[6] on materials and molecules containing Fe high-spin states and FeN_4 macrocycles as models for iron single atom catalysts for the oxygen reduction reactions in fuel cells. This research is now conducted within DFG collaborative research center (CRC) 1487 "iron upgraded" (2022-2025), in which A. Schnegg acts as PI. Studies in heterogenous TM (Co, Fe, Ti and V) oxide catalysts for liquid phase alcohol oxidation reactions are performed with the groups of Prof Muhler and Prof Barcikowski (U Duisburg -Essen).[2] within CRC 247 (2022 – 2026), in which A. Schnegg acts as Co-PI (PI Prof DeBeer). Further strong collaborations have been established within the cluster of excellence RESOLV with Profs Kasanmascheff (U Dortmund), Bordignon (RUB now U Genève, Switzerland), Tschulik and Neese on MF-EPR methods for studies in molecular solvation processes.

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Electrochemistry for Energy Conversion

The group primarily utilizes electrochemical methods to investigate the links between material properties and electrocatalytic activity supplemented by surface science techniques and instrumental analysis. The focus is on reactions that are of interest for energy conversion, storage and utilization.

In light of the current and impending energy challenges, the power-to-X concept, i.e., the transformation of energy to fuels or useful chemicals, is garnering increasing attention. Generation of fuels from electricity is one of the proposed ways of addressing the challenges of the intermittency of renewable energy sources. In this light, hydrogen is widely considered as a potential new fuel. In this concept, electricity from renewables at peak production would be used to produce hydrogen by water electrolysis. Such hydrogen could later be used in fuel cells to generate electrical energy, thus allowing energy storage from renewable energy sources. An alternative, or perhaps, rather complementary route for the utilization of renewable energy sources is the direct synthesis of wide-use chemicals. For instance, ORR can go through two different pathways, the so-called 4-electron one, which is desirable in fuel cells, and the 2-electron one, which is not desirable in that case, but results in the generation of hydrogen peroxide, which is a widely used chemical an oxidant and a disinfectant. Therefore, a good control of the selectivity of ORR is of high interest for both applications.

Out of the reactions taking place in electrolyzers (the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER)) and fuel cells (the are oxygen reduction reaction (ORR) and the hydrogen oxidation reaction (HOR)), in both cases, the reactions involving oxygen (OER and ORR) have slower kinetics and are the bottleneck to making these devices more efficient. Additionally, the catalysis of these reactions often requires costly noble metal catalysts (such as Pt), so there is considerable interest in finding alternatives that are more economical.

The Electrochemistry for Energy Conversion group investigates the influence of bi-, tri- and multicomponent alloys, surface and near-surface alloys, as well as surface structure and electrolyte composition on the electrocatalytic properties towards these key reactions [1]. In this regards we apply a wide range of electrochemical techniques, both in static and hydrodynamic conditions, coupled with complementary techniques such as electrochemical quartz crystal microbalance, FTIR, and various other surface science techniques, such as XPS, XRD, BET adsorption analysis, etc.

Pt-alloy catalysts have been used in electrocatalysis widely since the 1970s and have been considered as the state-of-the-art material. Alloying is a well-known strategy to modify the electrocatalytic properties of materials [2] and has been used to make various Pt-alloys with transition metals, lanthanides and other rare earths to create catalysts for the ORR [3, 4]. Despite the progress made in the last decades, there have only been modest developments in improving the properties of ORR catalysts in recent years. This is due to several factors, including the scaling relations between the adsorption energies of intermediates.

MPCAs for Oxygen Reduction

Multiple principal element alloys (MPCAs) and their special case - high-entropy alloys (HEAs), have recently received a lot of attention for their unique properties and the fact that the potential designs are exceptionally abundant. While, it is known that under ORR conditions polycrystalline bimetallic catalysts dealloy and form a core-shell structure, the promising property of multicomponent alloys, especially high-entropy alloys, is that they might not dealloy the same way as bi-metallic alloys. i.e., they could keep dissimilar atoms on the surface, and, therefore, have different atoms as active sites present [5]. This would mean that besides the well-investigated strain effects, ligand and ensemble effects would also be pronounced. The abundance of different active sites with different binding energies could, on one side, allow the identification of sites with optimal binding energies and furthermore, it could provide different optimal sites for multistep reactions, thus enabling overcoming the issues with the scaling relations. According to theoretical con-

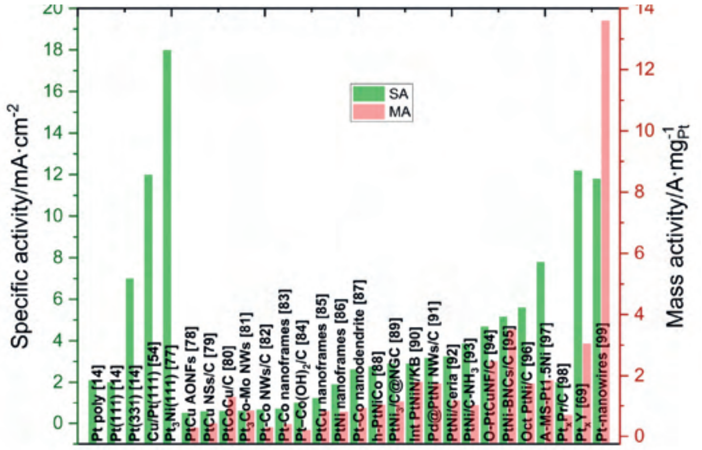

Figure 1. Specific and mass activity of selected bi- and tri-metallic Pt-alloys for ORR in 0.1 M $HClO_4$. Results obtained on Pt poly, Pt(111), Pt(331), Cu/Pt(111), and $Pt_3Ni(111)$ are shown as a reference for the specific activity, whereas Pt_xY, one of the highest SAs reported among lanthanide alloys and Pt-nanowires, displayed the highest MA to date.

siderations, HEAs should have a continuous distribution of binding energies. Therefore, they have been investigated in electrocatalysis, as catalysts for ORR, carbon dioxide reduction reaction, methanol oxidation, hydrogen evolution and others.

Considering the complexity of their structure, understanding the behavior of these alloys under reaction conditions is crucial to understanding their activity, selectivity, and stability. For this, it would be essential that these types of alloys are characterized not only as-synthesized, but also in situ, and after the reaction or, optimally, in operando conditions. Considering the above-mentioned reasons, the group aims to investigate the experimental challenges in the benchmarking of HEA and MPCA activity for ORR.

The overall number of desired active sites on these types of catalyst may be decreased, as the high compositional complexity also increases which necessarily leads to the fact that the number of optimal active sites may, statistically, be low. This raises the question of how to identify the optimal active site and distinguish it from a very large number of possible different contributions. The electrochemically active surface area (ECSA) determination is vital for the comparison of the intrinsic activities of different electrocatalysts and determining the activity per surface site (turnover frequency). Furthermore, the change of the ECSA before and after the reaction can help to rationalize the changes observed in the catalytic activity after continuous cycling. ECSA is determined using several methods, which all have their advantages and drawbacks. One of the most often used is based on the double layer capacitance (C_{dl}), determined from cyclic voltammetric experiments at different scan rates or from electrochemical impedance spectroscopy (EIS). The main concern about the ECSA determination from double layer capacitance measurements is the value of specific capacitance (Cs) such the error in the accuracy could be unacceptably high. CO-stripping, hydrogen underpotential deposition (H_{upd}), copper underpotential deposition (Cu_{UPD}) is another common choice to determinate the ECSA of Pt-containing alloys. EEC actively seeks to develop molecular probes that can provide electrochemical information about the surfaces of complex alloys. While the determination of the ECSA of such complex surfaces are not trivial and universal techniques are far from being applicable, specific information can be extracted using such techniques.

For the ORR, since the activities of the catalyst are benchmarked on the level of mV or tens of mV, it is of great importance to conduct the potential correction carefully. The most widely applied technique to find the uncompensated resistance (R_u) is the electrochemical impedance spectroscopy (EIS). The use of certain HEA or MPCAs materials might represents new challenges to ohmic compensation. They could form different phases and a (partial) passive layer under reaction conditions that increase the electrode resistance and complicate the compensation since the R_u value will change during the experiment.

The application of MPCAs and HEAs in electrocatalysis has many exciting prospects. The high complexity of the surface of such alloys (high-entropy alloys, multiple principal components alloy, and complex solid solutions) offers the possibility of identifying active sites previously not achievable by the manufacturing of "classical" alloy catalysts. Additionally, the presence of a multitude of active sites on the surface also offers new possibilities for breaking scaling relations, which have been the limiting factor for the development of improved ORR catalysts, as well as the catalysis of multi-step reactions. However, the high complexity of these materials offers significant challenges as well, particularly in surface site identification, selectivity control, the understanding of stability dependence and their in operando behavior. Additionally, the fact that the properties of such complex materials are difficult to predict based on the properties of components will offer new challenges to computational chemistry and high-throughput screening of materials, enabling researchers to navigate the multi-dimensional, highly complex compositional and structural space with an unprecedented number of degrees of freedom for the modification of their properties. The group seeks to further the prospects of rational catalyst design by linking the activity, selectivity and stability of these catalysts to assessable physical properties.

2-electron ORR

With the control of selectivity, the ORR can be switched to the 2-electron process which results in the formation of hydrogen peroxide H_2O_2. H_2O_2 is a wide use green chemical, used as a disinfectant, oxidant and in chemical synthesis. The group primarily investigates carbon-based materials as electrocatalysts for this reaction. The main challenge with such materials is reaching high selectivity and partial current density in acidic conditions, while ensuring sufficient durability. Acidic electrolytes have a significant advantage that they allow the use of solid state electrolytes and, therefore, the production of pure hydrogen peroxide in water. High selectivity is important to the energy efficiency of the system, while high current densities allow the production of higher concentrations of H_2O_2, since multiple-pass systems are often problematic due to H_2O_2 dissolution. In this regard EEC aims to electrochemically characterize carbon-based materials in terms of activity, selectivity and stability, as catalysts for oxygen reduction to H_2O_2.

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EPR Spectroscopy of Metallorganic Complexes

The Max Planck Research Group led by George Cutsail employs and develops new spectroscopic approaches to tackle difficult and challenging inorganic electronic structure questions. Primarily utilizing Electron Paramagnetic Resonance (EPR) spectroscopy, including a wide variety of advanced pulsed EPR techniques, rare and noteworthy systems are studied ranging from high-valent Cu and dioxygen activation intermediates to unusual mixed-valent complexes and heavy main-group radicals. However, not limiting ourselves to only paramagnetic species, various other X-ray spectroscopic approaches are also employed to further characterize systems of significance. Some selected studies are highlighted here.

Mixed Valent Transition Metal Cluster Electronic Structure

Iron sulfur cluster are ubiquitous throughout biology, fulfilling numerous roles from iron/sulfur storage to electron transfer and catalysis. These clusters form in a variety of nuclearities, from small 2Fe-2S dimers, to larger 4Fe-4S cubanes, and more complex heterometallic clusters such as the nitrogenase active site, a 7Fe9SMo-carbide cluster. To understand the electronic structure and reactivity of larger clusters, we must first fully understand the complexity of the minimal 2Fe-2S pairs that are constituent building blocks of these clusters.

The classic $S = 1/2$ spin-state of $[Fe_2S_2]^+$ clusters arises from the antiferromagnetic coupling of the high-spin Fe^{2+} ($S = 2$) and Fe^{3+} ($S = 5/2$) ions. In rarer cases, clusters have exhibited a maximal $S = 9/2$ spin with the Fe centers remaining uniquely antiferromagnetically coupled, rather than ferromagnetically coupled as one might expect. These observations require the implementation of a 'double-exchange' interaction (B) to explain the delocalization of the unpaired electron and the lifting of spin-state degeneracies. The most interesting consequence of this theory is the prediction of numerous intermediate-spin ground states, such as $S = 3/2$, 5/2 and 7/2 for iron-sulfur dimers. In the 70 years following the initial development,[1] there has yet to be a direct experimental observation of intermediate-spin ground state in a molecular dimer.

Recently, we characterized a new series of iron dichalcogenide dimers supported with bulky β-diketiminate ligands (**Figure 1**, Q = S, Se, Te). Ultimately, substitution with tellurium, Te, as a bridge between the iron ions had the most dramatic electronic influence. This unprecedented $[Fe_2Te_2]^+$ complex unequivocally exhibits a well-isolated $S = 3/2$ intermediate-spin ground state as shown by the low-temperature EPR measurements and the Mössbauer demonstrates that the unpaired electron is now completely delocalized at 80 K. Hence, our observation and characterization of an $S = 3/2$ spin-state for $[Fe_2Se_2]^+$ and $[Fe_2Te_2]^+$ clusters are a remarkable first for the field of mixed-valent chemistry and were published recently in *Nature Chemistry*.[2]

It is clear that the bridging ion influences the ability to trap intermediate spin-states, however, we have yet to spectroscopically understand the role of vibronic coupling in the core and how it controls the degree of electron delocalization. Computationally, we calculate a diminished out-of-phase breathing mode for the $[Fe_2Q_2]^+$ core with heavier dichalcogenide substitution. In the future, this study will be expanded to explore the influence of the supporting ligand and its ability to control fundamental vibronic coupling modes that dictate spin-states in these clusters.

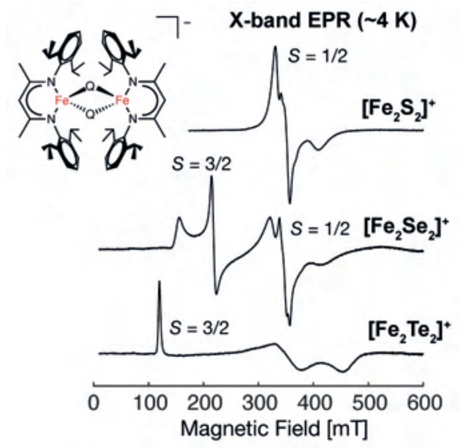

Figure 1. EPR spectra of $[Fe_2Q_2]^+$ complexes exhibiting $S = 1/2$ or intermediate $S = 3/2$ spin-states.

Characterization of Cu-centered Complexes and LPMOs by Advanced EPR Techniques

Both the cleavage and formation of the O-O bonds in O_2 through activation by transition metal centers are critical chemical processes for chemical energy solutions. We aim to understand the fundamental mechanics of O-O bond cleavage and formation facilitated by copper centers in metalloproteins and small biomimetic complexes by various spectroscopic techniques. One of our first goals is to expand the utility of advanced EPR techniques such as Electron Nuclear Double Resonance (ENDOR) and ELDOR-Detected NMR (EDNMR) spectroscopies to study and elucidate the structure and electronic properties of copper-oxygen intermediates, particularly copper. These advanced techniques possess the ability to produce high-level structural and bonding information of dilute catalytic intermediates. Here, we have established numerous ^{17}O hyperfine parameters using several small copper complexes with either bipyridine or tetraamine ligands and varying the identity of the oxygen ligand (H_2O, ^-OH, ^-OOH), **Figure 2.** These approaches for ^{17}O hyperfine couplings are complemented by $^{1/2}H$ hyperfine studies.

Our work on small molecules is being extended to mono-copper proteins such as lytic polysaccharide monooxygenases (LPMO). These proteins bind and activate O_2 to form a strong copper-oxygen oxidative intermediate that is capable of breaking the strong C-H glycosidic bond (>95 kcal/mol) of polysaccharide substrates.

While the copper active-site structure of LPMOs is well conserved among numerous organisms, with similar T-braces (bis-histidine, N-terminus amine coordination geometries), the modulation of the Cu(II) environment by either waters or hydroxo ligands as a function of pH is less understood. EPR spectroscopy evidences dramatic coordination geometry and electronic structure changes in a select AA10 family LPMO (*Sm*AA10A), **Figure 3**, as a function of pH. At more alkaline conditions, superhyperfine coupling of the ^{14}N ligands is observed in the EPR spectra, confirming that a 3N coordination sphere is present. Advanced pulsed EPR techniques, such as ENDOR, evidence unresolved ^{14}N hyperfine couplings and ^1H couplings of the exchangeable protons. These studies have allowed us to form the most complete coordination picture of LPMO to-date, highlighting its flexibility.

Copper X-ray Absorption and Emission Spectroscopy

We are currently studying the fundamental spectroscopic signatures of formal Cu(III) oxidation states and developing new methodologies for their study in tandem with computational analysis to yield a holistic interpretation of these high-valent centers. X-ray absorption spectroscopy (XAS) is able distinguish the various copper oxidation states by reliably measuring transitions as a function of the core Cu 1s binding energy. While XAS probes the lowest unoccupied orbitals, we extended the utility of Valence-to-Core (VtC) spectroscopy, which probes the highest occupied orbitals, to experimentally probe oxidation-state. For each organocopper complex in the

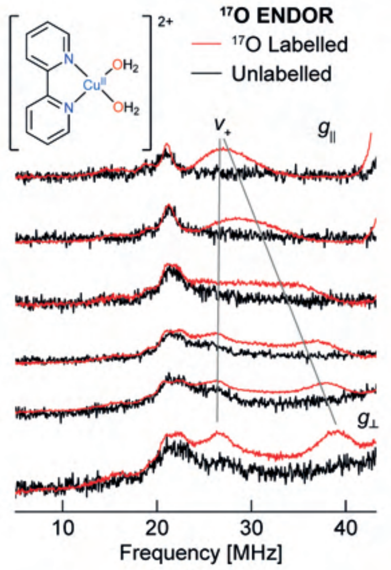

Figure 2. ^{17}O Electron Nuclear Double Resonance (ENDOR) Spectroscopy of an isotopically labeled copper bipyridine complex.

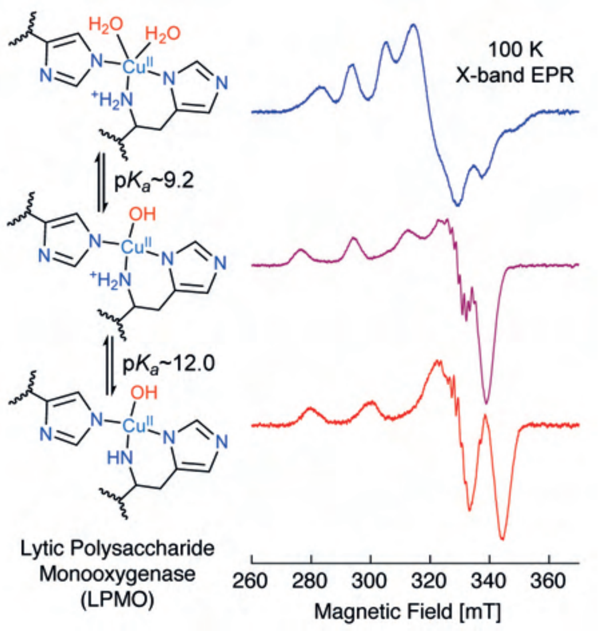

Figure 3. Structural formula of the copper active-site of LPMOs, also referred to as a histidine 'T-brace', as function of pH with CW X-band EPR spectra for each species.

series, a sharp feature with a clear correlated shift to higher energy with increasing oxidation-state is observed. This trend is identical to that observed in the XAS, suggesting that the VtC-XES technique is indeed sensitive to oxidation-state. This test of VtC-XES was the first demonstration of the sensitivity of technique to copper's oxidation-state.[3]

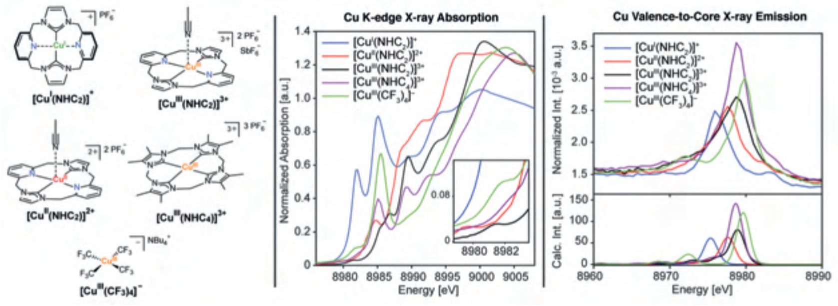

Figure 4. Various organocopper complexes studied by either XAS or VtC-XES.

Our approach was extended to the hotly-debated $[Cu(CF_3)_4]^-$ anion (**Figure 4**), which may be described either as a formal Cu(III) center with $4(CF_3)^-$ ligands or as a Cu(I) complex with a cationic ligand: $[Cu^{III}(CF_3)^-_4]$ or $[Cu^I(CF_3)^+(CF_3)^-_3]$. The unmistakable formal oxidation state assignment of $[Cu^{III}NHC_2]^{3+}$ and its remarkable similarities in electronic structure to $[Cu(CF_3)_4]^-$ lead to the same Cu(III) formal oxidation-state assignment. This pairing of core-level absorption and emission spectroscopies with computational methods have allowed us to make confident oxidation-state assignments with complete electronic structure understanding.

Heavy Main-Group Radical Characterization

The exploration and study of heavy main-group radicals is a rapidly expanding field of research, for which advanced EPR spectroscopic characterization plays a central role.[4] Our on-going collaboration with Prof. Stephan Schulz (University of Duisburg-Essen) has yielded numerous published studies in which we have applied multi-frequency EPR and ENDOR spectroscopy to As, Sb, and Bi centered radicals. Multi-frequency EPR spectroscopy elucidates the complex hyperfine patterns along with precise **g**-tensors. Furthermore, decomposition of the hyperfine tensors revealed the individual orbital components of the unpaired spin, confirming the predominately p-centered nature for most of these radicals.

Given that only a handful of stable bismuth radicals have been isolated to-date, our group is fortunate to be able to explore some of their unique properties.

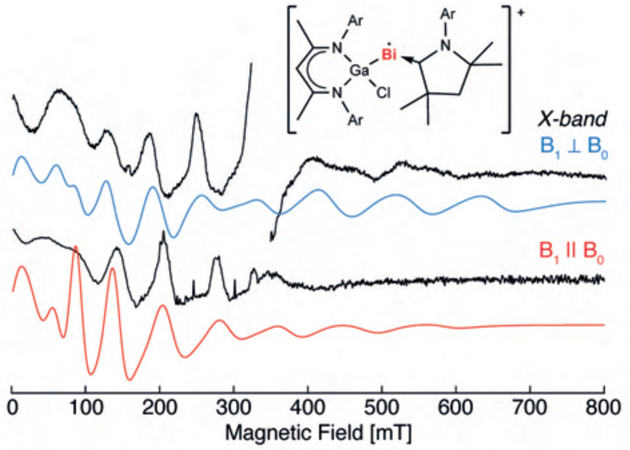

Figure 5. Perpendicular- and parallel-mode X-band EPR spectra and simulations of a Bi radical.

We have found that neutral Bi(II) radicals may exhibit a broad X-band (9.6 GHz) EPR spectrum of numerous transitions that span nearly 8000 G. Multi-frequency EPR, including Q- (34 GHz) and W-band (94 GHz) typically aid in resolving anisotropic *g*-values, however, severe spectral distortions are observed at higher frequency due to field-dependent strain. To overcome these problems, we have successfully employed parallel-mode EPR at conventional X-band frequencies to gain additional information. While parallel-mode is routinely described as only applicable to integer-spin (S = 1, 2, …) systems, the large hyperfine interaction of the bismuth radical profoundly changes the conventional selection rules at these relatively low magnetic fields. In the low field limit, M_S and M_I are no longer good quantum numbers and the *total* angular momentum, $F = S + I$, must be considered. Recognizing the selection rule $M_F = 0$ for parallel mode, transitions of simultaneous spin flips of the electron and nuclear spins are observed.

Our recent publication[5] of parallel-mode X-band EPR for bismuth radical is the first application of parallel-mode EPR to an $S = 1/2$ radical with large hyperfine coupling, **Figure 5**. The introduction of this approach to the characterization for bismuth radicals will undoubtedly be employed in the future by others, as access to parallel mode EPR spectroscopy is readily available on commercially dual-mode microwave resonators.

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Synergistic Organometallic Catalysis

Research vision: In nature, chemical bonds are constructed and ruptured with exceptional levels of precision. Synergies and cooperation within the constituent parts are crucial to these systems. As a catalyst works synchronously with its surroundings, it creates favorable kinetic and thermodynamic conditions for activating, breaking and transforming chemical bonds. By imitating this approach, researchers have been able to activate and convert a variety of small inert molecules with significant biological and industrial implications. Traditional catalytic protocols convert substrates into a single product, preferably or even exclusively. In contrast, catalysts can also be viewed as systems whose activity can be adjusted by fine-tuning reaction conditions to convey distinct product platforms. Developing dynamic and adaptive molecular systems[1] capable of controlling challenging bond activation processes is essential to our research program.[2]

Approach: We aim to design and understand catalytic systems in their full complexity. This may lead to responsive or adaptive catalysts for which it is possible to regulate and control their catalytic activity precisely. Here, reaction parameters are combined rather than isolated, and their interactions are studied within the entire system (Figure 1). This way, new synergies can be identified, ultimately creating new properties present in the system, not in its parts. As a result, the catalyst may appear to be self-adjusting, controlled, and regulated by the environment for a particular transformation. The ability to self-adjust is an essential prerequisite for developing universal catalysts. By creating such systems, laboratories could advance the fundamental understanding of the requirements to control various chemical transformation sequences; ultimately producing selectively different products from a vast array of building blocks.[3]

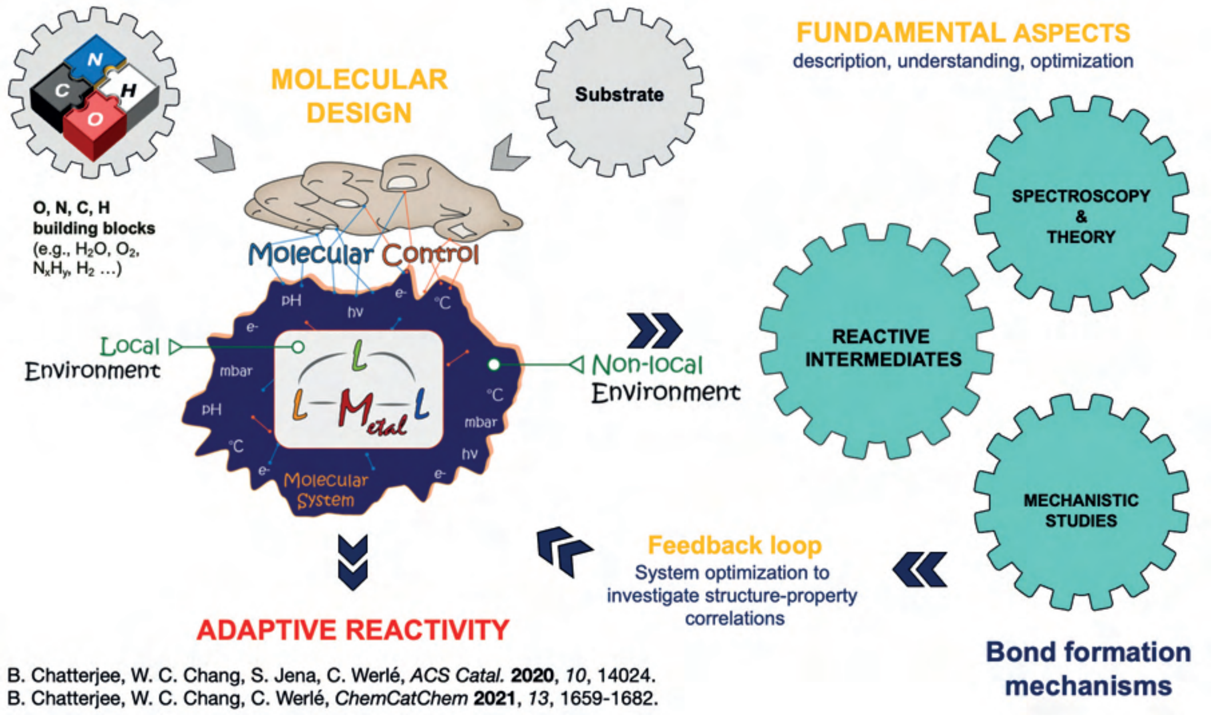

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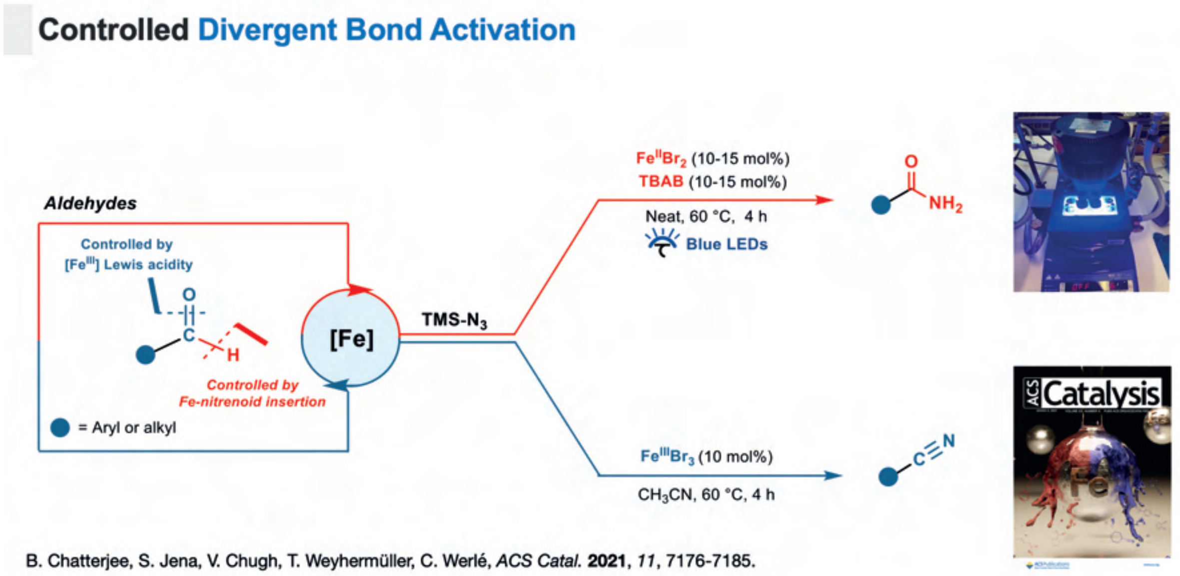
Figure 1. A schematic representation of the molecular approach to developing dynamic and adaptive systems.

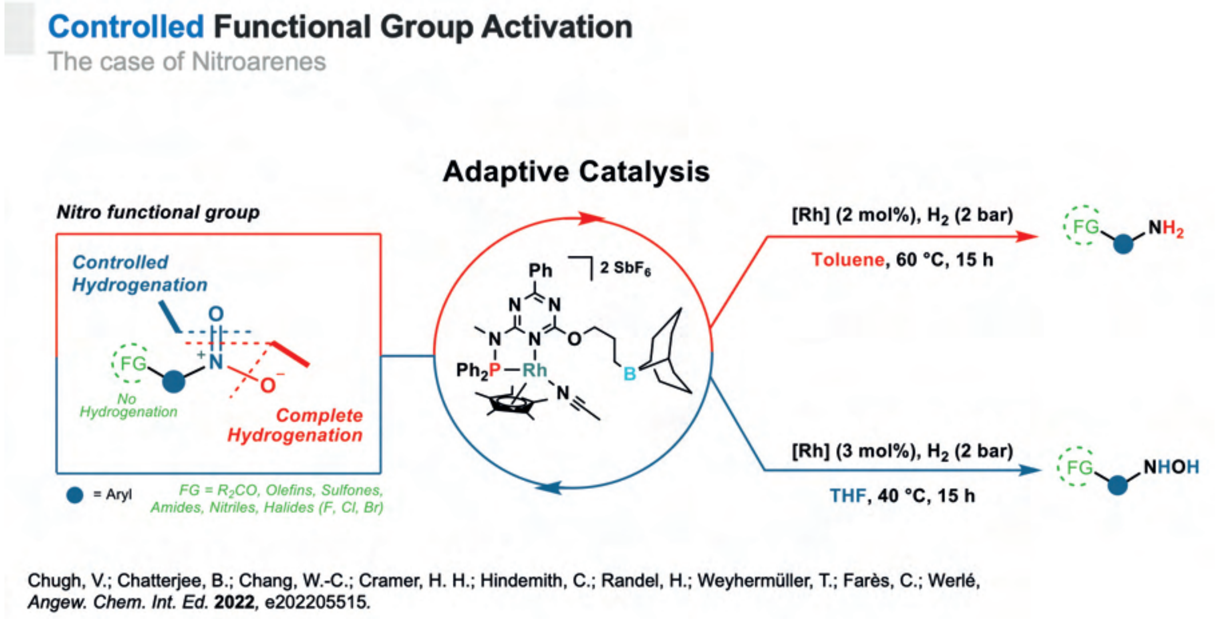


B. Chatterjee, S. Jena, V. Chugh, T. Weyhermüller, C. Werlé, *ACS Catal.* **2021**, *11*, 7176-7185.

Figure 2. Development of an Iron-based system for divergent bond activations in aldehyde.

One of our projects aimed to investigate whether a catalyst could, based on the reaction conditions, open divergent reaction pathways by engaging the intrinsic chemical bonds of a primary functional group (e.g., aldehyde, Figure 2).[4] Using aldehyde as an example, such a system might be able to address C=O (Figure 2, blue) and C-H (Figure 2, red) bonds separately in order to generate different products. The iron-based catalyst system we developed is based on these considerations. It provides unique molecular control over the formation of the product according to the nature of the active species (neutral versus ion pair) made operational under finely adjusted reaction conditions. By being able to selectively target the intrinsic chemical bonds of the primary functional groups, the reported system demonstrates that divergent reaction paths can be opened. As a result, nitriles and amides can be generated in highly selective manners under mild reaction conditions. Preliminary mechanistic studies have shown that nitrile is formed when neutral $Fe^{III}Br_3$ acts as a Lewis acid and activates the aldehyde bond C=O. This promotes the nucleophilic attack of TMS-N_3 and leads to the desired product after hydrolysis. On the other hand, amide synthesis involves the *in situ* generation of an ion pair $[Fe^{III}Br_4][N(C_4H_9)_4]$. This species acts as a molecular platform capable of producing and transferring an electrophilic nitrene radical to the aldehyde C-H bond.

In a complementary approach, we hypothesized that implementing a polarized cooperative domain within a catalytic system might develop in an adaptive platform.[5] Specifically, our approach involved using a ligand environment presenting an attached borane arm to challenge and tame the reactivity of the metal center (Scheme 1).



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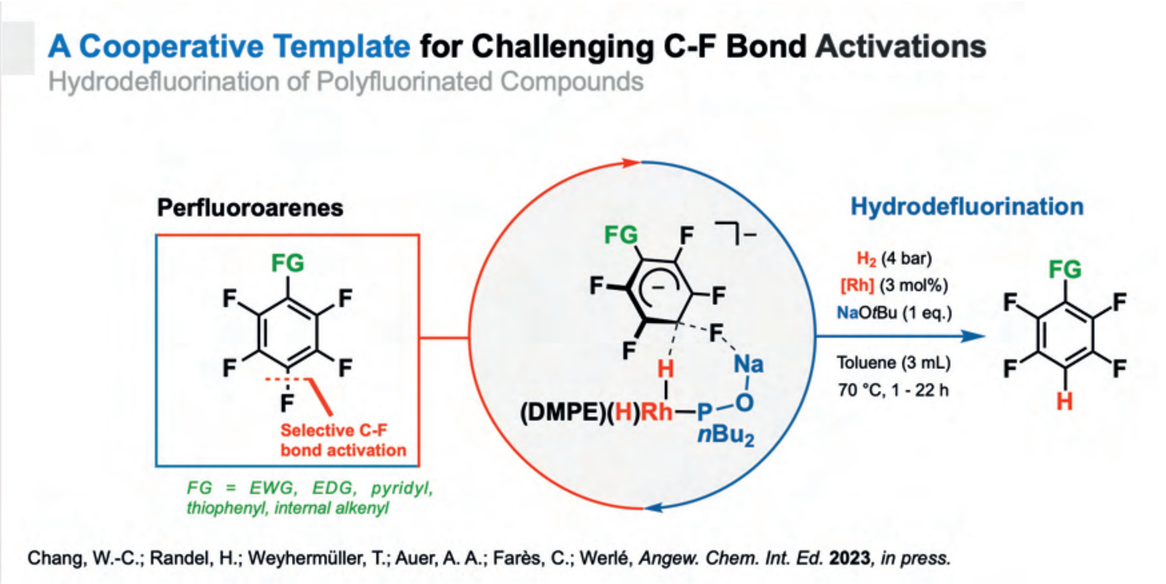
Scheme 1. Adaptive hydrogenation of nitroarenes.



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Scheme 2. A cooperative template for enhanced C-F bond activation.

Because both partners have unique electronic properties, a polarized environment is created, which can capture, lock, activate, and convert substrates. To this end, we decided to use rhodium as a metal center because of its high propensity to drive hydrogenation reactions. The developed system was tested for the hydrogenation of nitroarenes to evaluate the reactivity of the catalyst and its propensity to adapt its reactivity. We selected this specific class of substrates because several product platforms can be obtained on the way to fully reduced aniline. We, therefore, examined whether the designed system could control this hydrogenation network and selectively stop at the desired reduction levels. As a result, our system has been found to provide anilines (complete hydrogenation) and hydroxylamines (controlled hydrogenation) in excellent yields in mild conditions while preserving the integrity of other potentially vulnerable functional groups.

The selective activation of C-F bonds under mild reaction conditions remains challenging, particularly for electron-rich substrates. To tackle this challenge of bond activation, we took advantage of a delicate interaction between $Rh(DMPE)_2H$ fragments and secondary phosphine oxides ($HP(O)nBu_2$) to catalyze the hydrodefluorination of perfluoroarenes (Scheme 2).[6] Aside from substrates with electron-withdrawing functional groups, this system was highly tolerant of extremely rare electron-donating functionalities. This catalyst's high chemoselectivity and readiness to be used at a preparative scale demonstrate its practicality. Experimental mechanistic studies have identified a rhodium(I) dihydride as a relevant catalytic species and phosphine oxide as a determinant cooperative fragment. Our study shows that molecular templates can be assembled using these design elements to create catalysts with increased reactivity for challenging bond activations.

Future directions: Our research group aims to expand the potential of molecular catalysts for selective and effective activation of challenging chemical bonds. Our strategies have been developed directly at the molecular level in correlation with the characteristics and requirements of the targeted substrates. We believe that the synthetic protocols and the molecular insight from our work will encourage further investigations into the dynamic field of *synergistic catalysis*. In current projects, we are looking at finding sustainable alternatives to existing catalytic methods and challenging bond activations using dynamic catalytic systems in combination with sustainable energy.

Integration and future collaborations: Our research group is integrated into an interdisciplinary and international environment at the Max Planck Institute for Chemical Energy Conversion in collaboration with the Ruhr-University Bochum. We aim to pave the way for fruitful long-term partnerships between the two institutions. Our research group is also active in the Cluster of Excellence, "*The Fuel Science Center.*" In this project, we aim to advance fundamental knowledge to replace fossil fuel combustion in engines by developing adaptive production and propulsion systems utilizing renewable energy and alternative carbon sources.

Funding and acknowledgments: We are grateful for the generous financial support provided by the Max Planck Society, the IMPRS program, the "Fuel Science Center" funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany's Excellence Strategy Exzellenz-cluster 2186, The Fuel Science Center "ID: 90919832," as well as the outstanding support of our analytical departments.

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Magnetic Resonance of Complex Materials and Catalysts

Fields of research

Thomas Wiegand started his Max Planck Research Group at MPI CEC in November 2021 with a joint W2 professor appointment at RWTH Aachen University. The group studies catalytic processes in biology and chemistry by magnetic-resonance spectroscopy in close collaboration with research groups at MPI CEC, RWTH Aachen University and further national and international partners. The laboratory develops and employs solid-state Nuclear Magnetic Resonance (NMR) approaches to structurally characterize active centres in heterogeneous catalysts and to unravel the mechanism of catalytic reactions (e.g. hydrogenation reactions), as well as chemical-energy conversion processes in biological systems, such as motor proteins fuelled by ATP hydrolysis. A further focus lies on studying the molecular-guiding principles behind biomolecular phase separation events, which are currently intensively studied in cell biology due to their role in the onset of certain neurodegenerative diseases. The group also began to explore very recently solid-state NMR in the emerging field of mechanochemistry to disentangle the mechanisms of organic reactions performed in ball-milling devices under high pressures. A central research theme in the laboratory is the detection of weak chemical interactions, particularly noncovalent binding events, in the manifold molecular-recognition events mentioned above. The lab located at the Institute of Technical and Macromolecular Chemistry at RWTH Aachen University is equipped with NMR spectrometers up to 700 MHz and magic-angle spinning (MAS) equipment allowing to achieve 111 kHz spinning speed. Our vision is to develop unified concepts in catalysis bridging the gap between biology and chemistry. For an overview of the current research topics see Figure 1.

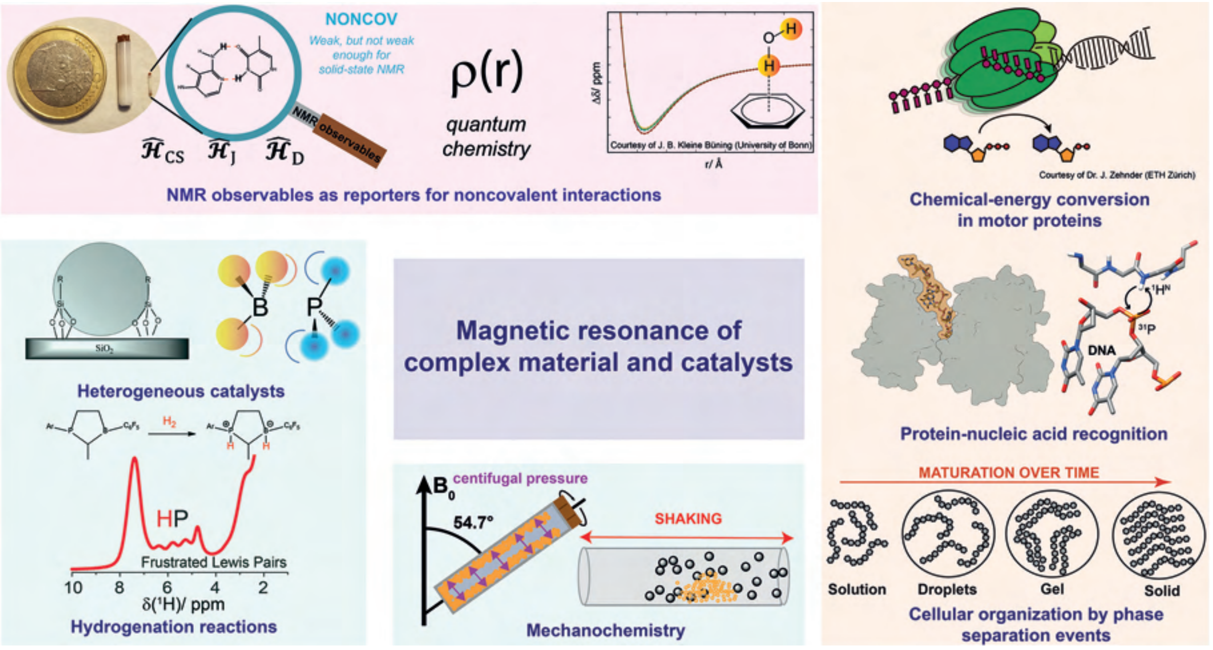

Figure 1. Overview of current research topics in the magnetic resonance of complex materials and catalysts group.

Solid-state NMR spectroscopy research

A focus of our research lies on the detection of protons by solid-state NMR, which often are at the heart of a molecular-recognition event initiating chemical reactions or assembly processes. Until recently their solid-state NMR spectra be uninformative due to lack of resolution caused by the sizeable proton-proton dipolar couplings, which are not fully averaged at previously used slow MAS frequencies. However, with the significant line-narrowing achieved with the advent of new fast MAS techniques (> 100 kHz), the protons engaged in various types of noncovalent interactions (hydrogen bonds, π–π– or hydrophobic interactions etc.) can be resolved and identified. We interpret our experimental results in feedback with quantum-chemical calculations on how NMR observables are influenced by noncovalent interactions.

Research topics

NMR observables as reporters for noncovalent interactions.
Our "NONCOV toolbox" development allows us to use NMR observables modulated by the strength of noncovalent interactions, e.g. proton chemical-shift values, [1] their temperature-dependence,[1a] hydrogen bond-mediated *J*-couplings and relaxation parameters. Supporting quantum-chemical calculations using density functional theory (DFT) of NMR observables help us to unravel the physical origin of such dependences. We currently use a variety of molecular entities to establish novel techniques at fast MAS, ranging from molecules related to phosphane/borane Frustrated Lewis Pair (FLP) chemistry, molecular Ru-complexes to lanthanide complexes trapping isolated water molecules.

Heterogeneous catalysts and hydrogenation reactions.
Solid-state NMR is employed in combination with DFT calculations to gain structural and dynamic information of active centres in heterogeneous catalysts. These insights will be used to (i) develop a mechanistic description of the underlying catalytic processes and (ii) further fine-tune the catalytic properties of the systems investigated. In close collaboration with our partners we study metal phosphide nanoparticles, particularly those immobilized on a supported ionic liquid phase, and functionalized Ru-polyphosphine polymers. Additionally, we use NMR to obtain mechanistic insights in hydrogenation reactions, for instance by unravelling the molecular-recognition process between catalysts and substrate molecules. Also Frustrated Lewis Pairs, whose potential is also recently explored in heterogeneous catalysis [2], are a long-standing research topic in the group. The group aims at developing solid-state NMR techniques at fast MAS to detect products of hydrogenation reactions. [2] Parts of the research are carried out within the DFG excellence cluster "Fuel Science Center".

Mechanochemistry.
The field of mechanochemistry has experienced an impressive development in the past years and a variety of organic reactions performed in ballmilling devices has been reported. We use ex- and in-situ solid-state NMR approaches to elucidate the structures of the materials formed in mechanochemically-induced reactions and to explore the whole branch of mechanochemical input on such transformations. We aim at deriving a mechanistic understanding of the molecular-recognition processes occurring under high pressures. The first reaction we have studied is a bromination of a cyclic sulfoximine (Figure 2). [3]

Additionally, we explore the influence of mechanochemical input on bond-scission events in biomacromolecules.

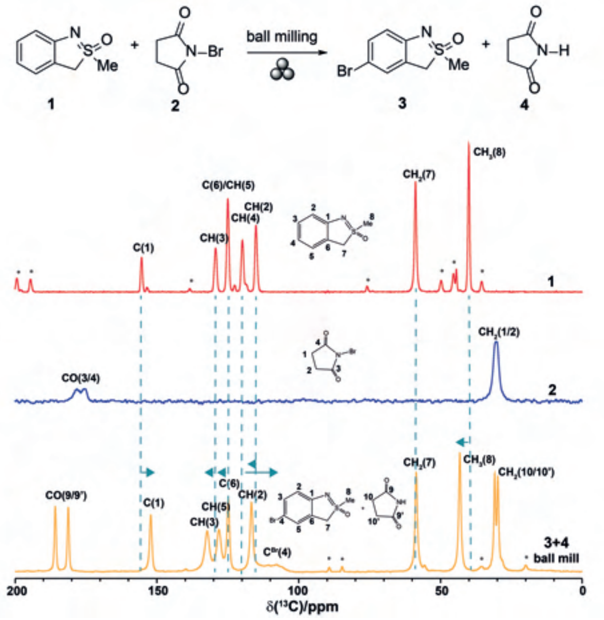

Figure 2. Investigation of a mechanochemical bromination rection of a cyclic sulfoximine by solid-state NMR spectroscopy. The ^{13}C cross-polarization MAS spectra of the two reaction educts and the reaction product directly taken from the ball-milling vessel are shown revealing both, a clean and fast product formation. The Figure has been adapted from reference [3].

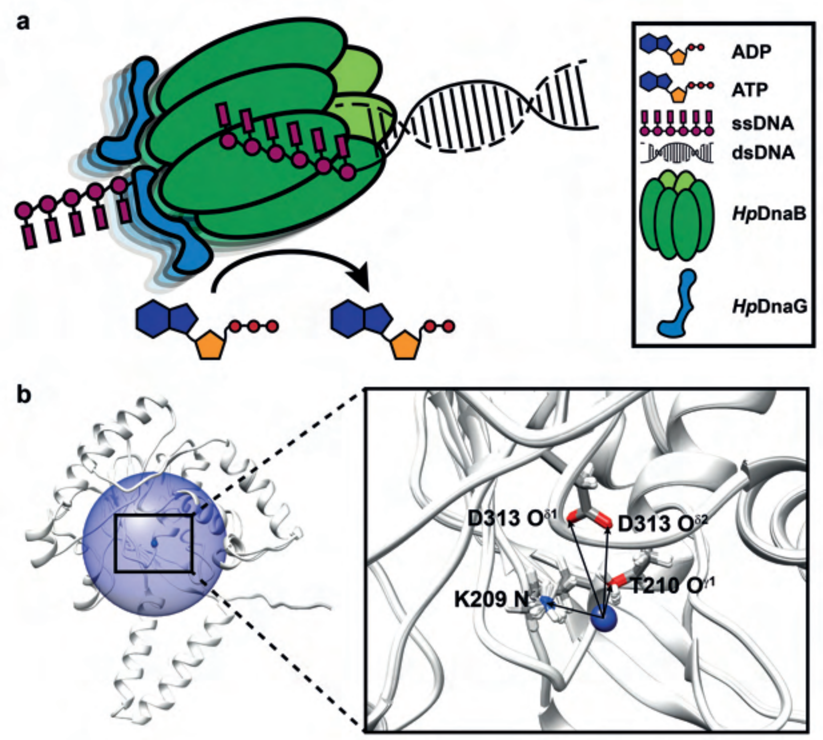

Figure 3. a) Schematic representation of the DNA-unwinding by a DnaB helicase. The chemical energy released during ATP hydrolysis is converted into mechanical functioning. b) Sketch of a DnaB monomer with the "blind sphere" around the metal ion co-factor, in which NMR resonances are broadened beyond detection. The Figure has been adapted from reference [6a]. A zoom into the nucleotide-binding domain with the metal ion color-coded in blue is shown on the right. Figure by Dr. Johannes Zehnder.

Chemical-energy conversion in motor proteins and protein-nucleic acid interactions.

ATP-fuelled proteins use the chemical energy released during ATP hydrolysis for biological functioning. Motor proteins, for instance, play an important role in DNA replication. We study helicases and primases focusing on deriving the molecular mechanism of ATP hydrolysis or primer formation, respectively. [4] A key research topic is to unravel the binding of nucleotides to proteins, allowing us to derive models for ATP-hydrolysis and its correlation with protein functionality. [5] We also develop paramagnetic solid-state NMR and EPR strategies, which for instance enable the localization of the ATP metal ion co-factor in large protein assemblies or pave the way for unravelling protein-protein interaction surfaces (Figure 3). [6] To probe protein-nucleic acid binding, we design novel solid-state NMR strategies at fast MAS, with a key focus on probing noncovalent interactions in such events. Distance restraints determined from solid-state NMR spectra will allow us to model the protein-nucleic acid complexes, for instance in the context of RNA-binding proteins (see beside) or proteins involved in DNA replication. A DFG Heisenberg fellowship and a Sachbeihilfe fund parts of this research.

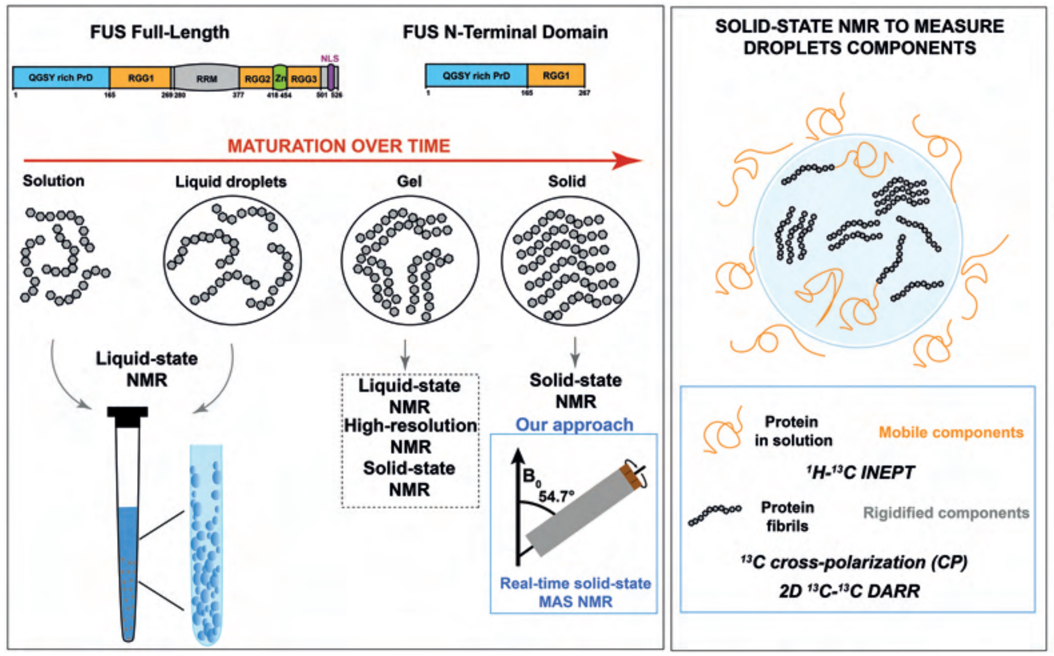

Figure 4. Liquid-liquid phase separation and the subsequent maturation of liquid droplets studied by solid-state NMR. The group currently focusses on the fused in sarcoma (FUS) protein and tries to unravel the molecular guiding principles behind biological phase separation events. Figure by Ettore Bartalucci.

Cellular organization by phase separation processes.

We study proteins related to neurodegenerative diseases (e.g. RNA-binding proteins), which are linked with liquid-liquid phase separation processes. Real-time solid-state NMR is applied to follow the maturation of liquid droplets into solid fibrils with the goal to unravel the non-covalent interactions guiding such events at the molecular level (Figure 4). Small peptide derivatives designed based on the sticker-and-spacer concept undergoing both, liquid-liquid and subsequent liquid-to-solid phase transitions, are studied as model systems. Currently our protein-of-interest is the Fused in Sarcoma (FUS) protein. The research is funded by a DFG Heisenberg fellowship.

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Heterogeneous Redox Catalysis

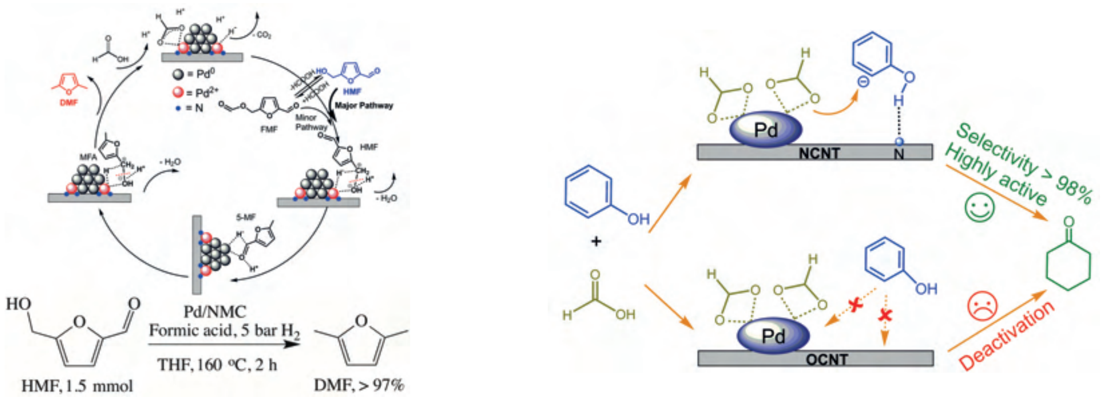
Introduction

The Max Planck Fellow group “Heterogeneous Redox Catalysis” has been established in October 2015. Dr. Baoxiang Peng joined as group leader in November 2015 and gradually set up the research group. Currently, the group mainly consists of three PhD students (Xiaoyu Li, Guilong Lu: CSC scholarship, Catalina Leiva Leroy: CRC/TRR 247 short-term scholarship) and one postdoc (Dr. Julia Büker: scholarship of Evonik Stiftung). In addition, Daniel Waffel funded by VCI scholarship contributed to the research group and successfully received his PhD in March 2022. Scientifically, the Max Planck Fellow group performs fundamental research in the area of heterogeneous redox catalysis in the liquid phase under mild conditions and aims at obtaining a comprehensive understanding for three-phase catalytic redox reactions. The scientific challenge is the elucidation of the reaction mechanisms and the interplay of the reactants with the complex surface chemistry of heterogeneous catalysts on the atomic level.

The reaction conditions of thermal redox catalysis experiments are chosen at temperatures below 200 °C in the liquid phase to guarantee conservation of the kinetic control of specific materials properties such as defects that have been deliberately adjusted by targeted catalyst synthesis. Reduction catalysis focuses on the hydrogenation and hydrodeoxygenation of biomass-derived platform chemicals such as phenol and 5-hydroxymethylfurfural (HMF), whereas oxidation catalysis comprises the selective oxidation of alcohols and the challenging C-H bond activation of hydrocarbons. Low temperatures also exclude the Mars – van Krevelen mechanism by avoiding bulk diffusion of oxygen anions in oxides. Liquid-phase oxidation requires a deeper understanding of solvation-related phenomena. Corrosion is a common phenomenon leading to catalyst deactivation or dissolution and re-deposition equilibria. The reactions are primarily performed in autoclaves at elevated pressure or self-built glass reactors at atmospheric pressure. *In situ* ATR-IR spectroscopy is used to investigate reaction mechanisms by monitoring concentration changes of key reactive and transient species. *In situ* EPR spectroscopy is applied to identify radical species in cooperation with AG Schnegg (MPI CEC). Products are mainly analyzed and quantified by GC and multi-channel gas analyzer.

Catalytic Reduction

The selective hydrogenolysis of biomass-derived HMF provides a valuable approach for the production of dimethylfuran (DMF) as higher-value-added fuels, chemicals, and solvents. We successfully synthesized Pd nanoparticles (NPs) supported on N-doped and N-free mesoporous carbon materials (NMC and CMC) via the immobilization method, which were systematically characterized, and applied in the hydrogenolysis of HMF to DMF. Density functional theory (DFT) calculations and X-ray photoelectron spectroscopy (XPS) measurements revealed the strong metal-support interactions between Pd NPs and pyridinic N atoms for Pd/NMC [1]. It also evidenced the presence of bifunctional Pd NPs containing Pd^0 and Pd^{2+} centers. When applied in the hydrogenolysis reaction, we were able to achieve a favorable HMF full conversion, DMF yield of > 97% and a higher turnover frequency (TOF) of 150 h^{-1} over Pd/NMC in the presence of formic acid and H_2 after 2 h (Scheme 1, left) [2]. Based on these excellent results, a trilateral transfer project was initiated and successfully funded by DFG and Fraunhofer society recently for three years, aiming at producing DMF from HMF on a large scale as a bio-based solvent for paints and coatings.



Scheme 1. Reaction pathway for HMF to DMF over Pd/NMC in formic acid and H_2 (left), and catalytic transfer hydrogenation of phenol with formic acid to cyclohexanone over Pd/CNT (right).

An important advantage of this process lies in the addition of formic acid as a versatile reagent for the conversion of HMF to DMF. The reaction mechanism (Scheme 1, left), especially the multiple roles of formic acid, was explored through a detailed comparative study. It was found that formic acid tunes not only the reactivity of HMF but also its reaction pathways, serving multiple roles, such as suppressing ring-hydrogenation, acting as a mild reducing agent, producing the formate esters as intermediates, and forming a protonated intermediate, thus lowering the activation barrier of the C-OH bond cleavage. The ATR-IR results clearly show that the presence of formic acid shifts the dominant reaction pathway from the hydrogenation of the aldehyde group to the hydrogenolysis of the hydroxymethyl group.

Since formic acid can serve as a hydrogen donor in the hydrogenation reactions, it is important to investigate the separate formic acid decomposition experiments by monitoring the gas evolution to better understand the hydrogenation reactions with formic acid. In our study of catalytic transfer hydrogenation of phenol with formic acid over Pd/CNT [3], separate formic acid decomposition experiments without and with the addition of phenol were performed to investigate the reaction mechanism, especially the deactivation behavior. It was found that deactivation is caused by the almost full coverage of active Pd sites by the strongly bound formates (Scheme 1, right), suppressing further formic acid decomposition on Pd NPs.

Furthermore, we developed a novel *in situ* auto-reduction strategy to encapsulate highly dispersed Pd clusters/nanoparticles in amino-functionalized Ti(IV)-based metal-organic framework (i.e., MIL-125-NH_2) [4]. It is demonstrated that the amino groups in MIL-125-NH_2 can be used to anchor formaldehyde to form novel reducing groups (-NH-CH_2OH), on which Pd^{2+} ions are *in situ* auto-reduced to metallic Pd NPs. The obtained Pd(1.5)/MIL-125-NH-CH_2OH catalyst with highly dispersed Pd clusters/nanoparticles exhibited full phenol conversion and 100% of cyclohexanone selectivity and remarkable reusability.

Catalytic Oxidation

Oxidation reactions are mainly investigated within Collaborative Research Centre / Transregio 247 (CRC/TRR 247), aiming at obtaining a comprehensive basic understanding of the processes at the solid-liquid interface for metal oxide catalyzed oxidation reactions. The core of the CRC in the first funding period is a comparative study, which delivers generic reactivity trends that allow the establishment and validation of (real) structure–activity–correlations. Employed catalysts include mixed transition metal-based spinel and perovskite oxides. These catalysts were tested in different oxidation reactions to comprehensively assess their chemical reactivity by finding activity and selectivity patterns in a reaction matrix. The reaction matrix is formed by variation of the substrate and the oxidant. After a successful first funding phase, the CRC/TRR 247 was extended by the DFG for a further four years from 1 July 2022, aiming at identifying the active sites and obtaining mechanistic understanding.

In the last three years (2020 – 2022), our subproject A01 resulted in 12 publications in peer-reviewed journals, of which 11 were joint work together with other subprojects of the CRC. In a study of the gas-phase oxidation of 2-propanol over $CoFe_2O_4$, it was found that mainly acetate species cause the deactivation of the spinel catalysts, which turned out to be fully reversible by oxidative treatment [5]. The mechanistic details of the gas-phase 2-propanol oxidation over Co_3O_4 were further investigated [6]. By thorough experimental evaluation in tandem with a DFT + *U* modelling, it became clear that on the {110} surface of the catalyst a Mars-van Krevelen mechanism takes place due to the faster reoxidation, while a Langmuir-Hinshelwood mechanism proceeds on the {100} surface. Unlike Co_3O_4 with smaller grain size (9 nm), larger Co_3O_4 particles (19 nm) showed no deactivation because of a higher fraction of exposed {110} facets.

Moving to the liquid phase, for the oxidation of 2-propanol in water and of benzyl alcohol, styrene and cinnamyl alcohol in dimethylformamide with O_2 over a $Co_xFe_{3-x}O_4$ series, it became clear that pure Co_3O_4 is the best catalyst, and any incorporation of Fe proved to be detrimental.[7,8] By modelling the surface composition as a function of the metal content of the spinel oxides, the hypothesis of an active ensemble consisting of at least six Co atoms was derived.[7] Contrary to the aerobic oxidation reactions, Fe incorporation in low amounts (≤ 10 %) proved to be beneficial for the oxidation of benzyl alcohol, styrene and cinnamyl alcohol with TBHP, emphasizing the difference between aerobic and peroxidic oxidants.[8] In addition, it was demonstrated that *in situ* solvent-derived hydroperoxide plays a central role during the oxidation of benzyl alcohol in *N,N*-dimethylformamide over Co_3O_4.

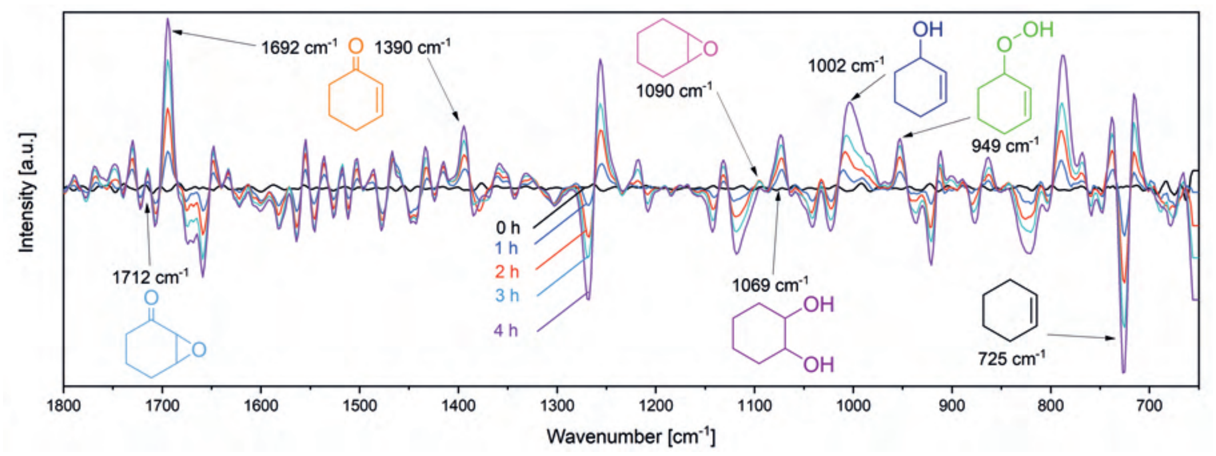


Figure 1. Time-resolved ATR-IR spectra for the oxidation of cyclohexene over $La_{0.6}Sr_{0.4}CoO_3$ with the assigned bands to track individual reaction components.

The oxidation of cyclohexene over a $La_{1-x}Sr_xCo_yFe_{1-y}O_3$ series showed that Fe incorporation into $LaCoO_3$ is not beneficial for either conversion or the allylic selectivity, while the substitution of Sr into $LaCoO_3$ is beneficial for the reaction [9, 10]. The optimum sample in terms of conversion and allylic selectivity was found to be $La_{0.8}Sr_{0.2}CoO_3$. As the Sr amount in the samples increased, the numbers of surface oxygen vacancies and exposed Co^{2+} centers were found to increase simultaneously. While Co^{3+} sites and oxygen vacancies are vital for the activation of O_2, Co^{2+} is an important factor for the decomposition of the formed 2-cyclohexene-1-hydroperoxide, the key intermediate of the reaction.[11] By *in situ* ATR-IR measurements, the complex reaction network of the cyclohexene oxidation was monitored precisely with enhanced time resolution (Figure 1).[10,12]

In addition to these metal oxide catalysts, Au-Pd alloy nanoparticles supported on various functionalized carbon nanotubes were tested in the oxidation of toluene with molecular O_2. Among these catalysts, Au-Pd/CKCNT exhibits the highest catalytic activity and the shortest induction period due to favorable basic properties of the support. A remarkable effect was observed when adding the products benzyl alcohol and benzaldehyde, which enhanced the reaction rate and eliminated the induction time without changing the product composition. The promoting effect can be attributed to a radical reaction mechanism related to benzaldehyde autooxidation via benzoylperoxy radicals. It is proposed that the observed retardation during toluene oxidation does not originate from catalyst deactivation, but from the formation of byproducts, which quench the radical mechanism.

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Solid Molecular Catalysts

Introduction

The Max Planck Fellow group "Solid Molecular Catalysts" has been established in November 2019. Dr. Anna Katharina Beine joined as a group leader in December 2019. Lea Hombach started her work as a PhD student in February 2021. The team is supported by the technician Maximilian Conradt. In January 2023, Jerome Hommes started as PhD student funded by a DFG project acquired by Dr. Beine.

Scientifically, the Max Planck Fellow group performs fundamental research in the field of solid molecular catalysts and aims to design and understand highly active, selective and stable molecular as well as single-atom catalysts. Enabled by progress in both synthetic procedures and analytical methods, tailored materials featuring defined nanoclusters or even isolated metal sites have become available and shown to be highly active catalysts. Such materials blur the lines between the traditional domains of homogeneous and heterogeneous catalysis, allowing to unite the advantages of both. Especially solid molecular catalysts based on polymers which structures composed of N- or P-containing ligand motifs, to which isolated metal species are coordinated, present a highly promising field of research. The resulting single-site catalysts feature catalytically active subunits with high similarity to homogeneous catalysts. Another concept in the transition between heterogeneous and homogeneous catalysis, between full catalysts on the one hand and the use of defined metal complexes in solution on the other, are single-atom catalysts. Increasing the metal dispersion of supported particulate species results in a change of electronic structure and transition to immobilized complexes as well as nanocluster, single-site and single-atom catalysts (Figure 1).

The metal species at uttermost dispersion (single-atoms), stabilized on suitable support materials, possess activity and selectivity profiles not previously available by traditional molecular or heterogeneous catalysts.[1] However, single-atom catalysts, unlike single-site catalysts, do not hold a uniform and fully defined coordination environment. Rather, in the case of single-atom catalysts, a large number of different active sites are present, depending on the coordination centres of the support material. The described material classes in focus of the Max Planck Fellow group find not only application in traditional chemocatalysis, e.g., for the hydrogenation of CO_2 or in (bio)plastic recycling,[2] but also possess a high potential for transformations in both electro- and photocatalysis.

Solid molecular catalysts based on single-site and single-atom catalysts

Because they contain nitrogen sites with tuneable electronic properties capable of strongly coordinating metals, covalent triazine frameworks (CTFs) recommend themselves for application as macroligand in solid molecular catalysts. Understanding the deactivation pathways of metals coordinated to CTFs, such as agglomeration, and

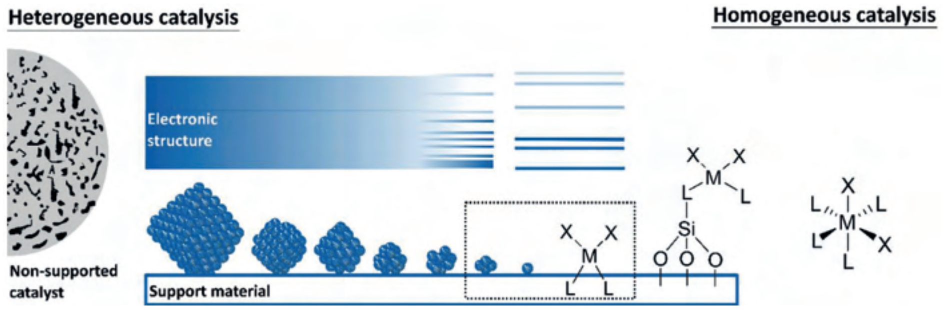

Figure 1. Landscape of catalysis in the transition between heterogeneous and homogeneous catalysis.[1]

exploring ways to increase their resistance to such is of utmost importance. Using a model system comprised of Ir(acac)(COD) immobilized on an N-rich CTF, it was possible to show changes to the catalytically active species depending on catalyst treatment. As evidenced by XPS and TEM analysis, reductive conditions above 400 °C lead to Ir agglomeration, while identical conditions at or below 400 °C instead cause the formation of highly active and selective iridium single-sites for formic acid decomposition and CO_2 hydrogenation.[3] We recently summarized the potential scope of CTFs as catalytic materials and supports for single-site and single-atom catalysts in a tutorial review article.[1]

Focusing on a currently intensively discussed class of single-atom catalysts, single Pd atoms stabilized on graphitic carbon nitride (g-CN) were investigated in the ethylene reduction as model reaction (Figure 2). In cooperation with Dr. Weidenthaler (MPI KoFo), thorough analysis of the metal dynamics under reaction conditions were carried out showing that a single-atom Pd catalyst agglomerates during ethylene hydrogenation at 100 °C. This agglomeration coincides with the appearance of catalytic activity, suggesting that small clusters, rather than single-atoms, are the active species.[4]

Single-site catalysts based on Ru supported on tailored poly-phosphines were tested as well in the synthesis and decomposition of formic acid. Catalysts based on 1,2-bis(diphenylphosphino)ethane moieties (pDPPE) showed superior activity in both reactions with a TON of 9680 for Ru@pDPPE in CO_2 hydrogenation in an aqueous amine solution. Switching between hydrogenation and dehydrogenation was possible enabling the application in H_2 storage systems.[5] In recent studies, the direct hydrogenation of CO_2 in a base free aqueous system was investigated. Therein, an optimized material synthesis gave rise to Ru@pDPPE catalysts reaching a TON of 2990 in aqueous DMSO solution and even pure water outperforming structurally comparable homogenous catalysts.[6] Currently, tailored polymer structures for catalysts active in hydroformylation are in the focus of research.

Further research topics

In addition to working on the main topic of the fellowship, the group also gives Dr. Beine the opportunity to develop her research profile and pursue her personal research ideas. Dr. Beine's research focuses on the development of tailored catalysts for the conversion of renewable energy and biogenic carbon sources to enable the transition from a fossil-based to a sustainable economy. Here, the focus lies on electrochemical water splitting and the conversion of hemicellulosic biomass to value-added products.

Catalyst development for the electrochemical water splitting reaction

Hydrogen economy is a central aspect of future energy supply, since hydrogen can be used as energy storage and fuel. To make this process economically feasible, it is particularly important to optimize the energy demanding oxygen evolution reaction (OER) which takes place at the anode. Therefore, carbon based composite materials containing the earth-abundant metals Fe and Mn were synthesised, characterised and tested for their electrocatalytic potential.[7] To synthesise the electrocatalysts, metal precursors and dicyandiamide (DCD) were ground together and pyrolised under N_2-atmosphere at temperatures between 600 and 900 °C. STEM analysis revealed the formation of N-rich multi-walled carbon nanotubes (MWCNT) for pyrolysis temperatures of 700 °C and above. From XRD analysis it was concluded that inside the tubes Fe_3C particles are formed, which decompose to metallic Fe and C at a pyrolysis temperature of 900 °C. Fe and Mn spinel particles cover the outer surface of the MWCNT. In linear sweep voltammetry the catalyst prepared at 700 and 800 °C showed a low overpotential of 389 mV (at 10 mA/cm^2), which can be referred to the presence of Fe_3C and conductive MWCNT. Chronoamperometric measurements reveal the highest stability of 22.6h for the materials prepared at 800 °C, which can be referred to the high coverage of the outer surface of the MWCNT by metal spinel particles, which protect the carbon matrix from oxidation. The different components of the composite thus contribute to either the activity or the stability of the catalyst and yield a promising electrocatalyst in combination.

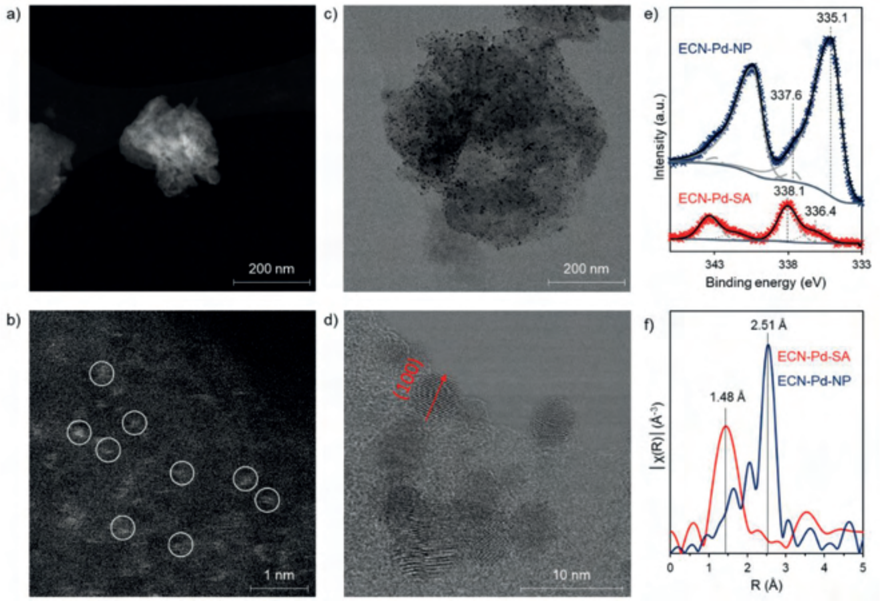

Figure 2. (a,b) Dark field AC-STEM images of single Pd atoms on g-CN (ECN-Pd-SA). As a guide to the eye, some single-atoms are marked with white circles. (c,d) Bright field AC-STEM images of Pd nanoparticles on g-CN (ECN-Pd-NP). (e) Pd 3d core level XPS spectra, with black lines showing fits to the raw data (crosses) and grey lines deconvolution into components. Positions of Pd 3d 5/2 components are shown by vertical lines. (f) Normalized magnitudes of the k^2-weighted Fourier transform (FT) of the extended X-ray absorption fine structure spectra in radial distance (not phase corrected).[4]

Since carbon-based catalysts tend to decompose by oxidation under the high potentials of OER, further research considered the use of all-metal oxide catalysts.[8] Mn and Co based catalysts were prepared by hydrothermal synthesis and varying pH value. Cubic particles with a size of 2 to 4 m resulted. The cubes are composed of varying amounts of $MnCo_2O_4$, $CoCO_3$ and a mixed $(Mn/Co)CO_3$ phase depending on the pH value of the synthesis. Structure–activity relationships were derived revealing a volcano-type correlation between the intrinsic OER activity and the fraction of spinel $MnCo_2O_4$ phase. A low overpotential of 370 mV (at 10 mA/cm^2) and a stability of more than 25 h were achieved in 1.0 M KOH using a rotating disc electrode (RDE) setup. The best performing catalyst was successfully tested under dynamic process conditions for 9.5 h and showed superior catalytic activity as anode for the overall water splitting in an electrolyser setup at 333 K compared to a reference NiCo-spinel catalyst.

As many catalysts for OER have been developed to facilitate the kinetics and to yield a high stability, we further summarised these efforts in a review highlighting especially deactivation processes, as stable catalysts are imperative for industrial application.[9] The main deactivation mechanisms for OER catalysts discussed in literature can be summarised as: dissolution, changes in the crystal phase or morphology, passivation, detachment and surface blockage by gas bubble formation. Further research should aim for a better understanding of the long-term stability of already introduced active catalyst materials and to further improve their stability. Therefore, studying catalyst performance under dynamic electrochemical conditions and in electrolyser cells are imperative.

Immobilisation of heteropolyacids for the conversion of hemicellulose

For a sustainable economy, next to the transition to renewable energies also the transition to renewable carbon sources is inevitable. One possibility is valorising lignocellulosic biomass, where the reaction types hydration and dehydration play a major role. The reactions proceed via acid catalysis and heteropolyacids (HPAs) proved to be highly promising due to their tunable acidic and redox functionality. As HPAs are very well soluble in water and many organic solvents, recycling strategies such as immobilisation or salt formation have been developed to ensure industrial applicability. We have summarised the findings in a review paper and found that mostly silica materials and metal oxides are applied as supports for HPAs.[10] Only few publications indicate that activated carbon might as well be a promising support for HPAs, while the interactions between HPA and support are only poorly discussed.

We have therefore impregnated the most acidic HPA phosphotungstic acid (PTA) onto an oxygen rich carbon support (AC).[11] ICP analysis confirmed a high PTA-loading of 473 mg_{PTA}/g_{AC}. From FT-IR analysis it becomes clear that the typically observed bands for PTA are preserved upon immobilisation indicating that the structural form of the HPA, the Keggin structure, remains intact (Figure 3a). The prepared catalyst was then tested in the hydrolysis of xylan to xylose, a bio-based platform chemical (Figure 3b). A high conversion of 92 % and full selectivity is reached after 2 h of reaction, which is comparable to the performance of the homogeneous PTA. The catalyst was removed from the aqueous solution by centrifugation and applied in a consecutive reaction. Over 20 runs, the conversion linearly decreases to 44 % while the full

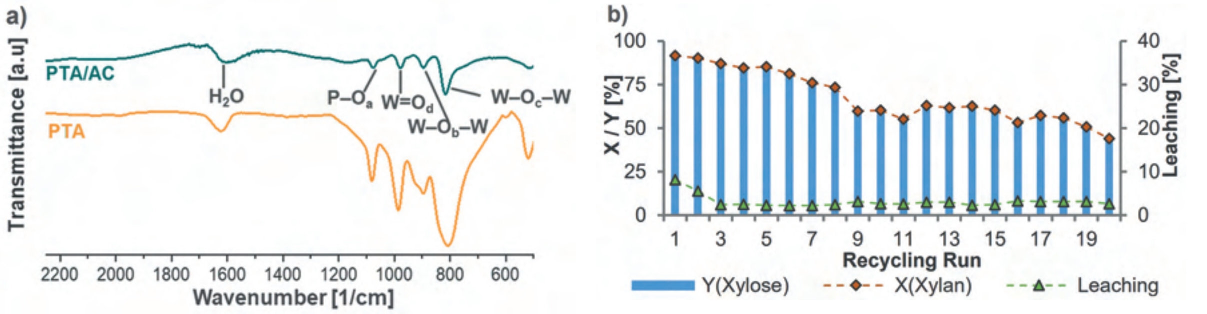

Figure 3. a) FT-IR spectrum of phosphotungstic acid (PTA) and PTA immobilized on an oxygen rich carbon support (PTA/AC) and b) catalytic performance of PTA/AC in the hydrolysis of xylan to xylose over 20 runs. Reaction conditions: T = 403 K, t = 2 h, m(xylan) = 0.345 g, m(PTA) = 0.118 g, V(H_2O) = 15 mL.

selectivity is maintained. The loss of activity can be attributed to the continuous leaching of PTA, which levels off at 2 to 3 % after three runs. Compared to other immobilised HPA catalysts applied in aqueous medium, the leaching is found to be low. FT-IR analysis of the spent catalyst confirms the Keggin structure to be maintained over the reaction and a molecular distribution of the PTA clusters on the surface is evident from TEM images of the catalyst before and after reaction. AC therefore represents a promising support material for the immobilisation of HPAs and polyoxometalates.

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MPI CEC IN SCIENTIFIC DIALOGUE

Carbon2Chem

The aim of the project Carbon2Chem® is to find suitable ways for the use of steel mill exhaust gases for the production of chemicals. By this, the overall CO_2 emission of a steel mill can be considerably reduced. In combination with the integration of hydrogen from electrolysis with renewable energies this provides also a more sustainable way to produce chemicals and/or fuels [1]. This project is funded by the Federal Ministry of Education and Research (Bundesministerium für Bildung und Forschung, BMBF) and contains 7 subprojects with numerous partners from industry and academia. Included in the project are also two kinds of laboratories for the partners of all subprojects: a general laboratory for basic investigations operated with commercial gases and a laboratory at a pilot plant scale, where the real steel mill gases are purified and provided for proof-of-concept investigations.

The main tasks of the MPI CEC within the project is the operation of a special Carbon2Chem® laboratory in collaboration with Fraunhofer Institute UMSICHT, characterization of the three metallurgical gases (coke oven gas, blast furnace gas and basic oxygen furnace) before and after the gas treatment as well as the materials used in the project and studies on methanol synthesis. This work is located in the Catalytic Technology group.

Gas Analysis

The activities regarding gas analysis focuses on the operation of an analytical container laboratory as well as an analytical laboratory for the online and on-site characterization of trace compounds in the raw and treated metallurgical gases at the Technical Center of the Carbon2Chem project in Duisburg. The characterization of these trace compounds before and after a purification process is of paramount importance, since such compounds even in the ppb-range could drastically reduce the catalyst lifetime in downstream processes like e.g. methanol synthesis. Therefore, a detailed knowledge of the gas composition and its time dependence is required for the design and operation of the gas-treatment unit. Furthermore, monitoring of the purified gases controls if the gas treatment is working properly and ensures reasonable interpretation of the subsequent processes investigated at the Technical Center where these gases are directly applied. While main and minor compounds are analyzed by gas chromatography, the characterization of trace compounds is performed applying high-end process mass spectrometer, so-called Proton-Transfer-Reaction Quadrupole interface Time-Of-Flight Mass Spectrometer (PTR-QiTOF-MS) [2,3]. Although PTR-MS is usually applied as a semiquantitative technique, calibration experiments proved that the obtained values are within a reasonable error range allowing to use the obtained values as starting point for the compounds of interest even without further calibration (Figure 1) [3,4]. Since up to date this technique had found mainly application in the determination of VOCs in air and environmental science, method development is required to adapt this technique to the analysis of industrial gases. Therefore, besides the characterization of the real gases, additional method optimization is performed with a gas mixing system in the Carbon2Chem® laboratory to further improve the application of PTR-MS in this field. Here, single compounds or complex gas mixtures are investigated, so that the substances found at the Technical Center in the metallurgical gases can be simulated under controlled conditions in order to study with an additional PTR-instrument possible side reactions and the fragmentation patterns inside the drift tube of the PTR-instruments.

Carbon2Chem® Laboratory

From the two laboratories, which are operated within in the project, MPI CEC - in collaboration with Fraunhofer UMSICHT - operates the general laboratory [5]. The intention of this lab is to offer all partners participating in the project the opportunity to combine their scientific efforts at one place and further improve the collaboration within the overall project. Furthermore, the lab is equipped with some standard sample preparation and characterization methods to support the work in the subprojects. The integration of the Carbon2Chem® laboratory into the overall concept of the project is shown in Figure 2.

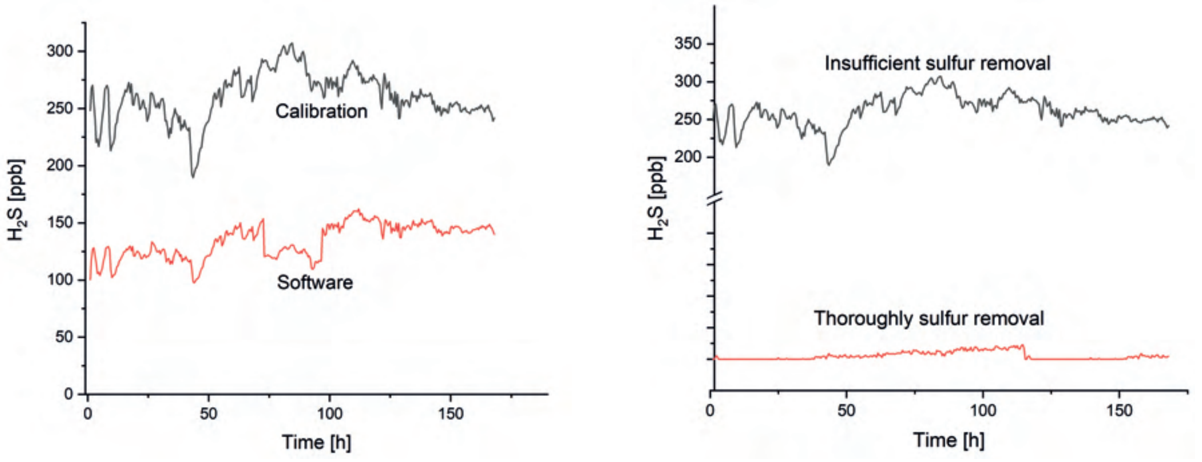


Figure 1. Left: Comparison of the H_2S concentration over time calculated by the PTR-MS software (red) and the external calibration (black). Right: Concentration profile of H_2S for a time period with insufficient (black) and with thoroughly sulfur removal (red). [3]

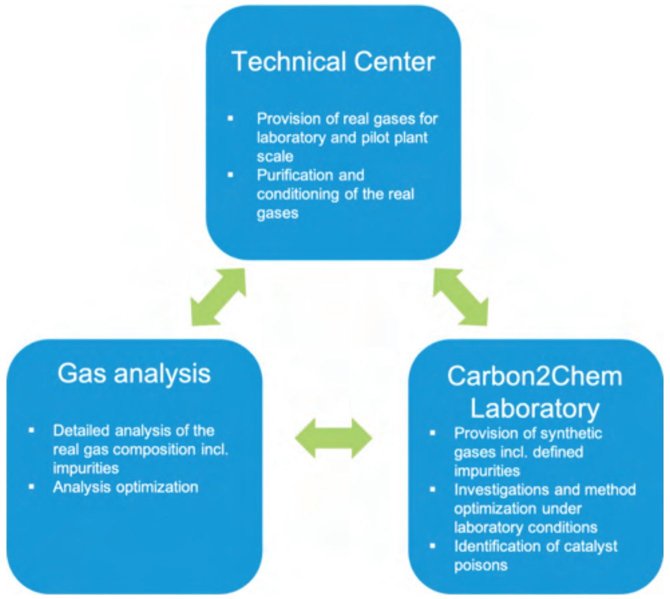
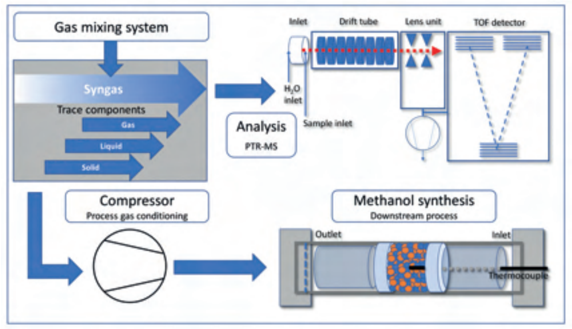


Figure 2. The role of the Carbon2Chem® laboratory within the Carbon2Chem® network. [5]

One important aspect is the additional gas mixing system, which was developed and installed as key set-up within the lab. A scheme of the interconnection of the gas mixing system with subsequent applications is given in Figure 3. In addition to the standard gases supplied by the overall infrastructure, with this gas mixing system it is possible to mimic the three metallurgical gases including main, minor and trace compounds. This offers the possibility to optimize the analytical methods applied in the real gas analysis as well as enables flexible catalyst poisoning studies at elevated pressures in subsequent flow set-ups.

For utilization in methanol synthesis, the typically hydrogen-poor steel mill exhaust gases have to be enriched with sustainably produced H_2 to achieve a sufficient methanol productivity. In principle, two basic scenarios for the utilization of the steel mill exhaust gases are possible. The first scenario is the utilization of H_2-rich coke oven gas combined with CO-rich basic oxygen furnace gas. A defined mixture of these gases will end up in a synthesis gas mixture consisting of the main compounds with a stoichiometric number similar to synthesis gas as it is nowadays applied in industrial methanol synthesis. Here, the major challenge will be the presence of minor and trace compounds, which may require a different purification procedure than the usually used feed gases to avoid a reduced lifetime of the applied catalyst. The second basic scenario is the utilization of the blast furnace gas. As it is related to the highest amount of CO_2 emission at the steel mill its utilization is crucial for a significant reduction of the overall CO_2 emission, but a high amount of H_2 is required for the realization. As the H_2 source has to be based on renewable energy sources to avoid additional CO_2 production, its supply will be intermittent following the availability of the renewable energy. Consequently, the methanol synthesis process has to be performed in a dynamic rather than the highly optimized stationary mode and its impact on the catalyst stability is unknown. These two important questions are addressed in the Carbon2Chem® laboratory accordingly and, therefore, research work on the influence of trace compounds as well as intermitting conditions on the stability of the catalyst is performed here.

Figure 3. Interconnection of the gas mixing system with subsequent applications within the Carbon2Chem® laboratory.



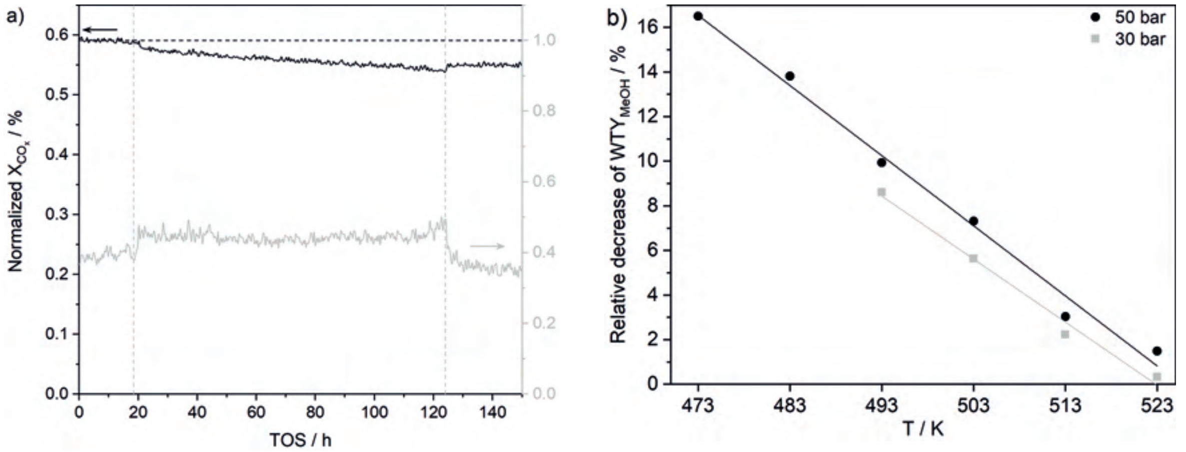


Figure 4. a) Continuous dosing of 0.06% O_2 over an industrial $Cu/ZnO/Al_2O_3$ catalyst under methanol synthesis conditions at 523 K and 50 bar for 108 h. Switching from clean syngas to syngas including O_2 and back is indicated with vertical dashed lines.
b) Relative decrease of WTY_{MeOH} while adding 0.06% O_2 into the feed gas in a temperature range of 473 K to 523 K and pressures of 30 bar (gray) and 50 bar (black). [7]

Investigations on the impact of intermitting conditions during methanol synthesis showed an unexpected high stability of the catalyst under these conditions [6]. These results are promising to realize a CO_2 hydrogenation to methanol under dynamic operation to compensate the fluctuations coming along with the integration of renewable energies in the process chain. Regarding impurities actual results show, that small amounts of nitrogen compounds as well as oxygen only act as reversible poisons [7].

On the other hand, long-term measurements with 500 ppm oxygen in the synthesis gas lead to an accelerated deactivation of the catalyst (Figure 4). Further detailed investigations will provide deeper insight in the interaction between these molecules and the active catalyst and their impact on the stability of the catalyst (see also report of the Catalytic Technology Group). Based on this, a judgement on the catalyst lifetime with respect to concentrations of trace components will be possible.

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Cluster of Excellence
The Fuel Science Center

Adaptive Conversion Systems for Renewable Energy and Carbon Sources

Building on the success of the Cluster of Excellence "Tailor-made Fuels from Biomass" the Fuel Science Center is creating a world-leading scientific environment as a structural unit of RWTH Aachen University in cooperation with Forschungszentrum Jülich and the two Max Planck Institutes at the Mülheim Chemistry Campus, MPI for Chemical Energy Conversion and MPI für Kohlenforschung.

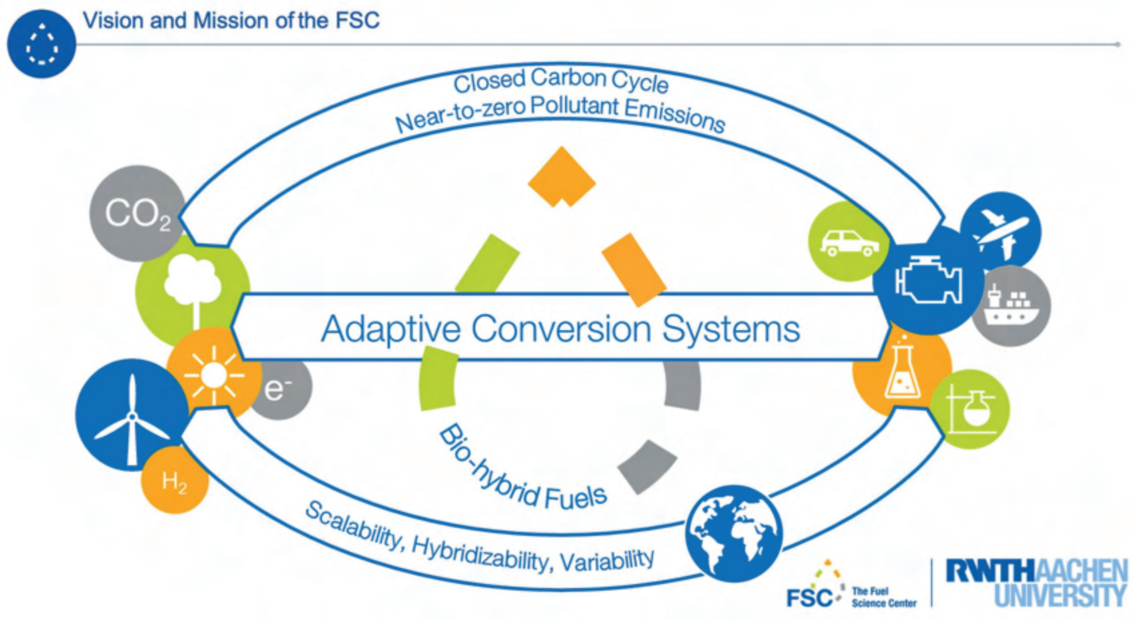
To enable highly efficient and clean combustion for sustainable mobility, fundamental knowledge and scientific methods are generated as the basis for the development of adaptive production and propulsion systems based on renewable energy and alternative carbon sources under dynamic boundary conditions. In its convergent approach, the FSC creates the scientific basis for an integrated design of production processes and engine technology. Adaptive technological solutions will be sought to respond to the increasing diversification of energy and raw material supplies and changes in the mobility sector.

Research of the FSC towards future fuels and their production creates the basis for the integrated conversion of renewable electricity with biomass-based raw materials and CO_2 into liquid energy sources with high energy density ("bio-hybrid fuels"). The (electro-)catalytic production of energy carriers and chemicals is considered to design flexible and economic value chains. Emission-minimized, molecularly controlled combustion systems are investigated for the reconversion of chemically stored energy. Methodical concepts are developed in order to move from an analytical description to reliable forecasts for the evaluation of environmental impact, economic efficiency, and social relevance.

Scientific Structure and Role of the CEC

The research activities of the FSC span two dimensions: Three Competence Areas (CAs) and the Translational Research Domain. The Competence Areas represent the required disciplinary methodologies and theoretical principles and are structured according to the time and length scales of the underlying phenomena (molecular, device, system). The Translational Research Domain addresses application fields according to potential product and market segments by dynamically forming Translational Research Teams (TRTs).

With Prof. Leitner acting as Co-Spokesperson, the strategic alliance between the University and non-University academic landscape is reflected scientifically as well as structurally. Further, the MPG Research Group "Magnetic Resonance of Complex Materials and Catalysts" of Prof. Thomas Wiegand was established with a tenure track option for a chaired W3 professorship at RWTH Aachen University. The MPI CEC currently accommodates two FSC projects located in the department "Heterogeneous Reactions" as well as in the Max Planck Research Group of Christophe Werlé.



Project "Heterostructured Ionic Liquid Metal Systems as Designer Catalysts (HILM-Cat)"

The HILM-Cat Project is located in the department "Heterogeneous Reactions" (responsible co-worker: Dr. Marc Tesch - Electrochemistry Group) and aims for the in-depth analysis of catalytic systems composed of metal nanoparticles (NPs) immobilized on molecularly modified surfaces, and in particular, supported ionic liquid phases (SILPs).[1] These NPs@SILP systems are highly flexible, and the appropriate choice of the support material, ionic-liquid-like structure, and NPs composition allow the development of multifunctional catalytic systems with tailor-made reactivity. In particular, the Multifunctional Catalytic Systems team (led by Dr. Alexis Bordet in the department of Prof. Leitner) developed this approach to prepare SiO_2-based powder catalysts capable of activating and transferring molecular hydrogen (H_2), e.g., to perform selective hydrogenation and hydrodeoxygenation reactions.[1,2,3] Within the HILM-Cat project, this concept is extended to well-defined flat silicon surfaces to prepare model materials allowing for a more advanced structural and electronic analysis by laboratory-based techniques at CEC and by synchrotron-based *in situ* and *operando* spectroscopy at CatLab (BESSY II, Berlin). Further, developing methods to modify (structured) wafers and thin film supports with ionic-liquid-like structures and NPs may enable an extension of the approach towards liquid phase reactions on electrified interfaces.

The long-term goal of the HILM-Cat project is to obtain a comprehensive and fundamental insight into the dynamic interaction between the metal catalysts, the self-organized ligand structure, and the support material under operation conditions. Thereby enabling a future knowledge-based design of such flexible or even adaptive catalytic systems and their application in novel approaches.

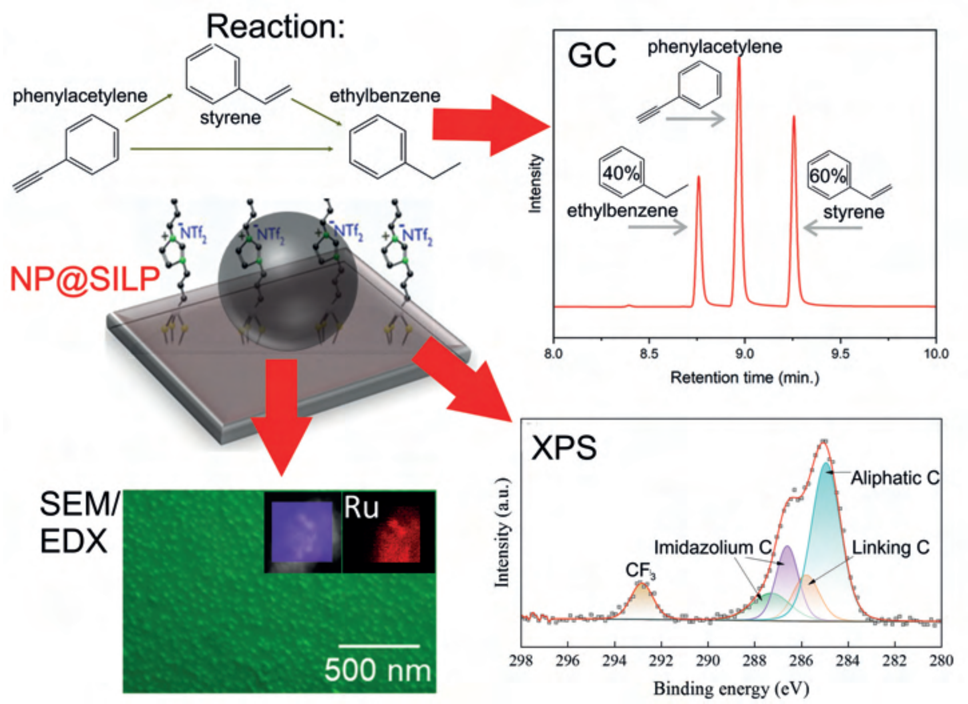


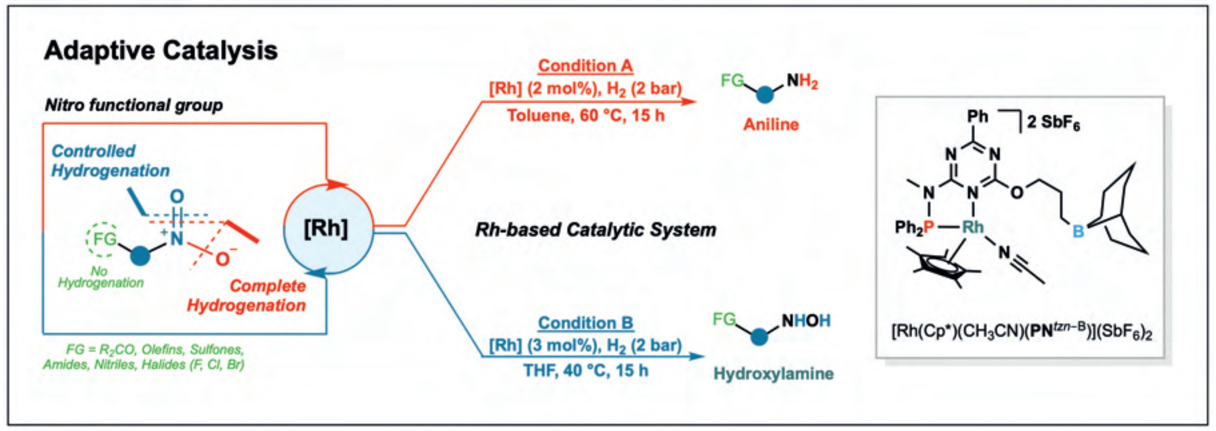
Figure 2. Scheme of the Si surface modified with the NP@SILP catalyst and the analysis of its particular structure via scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM/EDX), its activity by gas chromatography (GC) and its electronic structure by X-ray photoelectron spectroscopy (XPS).

Project "Development of Adaptive Catalysts: On the Road to a Controlled Photocatalytic Formation of Carboxylic Acid from Formate Salts."

This project aims to develop dynamic and adaptive catalytic systems incorporating cooperative designs to address and selectively control the bond activation steps. The molecular basis is developed for photocatalytic processes that convert renewable energy directly into chemical structures. In the long term, systems should respond *flexibly* to variations in single-electron supply and provide the potential to be implemented in scalable synthetic processes. Specifically, our approach involves using a ligand environment presenting an attached borane arm to challenge and tame the reactivity of the metal center. In addition, we decided to use rhodium because of its high propensity to drive hydrogenation reactions. To probe the reactivity of the catalyst and its propensity toward adaptivity, the developed system was probed in the hydrogenation of nitroarenes.

We are interested in this class of substrates because several product platforms may be obtainable on the way to fully reduced aniline. This study examined whether an adaptive catalyst could control this hydrogenation network and selectively stop at desired reduction levels. As a result, our system proved capable of supplying anilines (complete hydrogenation) and hydroxylamines (controlled hydrogenation) in excellent yields under mild conditions while preserving the integrity of other potentially vulnerable functional groups (Scheme 1). [4]

In future efforts, our group is interested in advancing alkene functionalization strategies designed to take advantage of attractive chemical building materials rather than high-energy reactants. Similar efforts to those for nitroarene reduction will aim to transfer the concept of molecular controlled catalysis to the photocatalytic functionalization of alkenes.



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e-conversion

The lifetime of proton-exchange-membrane fuel cells (PEMFCs) is one of the most critical factors for their successful implementation in transportation applications. During start-up and shut-down (SUSD) events, a hydrogen/air front moves through the anode leading to the oxygen reduction reaction (ORR), which, causes the degradation of the cathode catalyst by carbon oxidation.[1] While many solutions have been proposed for this in the literature, the development of a new catalysts with a suppressed ORR activity and a high hydrogen oxidation reaction (HOR) activity seems to be the most promising way to prevent SUSD-induced performance losses.[2] In a recent publication, the novel catalyst system Pt/TiO_x/C was proposed, which is characterized by a strong metal support interaction (SMSI) between Pt and reduced TiO_2 (TiO_x), resulting in a superior HOR-selectivity of Pt/TiO_x, keeping the high conductivity and low packing density of a carbon support.[3] Using rotating-disk-electrode (RDE) experiments and HR-TEM imaging, the lower ORR activities due to SMSI of the TiO_x layer encapsulating the Pt nanoparticles after reductive heat treatment were confirmed. This TiO_x layer is supposed to be permeable for protons and hydrogen, making hydrogen evolution reactions (HER) and HOR possible, but hindering ORR by impeding the permeation of larger oxygen-containing species.

In the framework of e-conversion project we tested an existing operando electrochemical cell available at BESSY II,[4] adjusted electrodes and manufactured a modified cell adapter for a standard PEMFC membrane electrode assembly (MEA), without any liquid electrolyte. We prepared the MEAs by hot pressing on a Nafion 212 membrane a coating of the synthesized Pt/TiO_x/C on the working electrode (WE) side, while on the counter electrode (CE) side we hot pressed a standard Pt/C coating. This CE, with a constant flow of humidified 3% H_2 in Ar, provides a constant potential and can be used as reference electrode (so-called dynamic hydrogen electrode). Commercial Pt/C was employed as benchmark catalyst also at WE, to confirm that the operando electrochemical cell provides expected results and compared them with those obtained from Pt/TiO_x/C. We confirmed the expected electrochemical results for both commercial Pt/C and Pt/TiO_x/C.

Using this operando electrochemical cell, we performed the intended investigation of strong metal support interaction (SMSI) on the novel Pt/TiO_x/C catalyst system by operando XPS at the ISISS beamline, in comparison to commercial Pt/C. As the interface between vacuum and WE, at the cell aperture where the beam illuminates, we used bilayer graphene, as reported in literature for the same cell[4, 5]. Collecting operando data, from the minor but evident energy shift on the XPS peaks upon applying potential, it was already tangible that the bilayer graphene allowed the X-ray illuminated portion of electrode to be in electric contact with the remaining part. This permitted to collect XPS operando data, in true correlation with the electrochemical behavior of both commercial Pt/C and synthesized Pt/TiO_x/C. Further data analysis will provide more structural insights on the difference between surface chemistries of the two system, allowing a further understanding of the SMSI in Pt/TiO_x/C.

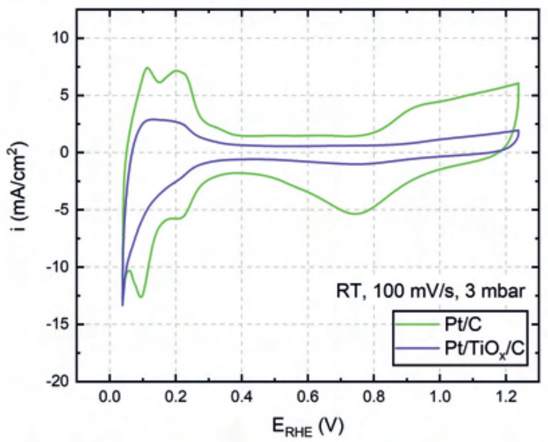

Figure 1. CVs measured in the two-electrode gas flow test cell at TUM utilizing a MEA with a Nafion 212 membrane at room temperature and a scan rate of 100 mV/s. The loadings of the studied catalysts Pt/C and Pt/TiOx/C are both ≈ 0.050 mgcatalyst/cm²MEA.

The test cell simulates conditions at BESSY II, whereas humidified 5% H2 in Ar is passing through the counter/reference electrode (Pt/C) and a vacuum of 3 mbar is applied to the working electrode side. The Pt/TiOx/C system clearly shows strongly diminished Pt-oxide features at potentials between 0.6 – 1.2 VRHE compared to the standard Pt/C catalyst, hinting a low ORR activity and therefore a higher selectivity towards the HOR/HER.

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CRC/TRR 247: A multi-modal perspective on the functional origin of cobalt oxide catalysts

In many catalytic processes, heterogeneous catalysis or electrocatalysis, there is the trend to replace expensive and rare noble metal catalysts by cheaper alternatives, often based on transition metal compounds such as cobalt or iron oxides.[1–2] These oxides introduce additional degrees of freedom into the task of understanding catalysis due to the flexibility in their redox states and phase diagrams. Here, we investigate the surface and bulk structures of cobalt-based oxides after various pretreatments and in selective oxidation reactions of CO and 2-propanol by several advanced X-ray spectroscopic and electron microscopic techniques.

By *quasi in situ* transmission electron microscopy (TEM), utilizing identical location imaging and spectroscopy (ILIAS), we characterize the electronic, crystallographic and morphological surface structures of the spinel oxide Co_3O_4 before and after different low-temperature pre-treatments in presence and absence of oxygen. The nanostructured features resulting from these procedures are correlated with catalytic CO oxidation results obtained after identical treatments: pre-reducing in N_2 leads to stepped surfaces that are inactive (Figure 1A), while pre-oxidation creates terraces and causes pronounced activity in CO oxidation, as evident from the data in Figure 1B.

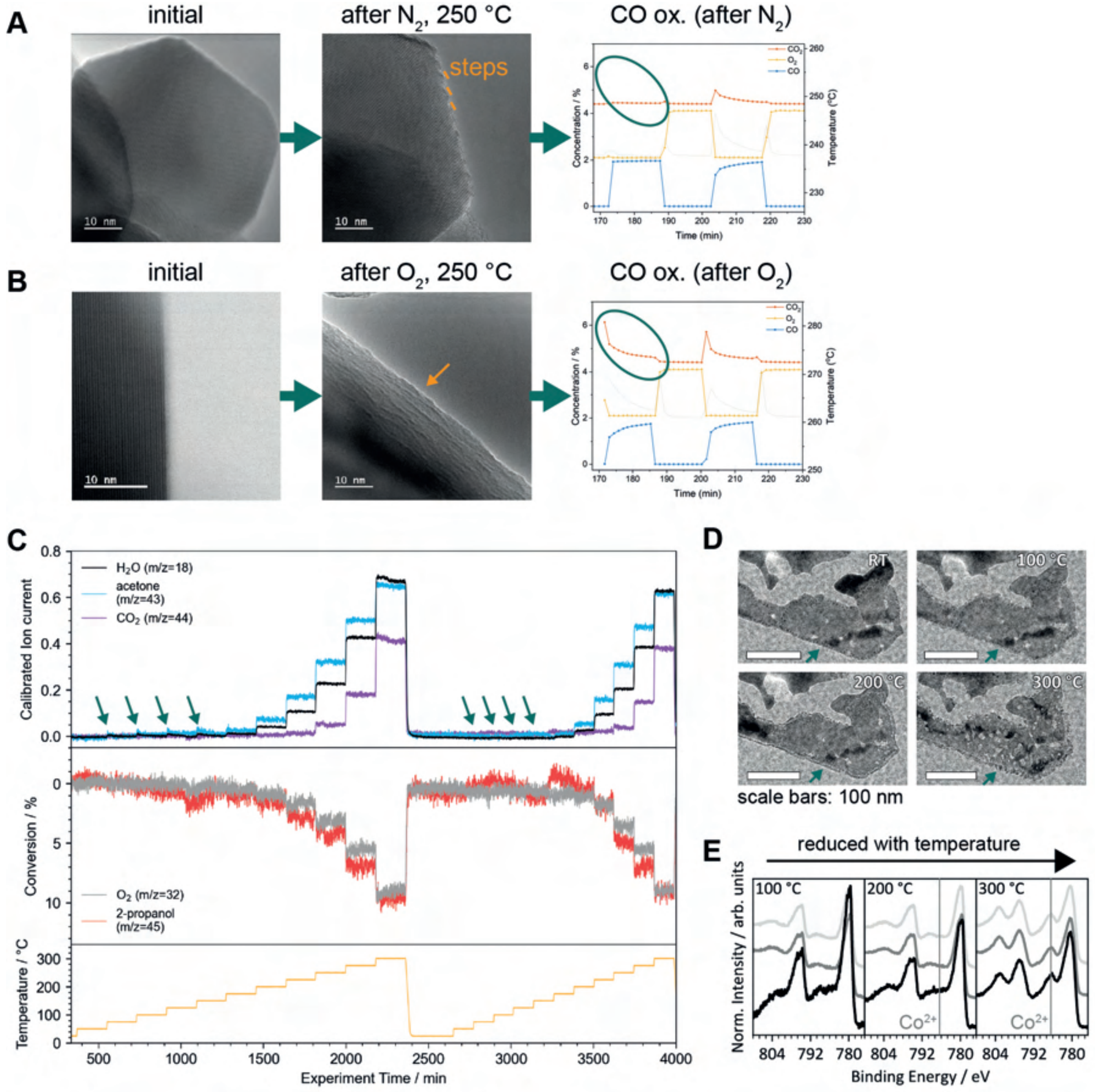

Figure 1. Identical location imaging data for Co_3O_4 particles after treatment in (A) N_2 and (B) O_2 at 250 °C, including the CO oxidation activity data after these procedures. (C) Reactivity data for the 2-propanol oxidation on Co_3O_4. The arrows highlight the low temperature channel (activity spikes) that is only present during the first temperature ramp. (D) OTEM images of a Co_3O_4 particle showing exsolution, overlayer formation and roughening, with (E) the corresponding Co2p XP spectra.

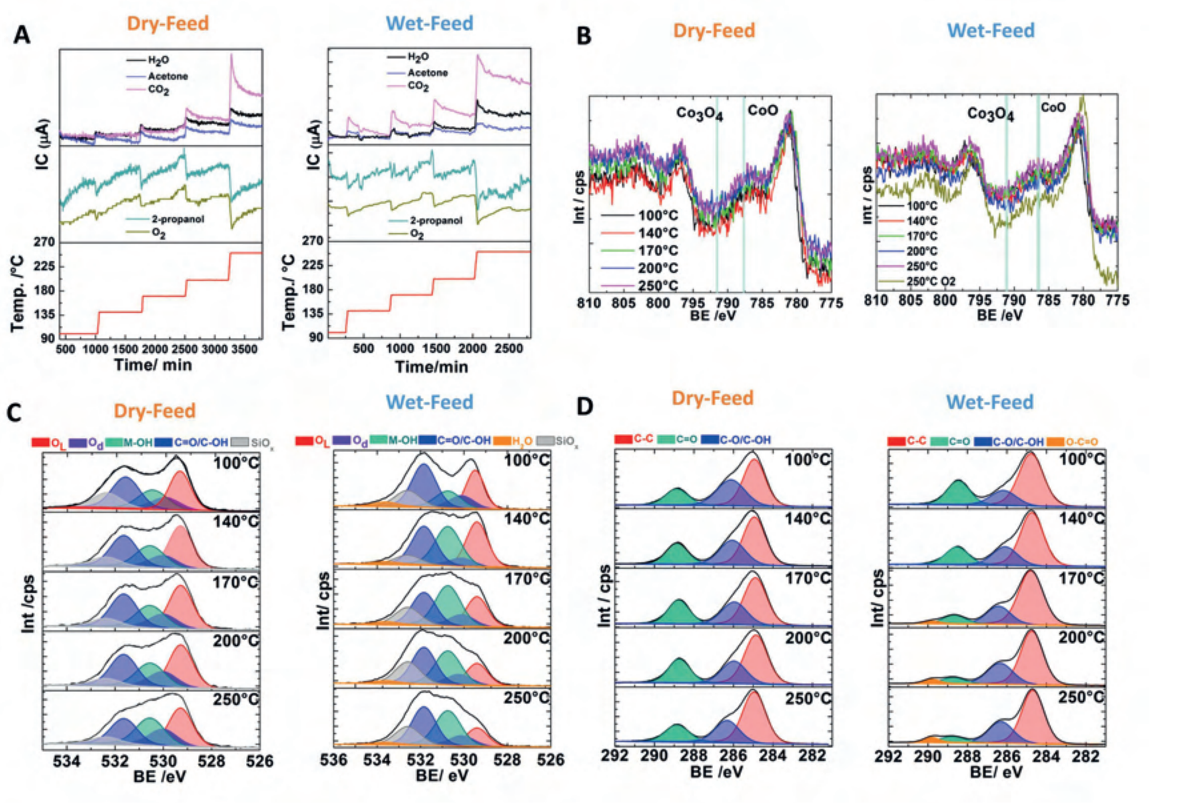

Figure 2. (A) Reactivity data for the 2-propanol oxidation on $LaFe_xCo_{1-x}O_{3-\Delta}$. (B) Co 2p (C) O 1s and (D) C 1s XP spectra under reaction conditions.

In order to further understand the selective oxidation of 2-propanol to acetone over unsupported spinel cobalt oxide (Co_3O_4) in the gas phase, a correlative combination of near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) and *operando* TEM (OTEM) were used to elucidate the electronic and crystallographic/morphologic evolution. In fact, the reaction is run at partial pressures of around 2 hPa in catalytic test reactors, which is virtually identical to the conditions used in NAP-XPS (0.25 hPa) and OTEM (10 hPa), thus effectively eliminating the pressure gap.

Characteristic for this reaction is the presence of two activity maxima: one at around 150 °C ('low-temperature'), the other at 300 °C ('high temperature'). Notably, the former reactivity channel is rapidly deactivated and is subsequently lost completely in further runs, as seen in Figure 1C (measured in the NAP-XPS systems at BESSY, refer to the arrows). However, this channel can be re covered by reoxidation.[3] Since this low-temperature regime features a higher selectivity for acetone, it is desirable to stabilize this channel, for which, however, it is a prerequisite to elucidate the mechanisms behind the deactivation.

Already at room temperature, the Co_3O_4 particles undergo significant changes in the reaction feed (2-propanol/O_2 1:1): the cobalt species on the surface are slightly reduced, as evidenced by Co 2p spectra, and small nanoparticles are formed inside the crystallites, just beneath the [111] facets. As the temperature is raised, these particles first segregate to the surface in order to form an overlayer at intermediate temperatures before they again roughen up around 300 °C (see Figure 1D). At the same time, the degree of reduction on the surface is continuously increasing, as determined by Co 2p spectra (Figure 1E), suggesting that the segregated particles are reduced CoO_x species. However, while electron diffraction reveals the formation of a small fraction of rock-salt CoO above 225 °C, the photoelectron spectra never fully resemble the signature of pure CoO, corroborating that this is a localized effect occurring only on some surfaces. When reoxidizing the system, CoO reflexes vanish above 400 °C and also the segregated particles are not observed on the surfaces anymore, indicating that these surface roughening and partial reduction processes might be related to the loss of low temperature activity.

In addition to Co_3O_4, this selective oxidation reaction was also investigated on perovskite oxides by NAP-XPS, with a focus on lanthanum iron cobalt oxide ($LaFe_xCo_{1-x}O_{3-\Delta}$). Hence, dry and wet oxidations feed scenarios were proposed to study the evolving species on the perovskite surface. In both reaction feeds, increases in temperature (in the range of 100°C to 250°C) are accompanied by acetone and CO_2 production (Figure 2A). However, the formation of reaction products is more substantial for wet than dry feed, likely by a water meditation of the transition states.

Tracking of chemical species involved on the surface during 2-propanol oxidation showed that a Co 2p satellite signal is arising at BE=783eV in both feeds, implying a total reduction to Co^{2+} (Figure 2B). This is in line with the behavior abovementioned for Co_3O_4. In wet feed, the different Co 2p peak shape compared to dry feed suggests an additional formation of Co hydroxide species. Simultaneously, the O 1s region exhibits a variation over the dynamics in the oxygen species at the surface (Figure 2C). The main difference between the feeds corresponds to an increase of the components related to hydroxide and carbonates/carbonylic oxygen species in wet feed and the simultaneous diminish of oxygen lattice features. Likewise, C 1s displays an intermediate species in both feeds (Figure 2D). Therefore, contributions of C=O (BE=288.7eV), C-OH (285.9eV), and C-C (284.8eV) were observed. The C=O species can be explained by intermediates of reactions or even adsorbed acetone, as shown for dry feed. Notably, under wet conditions, an additional signal at BE of 289.8eV appeared, presumably interpreted as carbonates.[4]

Compared with Co, a redox absence activity was observed for Fe and La, entailing the Co as an active redox site due to incorporation in the perovskite. Under the scope of this study, the enhanced interpretation of the chemical species involved during the 2-propanol oxidation was achieved. Part thereof is the critical role that plays water when the chemical potentials are changed during the feeds and its effect as a forcing character during the wet conditions. These effects induced modifications of the surface either by forming hydroxyl species attached or gas species production (acetone, CO_2) at the interface.

Furthermore, in order to lay the foundation for theory-assisted interpretation of *in situ* and *operando* absorption spectra, the oxygen K-edge spectra of Co_3O_4 were investigated in collaboration with theoreticians from the University of Duisburg-Essen.[5] Density functional theory (DFT) was used to describe these spectra, which are estimated to be very sensitive for oxidation reactions in particular.

Complementary information about the electronic structure of these materials can be obtained from hard X-ray (E>5 keV) experiments. A series of cobalt-boron oxides obtained by simple precipitation and thermal treatment, was studied using a combination of Co L-edge and Co K-edge XAS with Kβ XES (Figure 3). The boron-loaded samples (Co-B oxides) exhibited larger water oxidation current densities at moderately low overpotentials in KOH than the pristine Co_3O_4. The XAS data indicate that a rather amorphous Co^{2+} with an O_h geometry, as starting material, converts into a spinel-like structure when the calcination temperature is increased from 300°C to 550°C. Nevertheless, the Co-B oxides showed an average lower oxidation state than what it would be expected for a spinel. The resulting L-edges and XES could be well reproduced as a combination of 60% pure Co_3O_4 and 40 % of the starting material (for the sample calcined at 300°C), while for the sample calcined at 500°C the amount of Co_3O_4 was 80%, in good agreement with XPS measurements performed on the same samples. The same simple model used to fit the EXAFS data of the Co_3O_4 reference sample, could be used to fit the 550°C sample, but with worse fitting parameters, and even worse for the 300°C sample, which indicates more disorder in the sample. Interestingly, these samples showed a more intense pre-edge in the Co K-edge XAS spectra, which is indicative of a big deviation from a centrosymmetric geometry around the Co center.The increase pre-edge intensity could be caused by oxygen deficient Co centers, something that quite often plays an essential role in the electrocatalytic performance of the sample. Indeed, the 300°C was the most active of the measured samples. TEM and electrochemical Raman spectroscopy supported the relevance of these O-deficient sites and its involvement in catalysis.[6]

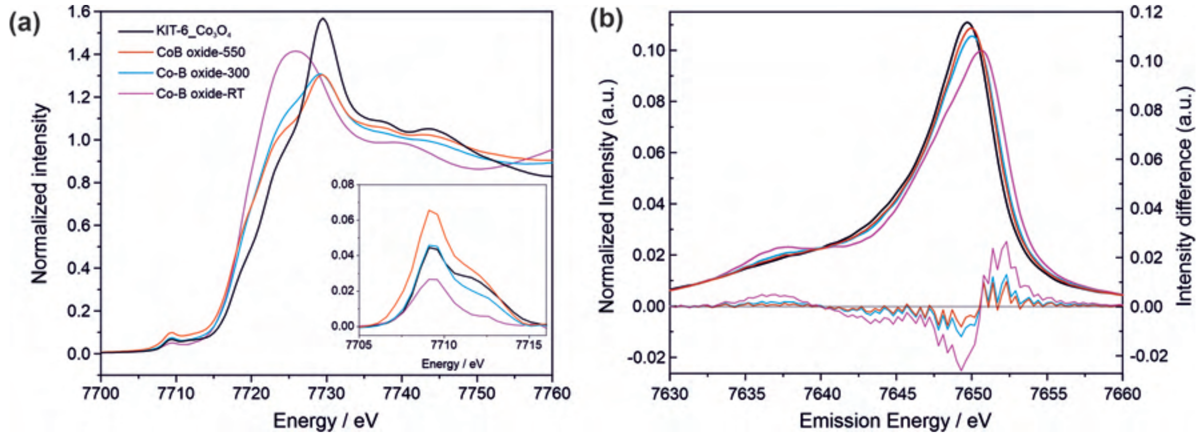

Figure 3. Co K-edge (a) XAS and K XES (b) spectra of Co-B oxide-RT, Co B oxide-300 and Co B oxide-550 and KIT-6_Co_3O_4. The inset in panel (a) shows the baseline corrected pre-edge region in detail including Co foil as reference. The subtracted spectra XES (Co-B oxide minus pristine Co_3O_4) is shown at the bottom of the spectra to highlight the differences.

In another study performed in close-collaboration with the group of Priv.-Doz. Harun Tüysüz, at the Max Planck Institut für Kohlenforschung, the spectroscopy of a series of cobalt spinels was investigated in order to understand how changes in the morphology of the material (nanocasted onto different templates) or changes in the ratio of Co and Fe in the composition, affect the water oxidation electrocatalytic activity. Using the site-selectivity of XES, it was possible to interrogate in detail a series of Co/Fe spinels. Spinels have the general formula AB$_2$O$_4$, where A is a metal in oxidation state +2 in a tetrahedral (T$_d$) geometry and B is a +3 metal in an octahedral (O$_h$) geometry. Co and Fe Kβ-detected high energy resolution fluorescence-detected X-ray absorption spectroscopy (HERFD-XAS) showed how increasing the Fe loading alters the electronic structure and geometry around the two different metals on spinel nanowires.[7] The pre-edge analysis of the Co and Fe HERFD showed increased pre-edge intensity for the Co/Fe 32 and Co/Fe 3 samples, compared to the pristine Co$_3$O$_4$. This indicates that at low Fe loading, the Fe preferentially occupies the spinel O$_h$ sites, resulting in an increase of ratio of Co at the T$_d$ sites and also the observed increase spin state from the Kβ mainlines.

EXAFS can also be used to characterize the geometric environment of the metal centers. This technique has been used also to provide structural information of a mixed silver-cobalt oxide used for electrochemical water oxidation catalysis.[8] Fe and Co K-edge EXAFS was also used in a series of Fe-loaded spinels and inverse spinels to analyze changes around the metal centers after catalysis.[9]

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CUBE – ERC Synergy Grant: Unravelling the secrets of Cu-based catalyst for C-H activation

In May of 2020, the ERC funded Synergy grant CUBE had its initial kick-off meeting. This six-year project is lead by S. DeBeer (CEC), together with S. Bordiga (Turin), U. Olsbye (Oslo) and V. Eijsink (NMBU) (Figure 1). The aim of this synergy proposal is obtain fundamental insight into copper-based C-H bond activation at the biological, homogeneous and heterogeneous limits. Specifically, the research in CUBE takes inspiration from copper-based enzymes that are able to activate strong C-H bonds (e.g. lytic polysaccharide monooxygenase (LPMO) and particulate methane monooxygenases (pMMO) enzymes) and copper zeolites, which can oxidize methane. Our goal is to identify the key underlying design principles for optimizing catalytic performance and to then engineer these motifs into optimized metal organic frameworks (MOFs). The CEC team leads the spectroscopic and computational investigations of the enzymatic systems (provided by the NMBU team), and also engages collaboratively in studies of the heterogenous systems (with the Turin team) and MOFs (with the Oslo team).

During this funding period, we have begun to perform experiments aimed at identifying the active intermediates in molecular, enzymatic and homogeneous catalysts. For the enzyme catalysts, we have focused on stop flow spectroscopic studies (utilizing both fluorescence and UV-Vis) to understand the intermediates that are formed in the presence of O$_2$ or H$_2$O$_2$. This work is supported by a collection of first and second sphere LPMO mutants that have been generated and characterized in the first two years. Some of these mutants have spectacular effects on copper reactivity, providing very useful tools in the hunt for the "hot" (i.e., catalytically relevant) intermediates. Several such mutants are currently being subjected to a range of spectroscopic studies, with an emphasis on EPR and XAS as complementary probes. In addition, we are performing parallel computational studies to calculate spectroscopic parameters and then using this as an informed basis to calculate mechanism. A publication describing the first LPMO work from CUBE is currently in preparation.

Moving forward, a particular challenge with LPMOs is the fact that natively the enzymes act primarily on insoluble substrates. This requires the development of setups in which solution/solid phase processes can be followed, and in parallel spectroscopic studies on LPMOs that are able to act on soluble substrates. These studies are planned, but are still in an early development phase. Importantly, the NMBU team has made major progress has been made in characterizing novel LPMOs that act on soluble substrates, including the generation of mutants that show different copper reactivities.

In addition, studies of pMMO, MOFs and molecular model complexes have already yielded results, with the CUBE team publishing 8 papers so far and many more in progress. More details on the CUBE project can be found at

https://www.cube-synergy.eu.

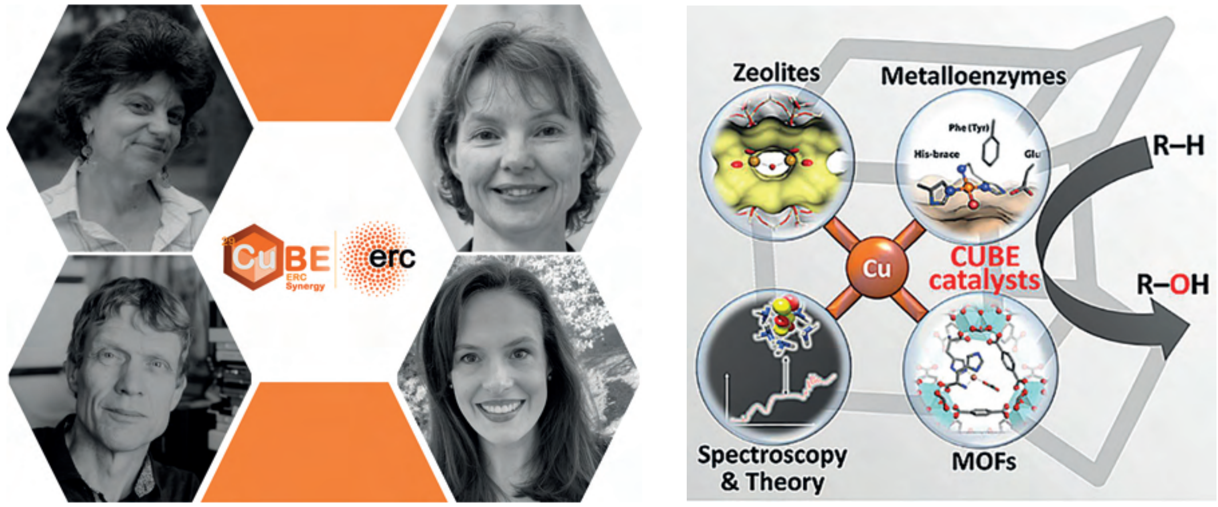

Figure 1. The PIs for the ERC funded Synergy project "CUBE". Bordiga, Olsbye, Eijsink and DeBeer (left) An overview of the approach that is being utilized to understand Cu-based C-H activation (right).

International Max Planck Research School on Reactive Structure Analysis for Chemical Reactions

The International Max Planck Research School on Reactive Structure Analysis for Chemical Reactions (IMPRS-RECHARGE) was established in 2015, and is a cooperative effort of the institutions and partners depicted in Table 1. The goal of the IMPRS is to establish the often desired but very rarely achieved unification of catalytic concepts in the education of specialists being trained towards a rational design of catalytic systems.

To this end the historic divides between molecular catalysis with dynamical structures and heterogeneous catalysts with assumed static structures must be overcome. The first running period of the IMPRS lasted from 2015 until 2020. In 2019 the first running period was evaluated successfully. The second running period started on January 1, 2021 and will end on December 31, 2026.

MPI für chemische Energiekonversion	MPI für Kohlenforschung	Ruhr Universität Bochum	Universität Duisburg-Essen	Universität Bonn
Inorganic Spectroscopy	**Homogeneous Catalysis**	**Chair of Physical Chemistry II**	**Faculty of Chemistry**	**Mulliken Center for Theoretical Chemistry**
Serena DeBeer	Ben List	Martina Havenith-Newen	Malte Behrens4) Stephan Schulz	Thomas Bredow Stefan Grimme Barbara Kirchner
Molecular Catalyis	**Organometallic Chemistry**	**Chair of Organic Chemistry II**	**Faculty of Engineering**	
Walter Leitner	Alois Fürstner	Wolfram Sander	Christoph Schulz Doris Segets2)	
Heterogeneous Reactions	**Molecular Theory and Spectroscopy**	**Chair of Industrial Chemistry**		
Robert Schlögl	Frank Neese1)	Martin Muhler Wolfgang Kleist5)		
Synergistic Organometallic Catalysis	**Organic Synthesis**	**Chair of Analytical Chemistry**		
Christophe Werlé3)	Tobias Ritter	Wolfgang Schuhmann		
	Heterogeneous Catalysis			
	Ferdi Schüth			

1) F. Neese is the spokesperson of the school. 2) D. Segets became IMPRS-partner in 2020. 3) C. Werlé, Max Planck Research Group Leader, became IMPRS-partner in 2021. 4) M. Behrens accepted an appointment as professor at University Kiel, Institute for Inorganic Chemistry since summer term 2020. He stayed for a transitional phase until summer term 2022 at UDE. 5) W. Kleist accepted a Chair of Technical Chemistry, Technical University of Kaiserslautern. The entire Kleist-group moved to Kaiserslautern and started working on Jan. 1, 2021.

Table 1. Institutions, departments, faculties and professors participating in the IMPRS-RECHARGE.

Doctoral Program and Teaching

The IMPRS-RECHARGE curriculum (Table 2) consists of obligatory as well as voluntary offers. With these offers the scientific background of the students is deepened and extended and the soft skills are enhanced. The block courses were carried out as a lecture series (90 minutes each lecture):

Advanced Courses on Catalytic Reactions (advanced course 2020)

- Bridging Heterogeneous Catalysis on Metals and Homogenous Catalysis in Molecules – Phenomena, Methodology and Theory *(Prof. Auer, MPI KOFO)*
- Electrocatalysis for Electrolysers and Fuel Cells *(Dr. Colic, MPI CEC)*
- Material Synthesis – Chemical Vapor Deposition *(Prof. S. Schulz, UDE)*
- Methane Chemistry *(Prof. Schlögl, MPI CEC)*
- Photocatalytic Activation of CO_2 *(Dr. Ristig, MPI CEC)*
- Synergistic Catalysis – Towards a Molecularly Controlled Catalysis *(Dr. Werlé, MPI CEC)*
- Synthesis Gas Chemistry *(Dr. Ruland, MPI CEC)*
- Utilization of CO_2 *(Prof. Behrens, UDE)*

Introduction to RECHARGE Theory and Experiment (basic course 2021)

- Chemical Reaction Engineering *(Prof. Muhler, RUB)*
- Electrochemistry *(Dr. Rüdiger, MPI CEC)*
- Introductory Band Structure *(Prof. Auer, MPI KOFO)*
- Ligand Field Theory *(Prof. Atansov, MPI KOFO)*
- Metal Organic Reaction Mechanisms *(Prof. S. Schulz, UDE)*
- Modern Simulation Techniques – Part 1 *(Prof. Kirchner, MCTC)*

	1st Year	2nd Year	3rdYear	
Block Courses	Course Area 1 (Basic)	Course Area 2 (Basic - Physical Methods)	Course Area 3 (Advanced - Catalytic Reactions)	**Final Oral Presentation**
	Summer School			
Organized by Student Teams	Student Conference			
	Student Retreat			
Supervision	TAC I	TAC II	TAC III	
	Discussion Meetings			
Soft Skills	Course I	Course II	Course III	

Table 2. Curriculum Structure.

- Modern Simulation Techniques – Part 2 *(Prof. Bredow, MCTC)*
- Nanoparticles *(Prof. Wiggers, UDE)*
- Organic Reaction Mechanisms *(Prof. Sander, RUB)*
- Organometallic Electrocatalysis *(Dr. Werlé, MPI CEC)*
- Solid State Chemistry *(Prof. Behrens, UDE)*
- Spin Hamiltonians *(Dr. Bill, MPI CEC)*
- Quantum Chemistry I *(Prof. Auer, MPI KOFO)*

Physical Methods in Homogeneous and Heterogeneous Catalysis (basic course, physical methods 2022)

- Absorption Spectroscopy *(Prof. Neese, MPI KOFO)*
- Characterization of Heterogeneous Single-site Catalysts *(Prof. Kleist, RUB)*
- Diffraction / Sorption / SAXS *(Prof. Schmidt, MPI KOFO)*
- Electrochemistry *(Prof. Schuhmann, RUB)*
- Electrocatalytical CO_2 Reduction *(Dr. Römelt, MPI CEC)*
- Electron Microscopy *(Dr. Hetaba, MPI CEC)*
- EPR Spectroscopy *(Dr. Schnegg, MPI CEC)*
- IR Spectroscopy *(Dr. Trunschke, FHI)*
- Magnetism *(Dr. SantaLucia, MPI KOFO)*
- Mössbauer Spectroscopy *(Dr. Bill, MPI CEC)*
- NMR Spectroscopy *(Dr. Farés, MPI KOFO)*
- Processing of Functional Electrode Layers *(Prof. Segets, UDE)*
- Resonance (Raman) Spectroscopy *(PD Dr. van Gastel, MPI KOFO)*
- Single-crystal X-ray Diffraction – Identification and Development of Catalysts at the Molecular Level *(Dr. Werlé, MPI CEC)*
- XAS/XES Spectroscopy *(Prof. DeBeer, MPIC CEC)*
- XPS Spectroscopy *(Dr. Knop-Gericke, MPI CEC)*

Soft Skills Courses

In addition to the scientific courses, the following soft skills courses were organized:

- Project Management, Dr. Simon Golin, GOLIN Wissenschaftsmanagement, July 27, 2020 (one day)
- Scientific Writing, Mark Buchanan and Justin Mullins, WriteAboutScience, November 8-11, 2021 (9:00 to 13:00 each day)
- Scientific Presentation, Dr. Bartlett Warren-Kretzschmar, GOLIN Wissenschaftsmanagement, November 11, 2022 (one day)

Scientific Output

Publications

The scientific performance of the IMPRS-students can be assessed by the number of publications and first author paper (Figure 1). The references are recorded in the bibliography of the institute.

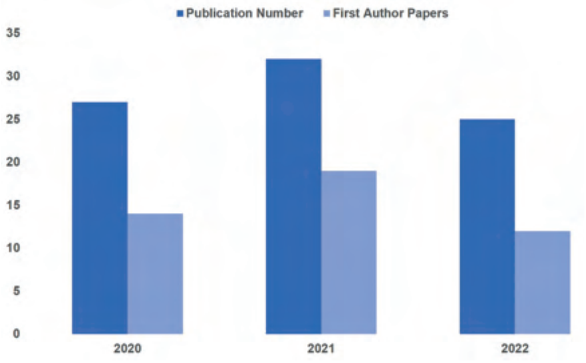

Figure 1. Scientific progress – measured by number of publications and first-author papers.

Awards, Fellowships and Prizes

- Hanna Cramer | ZAAC Poster Award | 54th German Catalysis Meeting, Online (2021).
- Julia Krüger | Poster Prize | GDCh-Wissenschaftsforum Chemie, Online (2021).
- Stanislav Musikhin | Best Poster Award | 11th Nanoontario Conference, Online (2021).
- Hanna Cramer | EurJOC Poster Award | 4th International Green Catalysis Symposium, Rennes, France (2022).
- Jil-Lorean Gieser | Poster Prize | 30th ATC Industrial Inorganic Chemistry – Materials and Processes, Frankfurt (2022).
- Jil-Lorean Gieser | Poster Prize | 55. Jahrestreffen Deutscher Katalytiker, Weimar (2022).
- Stanislav Musikhin was awarded with a Waterloo Institute for Nanotechnology Fellowship (2020 & 2021).
- Wenbo Dong was awarded with a 3-year China Scholarship Council (2020).
- Stanislav Musikhin received a student paper award by the University of Waterloo (2020 & 2021).
- Christine Schulz | Journal of Inorganic Biochemistry Elsevier Best Oral Prize | FrenchBic, Online (2020).
- Hanna Cramer | Research Stay at the LCMD laboratory of Prof. Clémence Corminboeuf, EPFL, Lausanne, Switzerland (June 2021 - August 2021).
- Rebeca Gómez Castillo | Ernst Haage Doctoral Award | Mülheim/Ruhr (2021).

Doctoral Theses

Successful IMPRS-RECHARGE students, who have completed the program requirements and obtained a PhD/doctoral degree by one of the participating universities receive a certificate from the IMPRS-RECHARGE additionally. The theses from 2020 until 2022 are specified in a chronical sequence:

- Alfarano, Serena: THz spectroscopy of aqueous solutions: conditions beyond the ambient, Ruhr-Universität Bochum, 2020.
- Joshi, Hrishikesh: Rattle-tape materials with spatially distinct functionalities for the cascaded valorization of glucose, Ruhr-Universität Bochum, 2020.
- Yu, Mingquan: Nanostructured transition metal oxides for electrochemical oxygen evolution reaction, Ruhr-Universität Bochum, 2020.
- Narangoda, Praveen: Influence of electrode structure and measurement parameters on the electrocatalytic alkaline oxygen evolution, Ruhr-Universität Bochum, 2020.
- Gehrke, Sascha: The influence of solvent reorganization on organocatalytic reactions, Rheinische Friedrich-Wilhelms-Universität Bonn, 2021.
- Gómez Castillo, Rebeca: Advanced X-ray spectroscopic techniques and new applications to metalloenzymes and biomimetic complexes, Ruhr-Universität Bochum, 2021.
- Ulpe, Anna: Quantenchemische Untersuchung der elektronischen Eigenschaften von Ferriten, Rheinische Friedrich-Wilhelms-Universität Bonn, 2021.
- Schulz, Christine: Multiscale computational modelling of metalloenzymes, Rheinische Friedrich-Wilhelms-Universität Bonn, 2021.
- Angel, Steven: Spray-flame synthesis of La (Fe, Co, Mn)O_3 perovskite nanoparticles for CO oxidation, Universität Duisburg-Essen, 2021.
- Salloum, Sarah: Synthesis and evaluation of thermoelectric group 15 chalcogenide nanomaterials, Universität Duisburg-Essen, 2022.
- Krüger, Julia: Ga-substituted pnictinidenes and gallapnictenes: suitable synthons for various open-shell and closed-shell species, Universität Duisburg-Essen, 2022.
- Cramer, Hanna: Rational design of transition metal complexes for the catalytic reduction of carbon dioxide: a synthetic, spectroscopic, and computational approach, Rheinisch-Westfälische Technische Hochschule Aachen, 2022.
- Spiller, Nico: Electronic structure studies of iron-sulfur clusters: from model compounds to the active site of nitrogenase, Rheinische Friedrich-Wilhelms-Universität Bonn, 2022.
- Dieckhöfer, Stefan: Insights into the confined pore environment of three-dimensional electrodes – operando SECM studies on CO_2-reduction gas diffusion electrodes, Ruhr-Universität Bochum, 2022.
- Musikhin, Stanislav: Microwave plasma synthesis of graphene and its laser-optical in situ characterization, Cotutelle de Thèse, Universität Duisburg-Essen and University of Waterloo, Canada, 2022.
- Kuß, David: Katalytische Hydrierung von Kohlenstoffdioxid mit Mangan-Komplexen: Konzeption und Mechanismus, Rheinisch-Westfälische Technische Hochschule Aachen, 2022.
- Elfgen, Roman: Structure-directing effects in microheterogeneous ionic liquids, Rheinische Friedrich-Wilhelms-Universität Bonn, 2022.

Student-organized Events

The doctoral students of the IMPRS-RECHARGE cooperate in the organization of international scientific conferences, which are held every two years. The students take all decisions relating to selection of topics, speakers and perform all tasks that are connected with the organization of an international conference independently. The costs are covered on the one hand by the registration fees of the participants and on the other hand by a given specific budget by the IMPRS. In 2021 a group of six IMPRS-students organized the third international scientific conference entitled "Exploring Reactivity with Spectroscopy (ExpReS)", which was held in an online format (May 19-21, 2021).

The conference brought together nearly 100 participants from 12 countries with a common interest in various spectroscopy techniques. Keynote lectures were held by Clare Grey (Cambridge), Lutz Gade (Heidelberg), Atsushi Urakawa (Delft), and Serena DeBeer (Mülheim/Ruhr). To convey the practical aspects of essential spectroscopic techniques, namely EPR, X-ray and Mössbauer spectroscopy, the MPI CEC group leaders E. Bill, A. Schnegg, and G. Cutsail III recorded virtual lab tours, in which they explained the whole measurement procedure from preparing the sample, acquiring the data to analyzing the final spectra.

In December 2021 a team of 12 IMPRS-students started the planning of the fourth international scientific conference entitled "Advanced Catalysis and Materials for Energy Conversion (ACAMEC)" to be carried out from April 24-27, 2023.

More information: http://imprs.cec.mpg.de

H2GIGA
DERIEL

Experimental and technical goals of the project

Hydrogen production via water electrolysis and its subsequent utilization into other reactors for example for the reduction of CO$_2$ to CO, constitutes a major part of the DERIEL initiative. DERIEL is part of the electrolyser scale-up work area of the H2Giga platform "serial production of water electrolyzers" and is intended to open up fields of application for series-produced electrolyzers up to the gigawatt range (Fig. 1), by bringing together different academic and industrial partners with the main goal of the project being the De-Risking of Electrolyzers. In order to achieve this goal, better understanding of degradation phenomena of Proton Exchange Membrane Water Electrolyzers (PEMWE) operating under dynamic conditions is imperative for the development and implementation of efficient and reliable energy storage from fluctuating renewable energy sources. However, still efforts are required to understand and address some limitations associated with technological requirements and material properties. The PEMWE allow significant permeability of gaseous products that decreases the efficiency and raises safety issues especially under imbalanced pressure operation. The harsh oxidative and corrosive environment (high electrochemical potential and low pH) necessitates the use of noble metal based electrocatalysts such as IrO2 (also to compensate for the low kinetics of the oxygen evolution reaction) and Ti current collectors and separator plates, contributing significantly to systems cost. Therefore, enhanced durability is essential, as extended lifetime can compensate for the high investment cost. Understanding the degradation modes of the individual system components, their interplay and the association with specific operating conditions are crucial for enhancing the durability of the whole system.

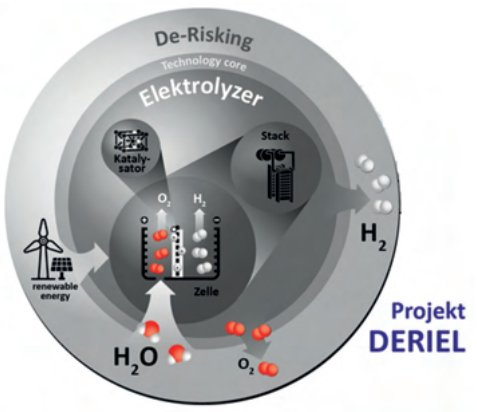

Figure 1. Scheme of the H2GIGA platform project DERIEL.

Chemical degradation is assigned to cross-permeation and mixing of H2 and O2 leading to H2O2 formation through the 2e- oxygen reduction reaction (ORR) in the cathode. In the presence of impurity ions from the stainless-steel based H2O reservoir and tubes, among others, H2O2 readily decomposes to active radicals that attack the PEM further decreasing stability. Thus, the electrochemical potential, the electrolyser operation mode and the electrolyzer parts affect stability, with Ir dissolution and ionomer degradation being the primary causes of instability in aqueous acidic media. Elucidating background phenomena that contribute to material degradation under more realistic application conditions is therefore crucial for the De-Risking of DERIEL.

Different modes of electrolyzer operation i.e. dynamic and stationary contribute differently to material degradation. It is thus essential to decouple these different modes of operation and study them with various in-situ and post-mortem techniques, which is a new technical territory and the novelty that the Electrochemistry group at MPI-CEC offers (1).

The first task will be to design a benchmarking protocol for catalyst screening in a single cell electrochemical flow cell (EFC). The EFC will be coupled to an Inductively Coupled Plasma - Optical Emission Spectrometer (ICP-OES) for continuous monitoring of catalyst material degradation. Scaling up catalyst benchmarking in a high surface area electrolyzer cell (50cm2) with continuous and dynamic modes of operation is the next task. Additionally, post mortem spectroscopic and microscopic and different times of life (DToL) degradation studies on Membrane Electrode Assemblies (MEAs) tested under high current loads (2A/cm2 at 700C) will give a better perspective on degradation phenomena at industrially relevant conditions. Monitoring by means of eQCM and ICP-OES the effect of impurities, originating from electrolyzer cell parts, on the stability of the Pt and Ir electrocatalysts on the cathode and anode respectively is fundamental for the understanding of MEA performance under industrial conditions. Finally, operando spectroscopic techniques such as in-situ Raman and X-Ray Absorption Spectroscopy will be used to monitor structural changes on the electrocatalyst material which will be linked to the MEA performance.

At MPI-CEC we have been specializing on studying degradation phenomena on various catalyst materials ranging from alkaline to acid based electrocatalysts such as IrO2, Ni-based oxides and their alloys and carbon materials. We have built different electrochemical flow cells (EFC) with the purpose on elucidating degradation at different modes of operation and at various pH and temperatures, at different catalyst loadings and electrolytes, thus gaining a better overview on the effect of each condition on the activity and degradation of electrocatalysts. Recently, during MAXNET Energy (2015-2019) we coupled a specially designed EFC with an ICP-OES. This setup allows the in-situ monitoring, of different modes of catalyst degradation electrolytes (2, 3). In our recent works, we have identified not only different modes of catalyst degradation but also identified the detrimental effect of electrolyte impurities on the catalyst performance and were able for the first time to quantify the uptake of such impurities during electrochemical testing. Additionally, we were able to investigate Ir-based catalysts and its alloys for the evaluation of their activity and stability (4, 5).

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H2GIGA
PrometH_2eus

Lab-scale synthesis and testing of catalysts very often do not match the harsh conditions and requirements that materials are exposed to in industrial manufacturing and application. Therefore, academic results on new catalysts are of limited use for applied industrial electrolysis. To bridge the gap between fundamental academic research and industrial application, the multipartner project PrometH_2eus was established as part of the BMBF lighthouse project H_2Giga, focusing on the development and understanding of Ni-based electrodes for the oxygen evolution reaction (OER) in alkaline media.

Research on new electrode materials within the PrometH_2eus consortium is performed in the context of technical relevance and applicability to guarantee a possible transfer of research outcomes to large-scale technical electrolysis and a reliable performance under industrial conditions. Thereby, PrometH_2eus contributes to H_2Giga by developing novel Ni-based prototype electrodes with a high technology readiness level (TRL) on the one hand and by establishing systematic and knowledge-based guidelines for an application-oriented research on electrode materials on the other hand. In particular, the latter can increase the number of future scientific publications with direct relevance for technical electrolysis, paving the way for innovations within this field.

The PrometH_2eus consortium comprises more than 20 research groups from universities and research institutes as well as industrial partners forming three interconnected research-clusters (Figure 1). The "Synthesis"-cluster works on the development of new catalysts, utilizing processes and materials that are suitable for large-scale production. The "Analysis"-cluster applies cutting-etch *in situ* and *operando* analysis techniques as well as theoretical simulations to obtain fundamental knowledge about material properties and (reaction) mechanisms that enhance or impair water electrolysis at harsh industrial conditions.

The "Application"-cluster focuses on modelling and simulation of technical processes and electrodes, scale-up processes, and the development of test-stations and protocols that are suitable to characterize new catalysts and electrodes in a technical relevant fashion.

The PrometH_2eus Consortium and the role of the CEC

The PrometH_2eus project was initiated at the MPI CEC in the "Heterogenous Reactions" department of Robert Schlögl as a follow up of the BMBF cluster project MANGAN by Prof. Anna Mechler (Coordinator, former group leader at MPI CEC and now located at RWTH Aachen) and Dr. Marc Tesch (Co-Coordinator, Electrochemistry Group). The consortium comprises 23 academic research groups located at University Kiel, TU Berlin, RWTH Aachen, University Duisburg Essen, TU Darmstadt, University Erlangen-Nürnberg, MPI CEC, MPI KOFO, MPIE, MPI CPfS, FHI Berlin, and Monash University (Melbourne, Australia), as well as the industrial partners thysenkrupp nucera, DeNora, and Umicore.

The coordination of PrometH_2eus is located at RWTH Aachen (Prof. Anna Mechler) including the coordination of the "Application"-cluster. The "Analysis"-cluster as well as the "Synthesis"-cluster are coordinated at MPI CEC, by Dr. Marc Tesch and Dr. Saskia Heumann, respectively.

Further, the MPI CEC accommodates three projects:

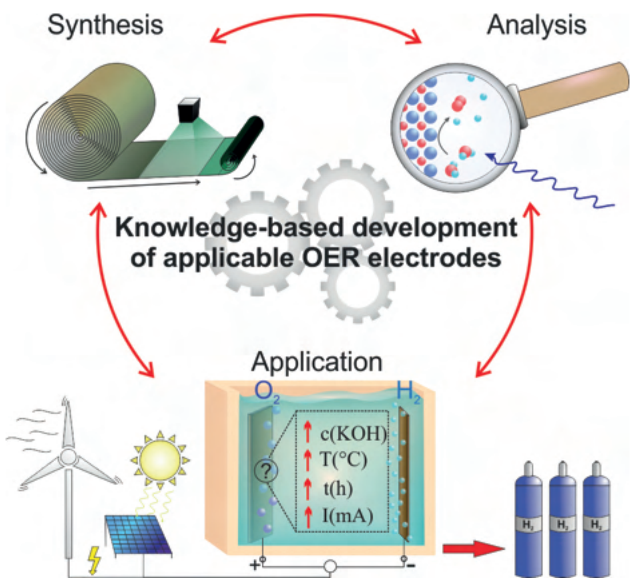

Figure 1. PrometH_2eus overview sketch.

Project "Scalable Synthesis of Ni-foam supported NixB@NiOOH catalysts for the oxygen evolution reaction"

PI: Dr. Justus Masa - Electrochemistry Group; Co-worker: Dr. Sayed Elrefaei

This project, located in the "Synthesis"-cluster, contributes to the overall goal of PrometH_2eus through knowledge-guided synthesis of nickel boride (Ni_xB) pre-catalysts that fulfil specified material parameters, such as the scale-up option for large-scale application. These materials are investigated at conditions that approach their envisaged industrial application, namely: high electrolyte concentration (30% KOH), high current densities ≥ 100 mA cm^{-2}, and high electrolyte temperature ≥ 60 °C. To obtain a comprehensive picture, in-depth physical-chemical characterization is performed prior-to electrocatalysis, during electrocatalysis (*operando*) and post-electrocatalysis. Chemical and electrochemical dissolution studies on individual and particle ensembles reveal spatio-temporal reconstruction and dissolution of the host-guest atoms under OER polarization with formation of $Ni_xB@BO_xH_y$ (Core@shell) transient structures, as previously observed for related Nickel phosphide (Ni_xP) materials using high resolution transmission electron microscopy (HRTEM) and atomic probe tomography (APT).[1,2]

In the presence of unpurified alkaline electrolytes containing iron impurities, a complex form of dynamic interaction ensues leading to activity enhancement. Elucidation of the interfacial electrochemical dynamics and role of dissolved polyborate anions are the subject of *operando* Raman spectroscopy studies to inform optimization and scale-up of synthesis of improved catalysts. Tracking the state of catalysts under reaction conditions is important in order to construct robust structure-activity correlations. Finally, optimized catalyst will be fabricated on 3-dimensional nickel meshes and foams by spray coating and high temperature annealing to form dimensionally-stable-anode like electrodes.

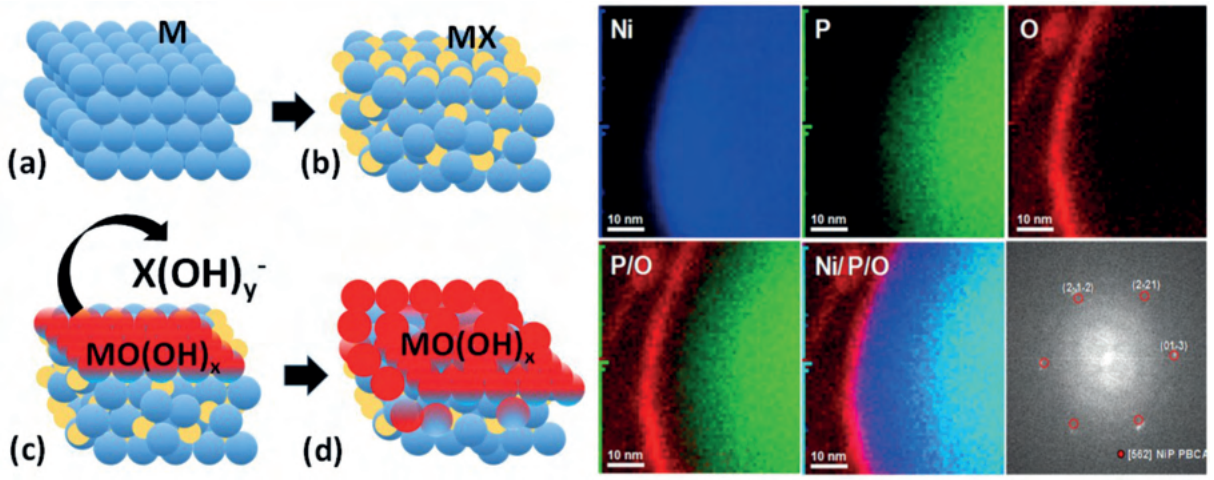

Figure 2. Schematic illustration of the mechanism of dissolution of the guest element (X) from a MX inter-metallic alloy and concomitant formation of a core-shell structure (left), and HRTEM images of an activated Ni_xP catalyst (right). [2]

References

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Project "Optimized Oxygen Electrodes by Plasma-Enhanced Surface Modification (VESPA)"

PIs: Dr. Saskia Heumann – Carbon Synthesis and Applications Group; Prof. Axel Lorke & Dr. Nicolas Wöhrl – University Duisburg-Essen (UDE); CEC-Co-workers: Dr. Sebastian Tigges – Carbon Synthesis and Applications Group

Within the framework of the "Synthesis"-cluster of the PrometH$_2$eus consortium, in order to develop electrodes that outperform existing materials in both energy and cost efficiency, the project VESPA deals with the physicochemical surface modification of materials by plasma treatment (Figure 3). Both our own preliminary work and results from current studies show that Ni-based materials can be plasma-treated in such a way that non-equilibrium phases with improved electrocatalytic performance are produced. In addition, it has been shown that the stability of these materials can be increased, significantly reducing reoccurring costs during the application. Samples of other project partners and partners from industry can be modified prior to or post synthesis to increase surface area and roughness, to introduce functionalization, or to deposit carbon via plasma-enhanced chemical vapour deposition.

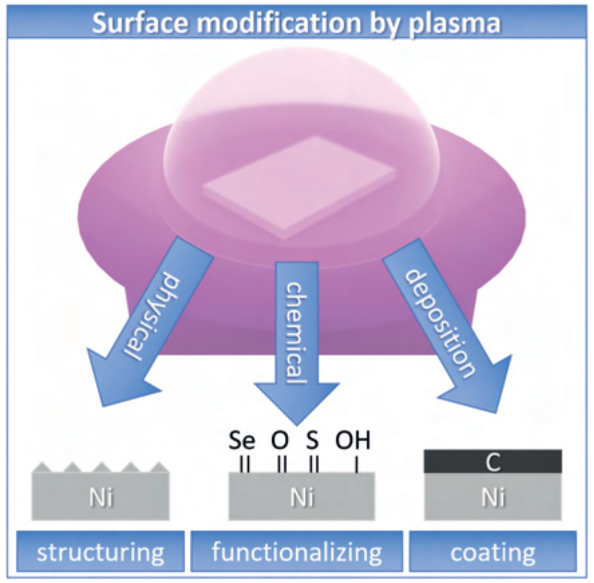

Figure 3. Schematic illustration of different surface modifications by plasma treatment.

Plasma treatment therefore provides a cost-effective and scalable way to optimise the materials independently of the pre-/post-process and is an important additional component in the materials synthesis of the PrometH$_2$eus project. Plasma treatment also offers the advantage that it can be integrated relatively easily into existing large-scale processes, for example roll-to-roll processes.

As part of the project, an industrial-sized plasma system was acquired at MPI CEC. This is the scaled counterpart to the existing laboratory facilities at the UDE and is intended to serve as a bridgehead between research and industry. Apart from successes in the planned physicochemical surface modification of samples, early experiments with the standard industry substrate material have shown the possibility to produce good performing electrocatalysts by plasma treatment alone (without the need for prior or further treatment) at industrially relevant yields.

Project "Application-oriented analysis of Ni-based OER electrodes by theory-supported *operando* X-ray spectroscopy (*op*Spec-X)"

PIs: Dr. Marc Tesch – Electrochemistry Group; Dr. Axel Knop-Gericke & Dr. Travis Jones – Electronic Structure Group; Dr. Katarzyna Skorupska – Catalysis with Metals Group at FHI Berlin, Dr. Alexandr Simonov & Prof. Douglas MacFarlane – Monash Univ.; CEC-Co-workers: Dr. Aliakbar Ghafari, Dr. Twinkle Yadav, Dr. Garlef Wartner – Electronic Structure Group

The *op*Spec-X project, located in the "Analysis"-cluster of PrometH$_2$eus, is a collaboration between MPI-CEC, FHI Berlin and Monash University (Melbourne, Australia). Based on comprehensive experience of the PIs in *operando* soft X-ray techniques (see e.g. Refs [1,2,3]), one aim of the *op*Spec-X project is to extend such *operando* experiments towards elevated temperature, current density, and pH by the development of according equipment (Figure 4a). The spectroscopic approaches comprise X-ray photoelectron spectroscopy, X-ray absorption and emission spectroscopy, and resonant inelastic X-ray scattering, used to obtain a fundamental understanding of the electronic structure of Ni-based catalysts for the OER. Experiments are conducted at different beamlines of the synchrotron radiation source BESSY II in Berlin. To elucidate structure-function relations, model systems as well as electrodes synthesized by project partners will be investigated. Importantly, this includes the analysis of electrodes that were applied in prototype electrolyzers in long-term tests to investigate electrode degradation.

The spectroscopic experiments are accompanied by theoretical approaches, in particular density-functional theory calculations and molecular dynamics simulations, to formulate adequate reaction/degradation mechanisms.

In first successful experiments, the oxidation behavior of an electrodeposited model NiO$_x$-catalyst was tracked as a function of potential (Fig. 4b), revealing a complete transformation of the Ni L-edge spectra when applying potentials up to 1.78 V vs. RHE accompanied by the formation of a pre-edge feature in the O K-edge spectra. The latter is assigned to the creation of new states in the bandgap when changing the electronic structure from a Ni(OH)$_2$ to a γ-NiOOH. By providing such element-specific *operando* spectroscopy, the opSpec-X project adds a powerful analysis tool to the toolbox of the "Analysis"-Cluster, enabling the identification of important aspects regarding the electronic structure during operation and thereby promoting the knowledge-based design of electrodes for the OER.

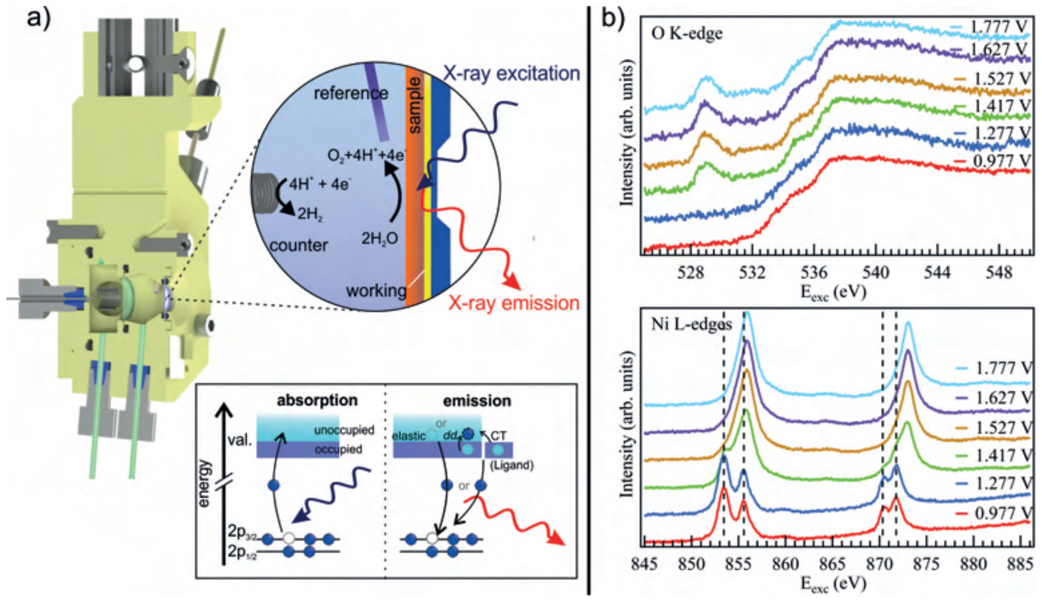

Figure 4. (a) Illustration of a flow cell[4] designed for soft X-ray photon-in-photon-out spectroscopy and its working principle, and (b) X-ray absorption spectra detected in fluorescence yield mode at the Ni $L_{2,3}$- and the O K-edge for selected potentials.

References

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[4] M. F. Tesch, S. A. Bonke, R. Golnak, J. Xiao, A. N. Simonov, R. Schlögl, *Electrochem Sci Adv* **2021**, e2100141. DOI: 10.1002/elsa.202100141

Kopernikus Project
Power-to-X

Exploration, validation and implementation of „Power-to-X" concepts

The „Kopernikus Projects for the Energy Transition" are funded as large scale national platforms with a 10 years horizon by the BMBF to develop technological and economic solutions for the conversion of the energy system in collaboration between academia, industry, and society.

The project "Exploration, validation, and implementation of 'Power-To-X' concepts (P2X)" is led by the coordination team Prof. Kurt Wagemann (DECHEMA), Prof. Rüdiger Eichel (Research Center Jülich and RWTH Aachen University), and Prof. Walter Leitner (spokesperson). The project partners of the consortium bring in scientific and technical expertise in the areas of electrolysis, catalysis, process technology, socio-economics and social acceptance research.

Following a successful 1st phase (2016-2019) the Kopernikus project P2X closely interlinked the fields of research and application in terms of content and structure during the 2nd phase (2019-2021) of „validation".

Selected technologies were developed in an integrated structure within the two technology pathways „hydrogen as energy vector" and „synthesis gas as energy vector". The technology pathways commence up-stream with the electrolysis of H_2O and co-electrolysis of CO_2, respectively, and arrive down-stream at a specific product or application. Reduction of greenhouse gas emissions in comparison to the corresponding petrochemical value chains defines the central evaluation criterion monitored closely in the Roadmap process.

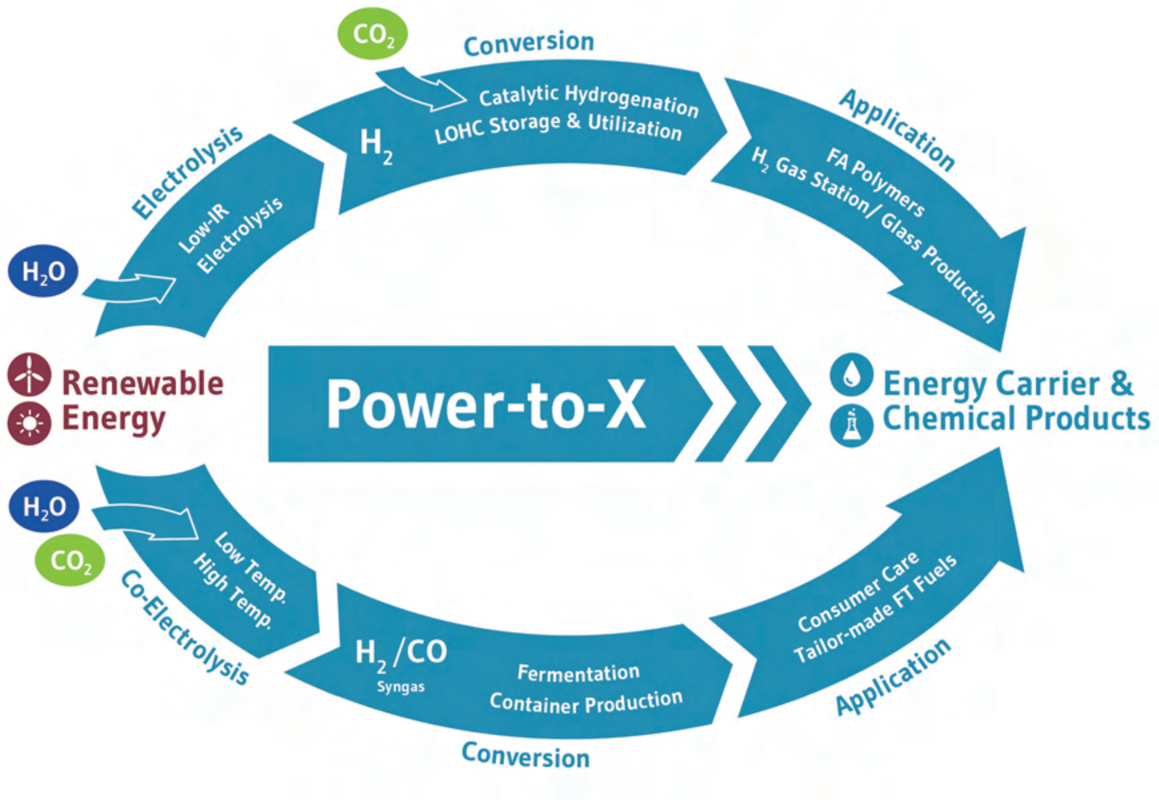
Communication to the general public defined a strategic measure for the second phase. The two NGOs BUND and WWF were project partners in this context. WWF contributed with workshops for students of various age groups and developed a virtual reality experience for "power-to-X" technologies

(https://www.wwf.de/fileadmin/fm-wwf/Publikationen-PDF/Bildung/Booklet-Power-to-X-VR.pdf).

The Kopernikus Project P2X is also a core partner of the Museums project "Power2Change"

(https://power2change-energiewende.de)

In order to achieve the ambitious goals of the second project phase, 14 research institutions, 6 associations and societies, as well as 26 industrial companies throughout Germany were participating within the project consortium. Currently, the transition into the 3rd phase "demonstration" is coordinated and negotiated with the German Ministry of Science and Education.



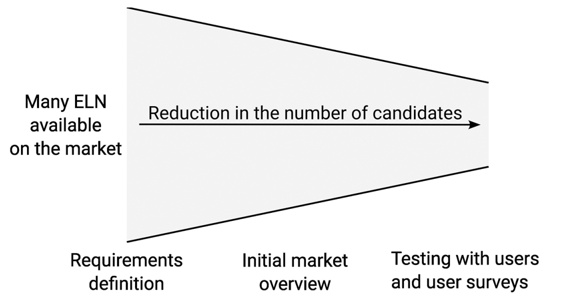
NFDI4CAT

Research Data Management

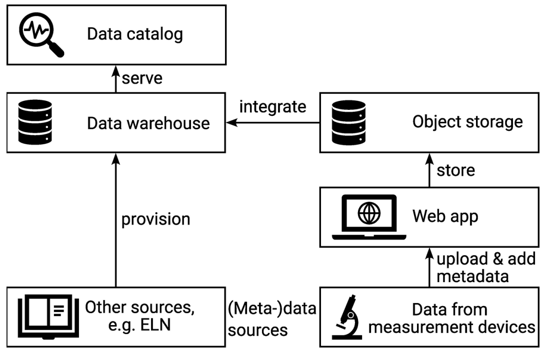
As part of the wider National Research Data Infrastructure (NFDI) association, 16 institutions from various fields of catalysis have partnered up to form the NFDI4Cat consortium, under the coordination of DECHEMA e.V. The goal of NFDI4Cat is to improve research data management practices in catalysis. MPI CEC is one of the partner institutions, represented by Prof. Walter Leitner.

The first area of research data management where MPI CEC has interfaced with NFDI4Cat has been a survey of the market for electronic lab notebooks (ELN). These software tools allow the digitization of laboratory note-taking, sample management, scheduling of experiments and inventory management, which facilitates or enables research data management practices. However, the ELN market is diverse, with different vendor categories (commercial and open source), and various degrees of feature richness. Moreover, products may be geared towards different research communities, which, in turn, may have different needs. Work at the institute has been to research the ELN market with a view towards catalysis research. Requirements from different research groups were gathered to define the requirements based on which ELNs would be assessed. Following an initial overview of the market, ELN solutions were tested and feedback was gathered through user surveys. The institute is now in an extended testing phase.

Furthermore, a task area of NFDI4Cat is the development of algorithms and analysis tools for facilitating the different steps of data processing in catalysis. Here, MPI CEC has been active with the development of a software architecture for storing and searching scientific data. The architecture is motivated by common concerns in data management. For example, data may end up in data silos, where it is accessible by only a few users. Furthermore, data may be spread out across different machines in an unstructured state. If no metadata is attached, the data is difficult to find. It is difficult to track data lineage, and the data is not easily accessible for large-scale analysis. Finally, existing workflows for data handling may involve repetitive manual work. The architecture under development at the institute would address these issues by combining a data lake with a data catalogue and a service for ingesting and enriching data. Data coming from instrument devices is uploaded using a website, annotated with metadata, and subsequently stored in an object storage, from where it is accessible and from where metadata can be retrieved to be exposed in a catalogue. The vision is that users maintain their existing workflows, while their generated data is automatically digitized and categorized for them, and is, subsequently, available and easy to find at a future time.



Scheme 1. Research of the market for electronic lab notebooks.



Scheme 2. Software architecture for research data management.

REDIFUEL

The goal of the REDIFUEL project was to develop a sustainable and innovative synthetic drop-in diesel (EN 590 compliant) that can compete with currently used fossil fuels. The concept is a three-step process, as shown in Figure 1.

This approach is common practice in the industry. Nevertheless, the process for effective hydroformylation of longer-chain olefins (C5+).

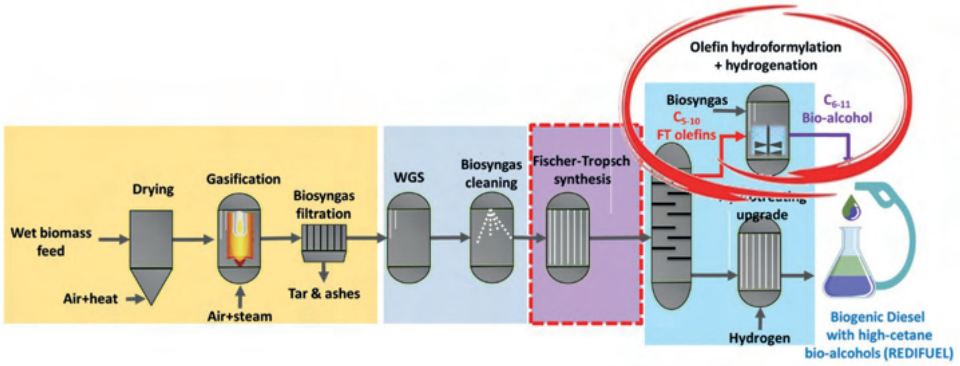


Figure 1. Redifuel concept

Starting from variable biomass, synthesis gas (CO and H_2) is first produced. Using the Fischer-Tropsch reaction, the syngas is converted to various alkanes and alkenes. While the alkanes make up most of the final fuel blend, some of the alkenes are converted to alcohols. In the final REDIFUEL fuel blend, these alcohols with varying chain lengths make up between 20% and 30% of the fuel matrix. The alcohols serve as high-value additives in the proposed synthetic fuel. They have been shown to provide improved combustion performance and reduce the amount of pollutants.

These alcohols are produced by converting C_5-C_{10} olefins into C_6-C_{11} alcohols. The hydroformylation/hydrogenation reaction is very effective for this conversion. The reaction has 100% atomic efficiency and can be carried out under mild conditions. Both steps of the hydroformylation/hydrogenation reaction must be catalyzed. In the project the Multiphase catalysis group worked on a two-step and a one-step sequence to yield alcohols.

The first approach was the development of a two-step approach, in which hydroformylation is carried out first with a homogeneous catalyst, then the products are separated from the catalyst and subsequently hydrogenated to alcohols in a second step.

The challenge to date is to create high reactivity, as this decreases dramatically in biphasic liquid/liquid systems with increasing chain lenght.In addition, complex mixtures, such as those produced by the Fischer-Tropsch process in the REDIFUEL project, have not been studied before and pose another challenge. A water based recyclable catalyst system was developed to successfully converted the complex FT-mixture from olefins and paraffins to the corresponding aldehydes. This system was then transferred in a custom-build miniplant to test to long term stability of the phase and catalyst system.[1] The system was very stable and showed a robust behaviour (figure 2). The Aldehydes were hydrogenated also in a continuous setup by a commercial catalyst with very high selectivity to the aldehydes.

The second approach is a single-step reaction (Figure 2, left) in which both reactions, hydroformylation and hydrogenation occur simultaneously. A reaction in which multiple catalysed reactions occur in a single step is also known as tandem catalysis. This catalysis system was developed and studied in deep detail.[2] An uncommonly selective alcohols selectivity by mild reactions conditions were achieved using amine ligand systems. A challenge was to recycle these unconventional ligands systems. Three different approaches were developed in order to separate the active catalyst and reuse it.

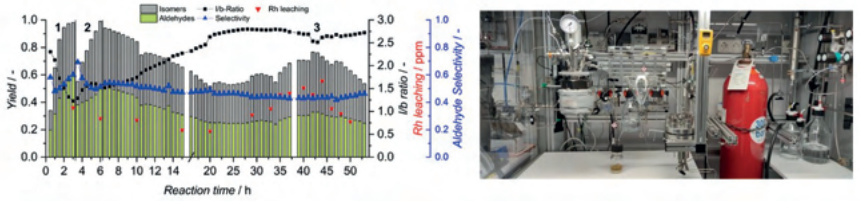


Figure 2. Yield time plot of a miniplant campaign (left), Miniplant (picture right)

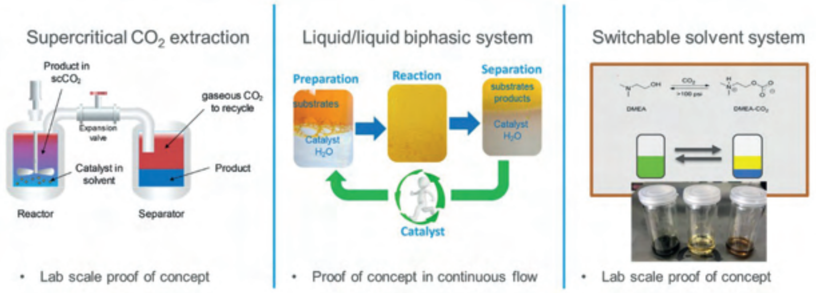


Figure 3. Developed recycling system for the newly developed Rhodium/Amine Catalyst system for the reductive hydroformylation.

First attempt was to create a solvent which has a amine functionality that is not soluble in supercritical CO_2.[3] This system was stable and showed high reactivity. The second development was the use a classic water-based system in with a water soluble amine ligand was used. This system was tested also in a continuous operated miniplant setup.[4] The leaching of the metal catalyst was higher than in the first recycling system while the phase system is very stable.

The last recycling system that was developed for the recycling was a monophasic system in which a second phase was induced by adding CO_2 which is reacting with the ligand to a polar salt.[5]

The overall Rediful project was very successful by guiding a way to a CO_2 neutral fuel of the future.

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EU Project e-tandem

The EU target for 2050 to achieve a net-zero greenhouse gas (GHG) emissions economy is crucial to cease global warming and its consequences on climate. While electrification is the blueprint for short-range passenger transportation, the defossilization of other transportation sectors such as heavy-duty, long-haul ground transport, shipping and aviation relies on the availability of higher-energy-density and carbon-neutral fuels. Synthetic paraffinic liquid hydrocarbons and light (C1) oxygenate (DME, methanol) renewable fuels stand as the current options. Higher (C3+) oxygenate compounds (alcohols and ethers) could prove a highly preferred alternative, due to their exceptional capacity to reduce (even eliminate) tailpipe hydrocarbon and soot emissions compared to paraffinic fuels, and their advantageous logistics and compatibility with current-fleet infrastructures compared to lighter oxygenate compounds.

e-tandem is an international cooperative effort set to unlock an efficient and direct production of higher oxygenate (aliphatic alcohols and their derivative ethers) diesel-type e-fuel for the marine and heavy-duty transport sectors. Said oxygenated e-fuel is carbon-neutral and directly produced from CO_2, as the sole carbon source, and renewable power as the sole energy input, in a once-through hybrid catalytic process which integrates three major catalysis branches in a tridem fashion, i.e. electrocatalysis syngas production, solid thermocatalysis for syngas conversion into hydrocarbons, and molecular catalysis for in situ hydrocarbon oxo-functionalization (figure 1).

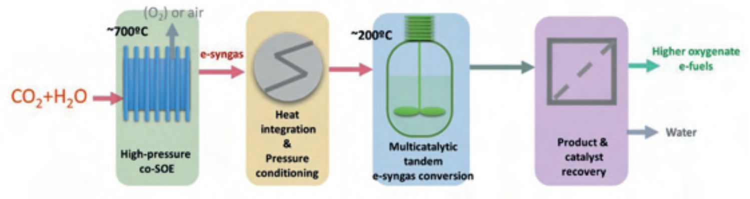

Figure 1. e-tandem concept

The project's ambition builds on very recent findings made by consortium of MPI CEC and CSIC/ITQ Valencia with catalyst materials which, owing to their unconventional performance, enable for the first time the integration of reductive polymerization and oxo-functionalization reactions from renewable syngas in a single-step process with greater carbon and energy efficiency than conventional multi-step conversion schemes and essentially no CO_2 side-production (Figure 2).[1]

e-tandem will demonstrate the process at bench scale, validating the technology at TRL 4. The Multiphase catalysis group in the MPI CEC is engaged in the development of the tandem catalyst for the direct production of alcohols from synthesis gas and the design and operation of a lab scale miniplant to demonstrate the feasibility of the concept.

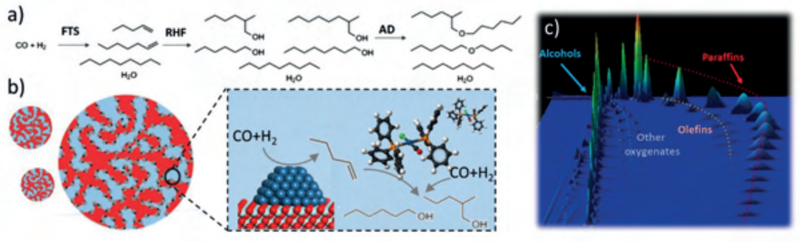

Figure 2. Reaction sequence of the new developed tandem catalytic system from CO/H2 syngas to long chain alcohols and ethers.

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TransHyDE

The definition and development of a storage and transport infrastructure is essential for the ramp-up of a hydrogen economy. The project is funded by the Federal Ministry of Education and Research (Bundesministerium für Bildung und Forschung, BMBF; support codes: 03HY200_ - 03HY209_, where "_" is amended with an individual letter representing the partners in the respective project).

The hydrogen flagship project TransHyDE with its five research and four implementation projects (compare Figure 1) is developing solutions how ideal hydrogen infrastructures could be designed in order to create the greatest possible efficiency and resilience. The communication and coordination office is part of the overarching project structure and is reporting to the three coordinators Prof. Dr. Robert Schlögl, Prof. Dr. Mario Ragwitz and Jimmie M. Langham in an advisory and supportive capacity. In addition, the office is intended to strengthen the transfer of information between the coordinators and the entire TransHyDE technology platform as well as between the individual TransHyDE projects.

The technological focus of TransHyDE is research, development and implementation of transport and storage options for the following molecular energy carriers: gaseous hydrogen (gH_2), liquid hydrogen (LH_2), ammonia (NH_3) and liquid organic hydrogen carriers (LOHC). An overview of the different topics tackled in the individual TransHyDE projects can be found in Table 1.

The project structure of TransHyDE ensures a continuous and mutual exchange between the research and implementation projects. The close information coupling ensures on the one hand application-oriented research and on the other hand state-of-the-art technical implementation. In addition, the results obtained are directly incorporated into roadmapping processes for the development of a hydrogen infrastructure up to 2045 and the closing of standardization, certification and regulatory gaps.

The agile project structure of the TransHyDE ecosystem, consisting of projects and work packages, enables continuous adaptation to the requirements of the dynamic and techno-political project environment.

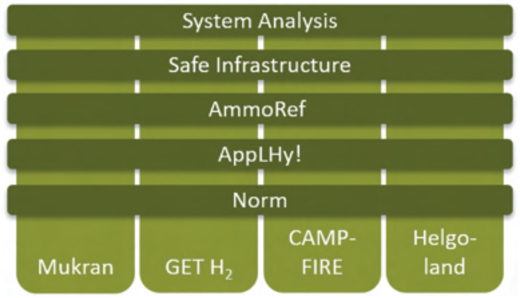

Figure 1. Breakdown of TransHyDE into projects with focus on research (horizontal) and implementation (vertical).

Table 1. Brief description of project content of individual TransHyDE projects.

TransHyDE Project name	Brief description of main activities within the project:
Communication and Coordination	Internal coordination, external coordination, public relations, regulatory framework considerations
System analysis	Synthesis of major project results, roadmap of infrastructure development until 2045
Safe Infrastructure	Material and technical foundations for the safe operation of a hydrogen pipeline network
AmmoRef	Catalysts for industrial NH_3 reforming
AppLHy!	Transport and synergies of LH_2
Norm	Status quo of technical regulations, needs analysis and recommendations for action to close standardization and certification gaps
Mukran	Trimodal H_2 transport in high-pressure spherical storage vessels
GET H_2	Conversion of natural gas transport grids to H_2 and safe operation of H_2 pipeline networks
CAMPFIRE	NH_3 value chain as an energy carrier and H_2 storage medium
Helgoland	H_2 storage and transport with LOHC (liquid organic hydrogen carriers)

The MPI-CEC is involved in activities in the TransHyDE Communication and Coordination Office that coordinates the flagship project (support code 03HY200A) and the research project AmmoRef, which focusses on enabling and optimising an efficient catalytic reforming process of ammonia (support code 03HY203A).

TransHyDE – Communication and Coordination

The overall communication and coordination of TransHyDE ensures achieving the objectives set by the individual projects and coordinates both internal and external communication to strengthen professional and societal networking. Additionally, the communication and coordination project within TransHyDE investigates regulatory aspects of an hydrogen economy and formulates recommendations and suggestions to enable upramping such an economy.

The communication and coordination team consists of the three project coordinators (Prof. Dr. Robert Schlögl, Prof. Dr. Mario Ragwitz and Jimmie M. Langham) and the TransHyDE office, which is composed of employees of the former/current affiliations of the coordinators (MPI-CEC, Fraunhofer IEG and cruh21).

Main aspects of the work the MPI-CEC was leading or involved in within the communication and coordination team in 2020 – 2022 were focussed on public relations and coordinating informational exchanges between the different projects within the TransHyDE framework. Noteworthy in the field of public relations are, among others, organising the representation of TransHyDE on trade fairs like the ACHEMA 2022 and the WindEnergy Hamburg as well as multiple articles on TransHyDE that were publicised in the "energie | wasser-praxis" and the "3R".

TransHyDE – AmmoRef

The low density of gaseous hydrogen and the high energy required to liquefy hydrogen make transport and storage of hydrogen a challenging task. Gaseous hydrogen is stored in gas tanks at up to 800 bar and, in addition to special embrittlement-resistant materials, requires an enormous amount of safety technology for safe logistics, mainly because of the high pressure. In its liquid state, hydrogen can be stored in cryo-vessels at -252 °C. Due to the physical properties of hydrogen, however, a constant evaporation process takes place. Together with the energy required for the liquefaction, this lowers the energy balance for such hydrogen storage.

Chemical storage of the hydrogen can provide a remedy. In addition to other possible alternatives, ammonia (NH_3) as a storage molecule is a promising alternative that is already close to being ready for use. Other advantages are that ammonia has a very high gravimetric and volumetric hydrogen density, can be easily liquefied and is already being transported safely over long distances on various routes. Thus, a transport chain for hydrogen is possible according to the scheme presented in Figure 2.

Ammonia is well known as an important component of artificial fertilizers, but it is also used in other important technologies. For this reason, ammonia is already being produced on megaton scale via the extensively optimized and comparatively well understood and efficient Haber-Bosch process. In order to establish a sustainable process, the ammonia must be synthesized using green hydrogen and renewable energies. However, the catalytic recovery of hydrogen from the ammonia (reforming) is less optimized and researched. [1]

This is exactly where the work of the TransHyDE research network AmmoRef comes in. 7 partners from research and industry are involved in order to achieve the balancing act between understanding-based optimization and, at the same time, faster implementation in pilot plants. The overall goal of the AmmoRef network is to research an application-related, industrially feasible, safe and cost-effective technology for the reforming of ammonia.

On the one hand, technical questions have to be answered that have to be thought through and processed specifically for the respective applications. The AmmoRef project is therefore researching two routes (low pressure and high pressure). This includes reforming at elevated pressure (~30 bar), which requires less downstream compression of the hydrogen obtained for certain applications. However, efficient catalysis will occur at atmospheric pressure. In addition, care must be taken to ensure that the recovered hydrogen is as free as possible of ammonia residues and other by-products in order not to endanger subsequent processes.

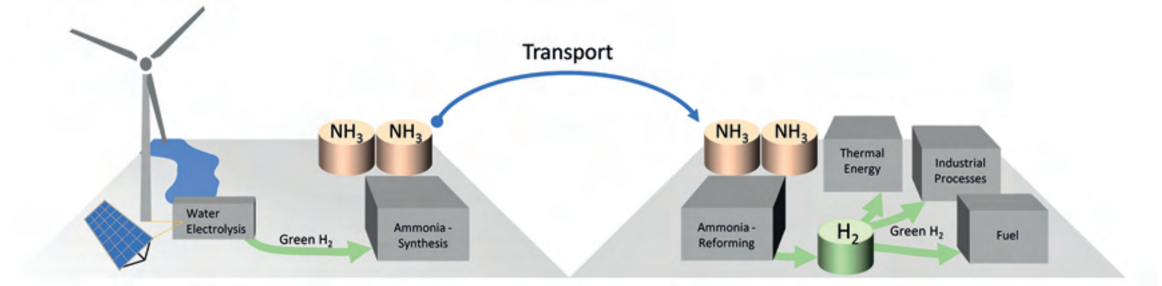

Figure 2. Schematic representation of the use of ammonia as a chemical hydrogen storage medium.

On the other hand, a screening of various catalyst materials must be carried out in order to understand chemical relationships and structure-activity relationships. Highly developed and specialized characterization methods are used here, which are supported by theoretical models. Subsequently, with this knowledge, a strategic catalyst design can take place to optimize the properties.

Ruthenium based catalysts are known to show best activities in ammonia reformation catalysis. However, Ruthenium is an expensive and low abundant precious metal. High-abundant metals like Nickel, iron and cobalt show as well promising activities in ammonia reforming, though, only at higher temperatures and with lower conversion rates. Therefore, the project focusses on the improvement of the catalytic properties of transition-metal-based catalysts.

Beside the coordination of the AmmoRef project, the MPI CEC conducts as well the synthesis and investigation of carbon-based catalysts (working group of Saskia Heumann), the fast screening of catalytic properties in the ammonia reforming (working group of Holger Ruland), the kinetic and long-term stability testing of catalysts (working group of Martin Muhler, Max Planck Fellow) and in-operando spectroscopic investigations during catalysis (working group of Serena DeBeer).

Reference

[1] Ristig, S., Poschmann, M., Folke, J., Gómez-Cápiro, O., Chen, Z., Sanchez-Bastardo, N., Schlögl, R., Heumann, S. and Ruland, H. (2022), Ammonia Decomposition in the Process Chain for a Renewable Hydrogen Supply. Chemie Ingenieur Technik, 94: 1413-1425. https://doi.org/10.1002/cite.202200003

The institute in the public eye

The Research Communication team is responsible for press and public relations, the graphic design of all Institute media as well as for photos and the documentation of Institute activities. In addition, the team is responsible for the organization, implementation and follow-up of various scientific and public events.

The team strives to act as an interface between the institute and the public and to create awareness of the important role of basic research in the field of chemical energy conversion. The aim is to promote the perception of MPI CEC's research but also of basic research in general in society, among corporate partners, prospective students, alumni and also internal interest groups. To this end, the team informs journalists and interested citizens with press releases, provides background knowledge and also invites them to visit the institute.

Communication channels and platforms

In addition to direct communication with the press, citizens and scientists, the Institute's website is an important part of its communication work. The Research Communication team regularly maintains and updates the website, preparing scientific topics for both the general public and the scientific community.

Social media

The Research Communication team regularly posts news from the Institute on the Institute's Facebook page and via the Institute's Twitter account.

Event announcements, but also publications and research results, are shared and published here. The team helps scientists of the Institute to share their knowledge, news, publications or job postings. The number of CEC scientists who use their own Twitter account is growing steadily, so that a lively exchange takes place online. The Research Communication team supports scientists in setting up and maintaining their own accounts on social media platforms.

Events

The organization of various scientific and public events is an important part of the team's work at MPI CEC.

Due to the Corona pandemic, numerous events had to be cancelled at short notice in 2020 to 2022 or could not be planned at all. Nevertheless, the institute managed to stay in contact with the public and scientists in other as well as new ways and to hold various events.

The annual call for nominations for the Ernst Haage Prize was continued in 2020, with the award ceremony in 2020 being postponed to the following year, so that in 2021 not only the prize winners of 2021 but also those of 2020 were honored. The event took place as a hybrid event with live broadcasting of the award ceremony on YouTube. In 2022, the Ernst Haage Prize could again be awarded on site at a festive reception.

Ernst Haage Award Ceremony 2022

A special highlight was the celebration of the 10th anniversary of the MPI CEC. In May 2021, the institute celebrated the successes of the last ten years with all staff and invited guests as well as citizens of Mülheim from the neighborhood. The two-day event was dedicated to science and successful cooperation with numerous partners. Guests such as State Secretary Dr. Dirk Günnewig (MKW NRW), Mayor of the City of Mülheim an der Ruhr Marc Bucholz, Dr. Christoph Rövekamp (BMBF) as well as directorate colleagues from the neighbouring MPI Kofo attended the event.

Anniversary celebration "10 years of MPI CEC"

The Frontiers Awards 2021 and 2022 were also presented during the anniversary celebration and honored two outstanding scientists.

For many years, the MPI CEC has presented the Frontiers in Chemical Energy Science Award to internationally renowned scientists for special achievements in the field of chemical energy conversion. During the award ceremony, the award winners gave a keynote speech and were available for scientific discussions, especially with young scientists from the institute.

In 2022, the MPI CEC was again able to open its doors to school classes and other visitor groups. This offer of scientific experiments and guided tours through the laboratories of the new buildings is especially popular with nearby schools and residents from the institute's neighborhood.

In addition, the communications team organizes a Girls' Day every year to get girls interested in scientific and technical professions. In 2020, the event was cancelled by the nationwide organizing team, however in 2021, the Research Communication team held a digital Girls' Day with female scientists from the Institute, in which girls from all over Germany participated. In 2022, Girls'Day took place again at the Institute with over 25 enthusiastic girls.

As a partner of the JuniorUni Ruhr, the MPI CEC held a seminar consisting of four individual events for 11 to 14-year-olds for the first time as part of a local project. The seminar series will also be held in the future with scientists from the institute and offers young, science-loving pupils the opportunity to get a taste of the everyday research life.

Internal communication

Another important aspect is also the implementation of internal communication measures to create transparency and keep all employees informed about what is going on in the Institute.

This is mainly done via the intranet, e-mails and a screen in the foyer. An internal newsletter is being set up and will promptly make internal circulars easier.

Impressions Girls' Day at MPI CEC

IMPRESSUM

Publishers Max Planck Institute for Chemical Energy Conversion
Editor Esther Schlamann · Dr. Marion Tiedtke · Sarah Troska
Reproductions Thomas Hobirk
Layout Sigrid Schelonka, Düsseldorf
Printing Scholz Druck, Dortmund

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