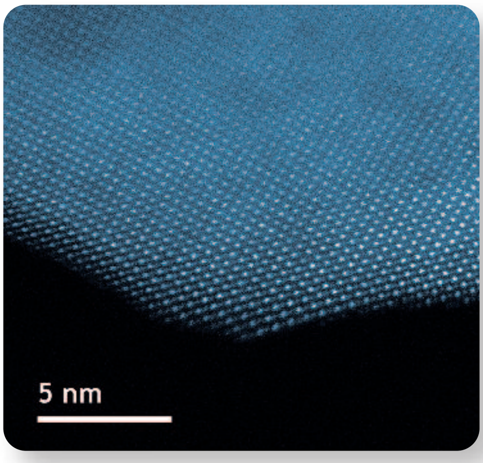
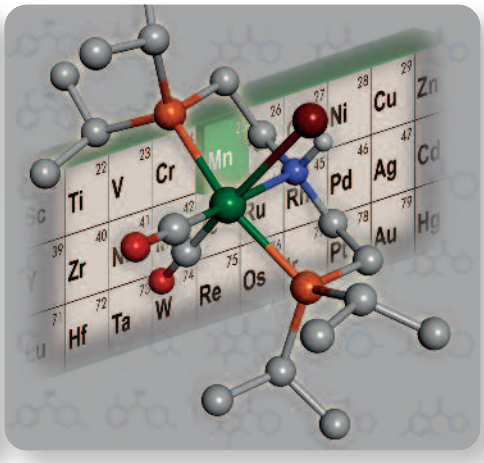
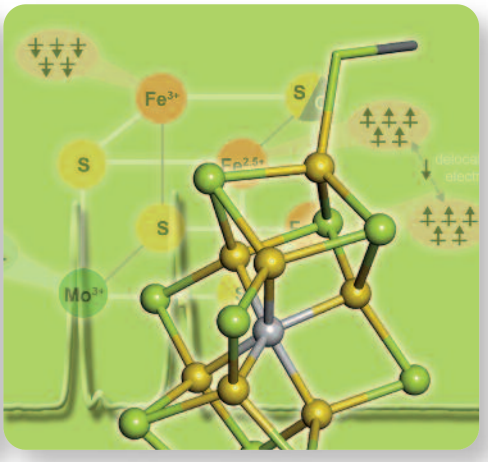
SCIENTIFIC REPORT

2017–2019

MAX PLANCK SOCIETY







MAX-PLANCK-INSTITUT FÜR
CHEMISCHE ENERGIEKONVERSION

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

General Development

At the time of the last report the Institute was about to appoint the first two directors in a novel structure. These attempts led to tow appointments of Serena DeBeer and Walter Leitner who form the core of the future MPI CEC. The relocation of Frank Neese to the MPI KOFO eventually worked out. The concept to link the two institutes to a Mülheim Chemistry Campus through a joint workspace in which the experimental activities of F. Neese remaining in the MPI CEC connect to the experimental work largely of S. DeBeer and increasingly also of W. Leitner was realized and is now in stable operation. This was only possible through special efforts of the Administration and of the General Administration in Munich as the hurdles created by different legal forms of the two MPI were enormous and needed year-long negotiations. During this intense period the institute lost the head of the Administration. Helga Oppenberg took over and had to restructure the Administration to make it fit for the challenges coming with the extension of the MPI CEC into its full dimension.

Serena DeBeer erected her Department in the existing building. She integrated some activities of W. Lubitz and integrated the spectroscopic analysis of biological systems related to chemical energy conversion in her research program. She further installed instrumentation for in-house X-ray spectroscopy. The creation of the Leitner department is more challenging as he will use the novel chemistry building that was not even started to be erected by the time of his appointment. A combination of provisional refurbishments in the old laboratory annexe (that will be demolished within the forthcoming 12 month) and the possibility to leave a substantial part of his operation at RWTH Aachen plus the re-structuring of the occupation in the existing building created a provisional operating environment. The creative phase of moving and reinstallation within all groups of the MPI CEC during the years 2017 and 2018 was conducted with excellent support from the technical staff and all co-workers of the institute. At present the institute is in an intermediate stable situation that will come to an end with the movements needed to populate the new buildings.

Mission of the Institute

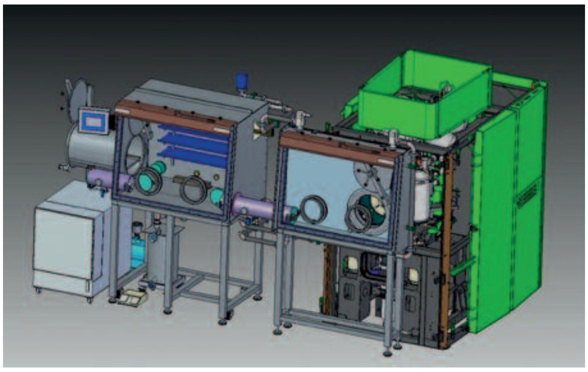
Resulting from the advent of the two new departments in combination with the fractional department of Robert Schlögl and their working structure through the various group leaders the Institute organized in 2019 a discussion day to reflect and define its scientific mission. The consolidated outcome is that the Institute defines its mission as creating a comprehensive understanding of the generation and function of active sites. A limited set of chemical transformations will be studied in this endeavour that all relate to the needs of future de-fossilized energy systems. The understanding to be reached should be universal across the various brands of catalysis namely molecular, biological and interfacial. The reactions are chosen as to delineate a system of sustainable processes required for the energy transformation. Storage and transportation of renewable electricity (hydrogen and its transport forms), fuels for mobility and materials from chemical industry transformations are target areas.

Reactions of common interest are the generation of hydrogen (electrocatalysis, dehydrogenations), the conversion into transport forms of ammonia and methanol and a range of hydrogenation reactions as applications for green hydrogen. Transformations of biomass are studied as well as novel concepts of streamlining multistep transformation with the concept of saving energy and resources. The research is organized according to two selected key challenges. One is the definition of size and structure of active sites in operation including its dynamical transformations. The other one is the identification of a strategy allowing the transition from noble metals to non-noble metals as active site components.

A key element in the profile of the institute is its desire to unite under its roof catalysis competence with molecules as well as with interfaces. The practical cooperation between these fragmented branches of science is considered as a critical element in the overall mission. It is a working hypothesis in the MPI that working catalysts consist of active sites coming about from dynamical fluctuations of an active material. This applies to molecules with exchanging ligands as well as to termination layers of solids undergoing frustrated phase transitions inhibited by the lack of nucleation of an ordered stable phase.

Analysis of the state-of-the-art reveals that these challenges require dedicated and tailored methodical developments. The Institute is determined to develop methods in synthetic chemistry and functional analysis according to the needs of elucidating the general questions named above. The institute will, however not invert the approach by developing methods and search for applications. The institute performs thus problem-oriented research. The problems tackled are in the science domain. The institute does not intend to develop or implement technological solutions per se. It rather relies on external collaborations to get in dialogue with the technology sphere. From there critical problems will be taken into research and scientific solutions and insights can be verified in a real-world technological environment.

Each department will define its research agenda independently. The discourse about the unifying concept of the function of active sites is taken as the common platform on which collaborative activities will be developed. From the year 2020 onwards a set of instruments is executed that in addition to intra-departmental activities will create the joint scientific exchange. One activity concerns methanol synthesis through molecular and interfacial catalysis as a common research focus. Here the state of reducing equivalents will be a particular focus (hydrogen atoms vs PCET and hydride transfer). Another joint activity is the creation of a new central scientific unit dealing with all aspects of electrocatalysis and serving as cross-sectional resource for experimental and analytical knowledge. The joint scientific facility "EPR spin probes" with the permanent leader (W2) Dr. Alexander Schnegg inherited the excellent knowledge base from the late department Lubitz for the future. It forms a strong relation to the EPR activities in the joint workspace and widens the methodical scope to applications in the area of interfacial catalysis. The project "EPR on a chip" jointly with the HZB Berlin underlines the independence of the leader. The joint facility "chemical reactor hall" supervised by Dr. Holger Ruland will come into operation throughout the year 2020 and provide a platform for joint activities in building and using chemical reactor infrastructure for various catalytic testing activities including operando monitoring of the reaction progress. An interfacing activity was the technical development of a semi-automatic transmission electron microscope with the ability to handle air-sensitive samples in a glove box environment. The development was performed with Thermo-Finnigan at the FHI and led to the installation of a custom-designed "ChemiTEM" instrument in Mülheim. Figure 1 presents a layout of this unique infrastructure.



Annual retreats with the directors, research group leaders and all group leaders and a regular open-topic group leader meeting complement the joining activities. Here the prospects of utilizing the joint scientific infrastructures (EPR, electrochemistry, electron microscopy, synchrotron radiation) will be discussed in a strategic context and options for common research will be developed resulting from the insights gained within the departments and research groups.

MPG Research Groups (MPRG)

From the beginning of the MPI CEC the instrument of MPG research groups was intended for making strong contacts to the neighbouring universities. The model is to create MPRG through joint selection of candidates with the colleagues from university and install the groups at the university with MPG providing the funding and the university providing the space and access to technical infrastructure.

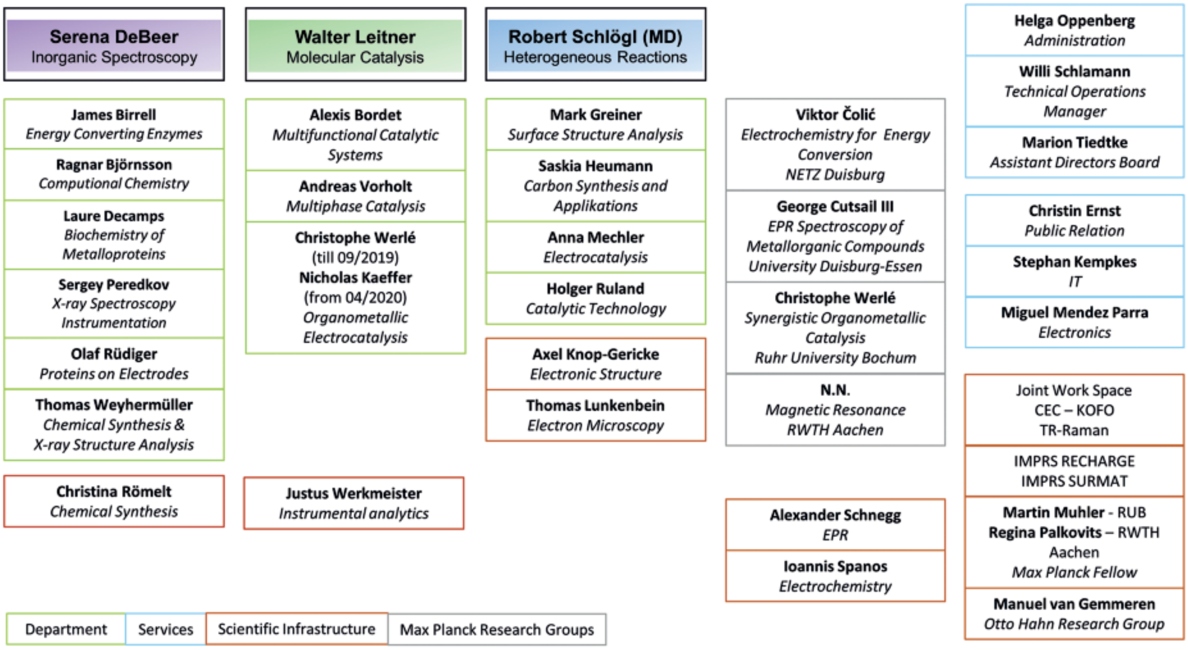
The first successful MPRG was created at the university of Duisburg-Essen (UDE) with Dr. Jennifer Strunk as leader of a group dealing with photocatalysis. The aim was to verify the possibility to perform a one-pot photoreduction of CO_2 to methane. This intensely researched subject was found to be based upon an artefact. In a stoichiometric and thermally driven reaction CO_2 and hydrocarbon impurities react with defect sites of the photocatalyst. In a series of publications describing methodical improvements and the core findings this subject was brought to a certain rest. During this work Dr. Strunk was awarded a W2 position at Rostock university in 2017 and the MPRG was terminated in 2019.

In a second round of implementations 3 new MPRG were created in 2019. Dr. Victor Čolić sets up a new group at UDE in the NETZ research centre in Duisburg dealing with oxygen electrocatalysis. Dr. George Cutsail set up an MPRG at UDE in Essen dealing with advanced EPR spectroscopy and metal organic chemistry. He will intensely use the EPR infrastructure at MPI CEC. Dr. Christoph Werlé sets up an MPRG at Ruhr University Bochum (RUB) dealing with synergistic organometallic catalytic reactions. All 3 MPRG are closely connected to departments in the MPI CEC such that a true collaborative contact is established between the MPI and the hosting universities and their contact chairs.

Structure of the Institute

Following the multiple changes in the institute its present structure is as outlined in the organigram. The managing Director wishes to thank all members and co-workers of the Institute for conducting the transformations pro-actively. The following comments help to understand the structure:

1. The only fully expanded department is that of Serena DeBeer.
2. The department of Walter Leitner is only partly complete as available space restricted the transfer of all activities from Aachen. It is expected that this will change within the next 12 months.
3. The fractional department of Robert Schlögl will cease to exist within the upcoming 3 years due to retirement of the director. Anna Mechler will leave the institute in 2020 as she obtained a W2 professorship at RWTH Aachen. Holger Ruland will switch position and become the manager of the chemical reactor lab as central facility. Some infrastructure for catalyst testing was created from external funding and is presently located in rented space in Oberhausen (C2C laboratory) This equipment will be brought to MPI CEC when it is no longer needed in the C2C laboratory. It will form a basis for interfacial catalyst testing that is expected to remain a core capability of the MPI CEC. The continuation of the remaining groups will be decided as the future expansion of the institute becomes clearer.



Organigram of the MPI CEC at the end 2019.

4. The institute has installed several scientific central units (red boxed) dealing with methods that are accessible to all members of the Institute. These groups are managed independently but attached to a scientific. Department. This will represent the group s needs and interests in the Kollegium and Administration.

   In this category also the local IMPRS (RECHARGE) is listed. It is directed by Frank Neese forming another common activity of the Mülheim Chemistry Campus. It is administered by Rita Groever located at the MPI CEC who carefully looks after the students and extends her support to other PhD students of the MPI CEC.
5. In addition, there exist service units in departments (blue boxes) that provide service mainly to the Department where they are attached to. They also reach out to support other departments in matters that are not common to all.
6. The Institute can support a total of 4 MPRG (grey boxes). Three groups are currently operating. The fourth group is in the process of selecting the leader. It is a special construction, as this group at RWTH Aachen will after its end in 2026 be converted into a regular chair of the university. Accordingly, an extended selection process under the lead of the university and with MPS directors not from the MPI is being conducted. The intention is here to build a strong and continuous relation to the prominent NMR tradition of the RWTH. In this way a strong synergy is formed between the MPI and the RWTH in a critical competence for this increasingly versatile and rapidly developing group of methods.
7. The non-scientific support groups (blue boxes right side) were also re-organized and unbundled from their former convoluted structure. The MPI is here particularly grateful to the General Administration who supported this process and helped with the creation of several necessary new positions.

Building Operation

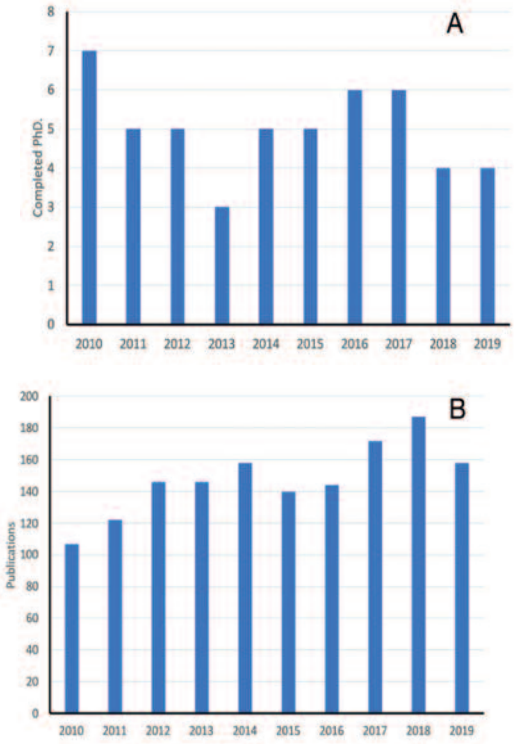
The completion of the Institute with 4 departments and the necessary common infrastructures requires substantial expansion of the space available. Forming the concept, acquisition of the land needed, planning and execution of the building was a key occupation of the MD over the last 8 years. Now as the buildings begin to reach their completion the institute sees the chance to grow into its final structure. This is only made possible by the professional support through the building department of the General Administration and through the enthousiastic engagement of Willy Schlamann and Kerstin Neurieder acting as the building representatives for the institute. Numerous smaller and larger difficulties endangered the execution of the buildings but were handled such that no relevant delay of the completion is expected. Proactive action of all involved allowed to combine several steps of the execution plan and to arrive in 2020 at a stage of the operation that Walter Leitner can move his operation into the chemistry wing of the buildings.

Selected Descriptors

The MPI CEC is still in a provisional state with less than half of the workforce that is intended for its full operation. In addition, there were multiple far-reaching changes in the institute concerning co-workers and infrastructure. In such a dynamical state it is challenging to retain stable output. This is seen in the limited number of graduate students admitted. The present state is not the foreseen normal operation. It is not easy to ensure adequate supervision in the growing state of the institute. The passion of the co-workers in the institute to perform science also in changing situations can be seen from the publication output. Naturally, the productivity as measured by this number varies over the research groups. Many of them were inhibited by moving operations. Several of them are new or are setting up their research infrastructure and are thus inhibited in executing their projects. The institute expects substantial dynamics in these figures with the upcoming consolidation of the operation.

Status of the building operation as of Nov 2019.

The photograph indicates status and dimension of the operation. The building at the right side will be the new central office building. Behind it the new chemistry building is situated offering sufficient space for 2 full departments with highly functional synthetic infrastructure. The existing building will then serve as the physics building housing the spectroscopy and advanced characterization infrastructure of the MPI. The picture does not show the last part of the operation in which two old building behind the existing wing (white in the photograph) will be removed and replaced by a dedicated building, housing electron microscopes that will be needed for catalyst nano-analysis and operando studies.



Selected output figures of the MPI.
(A) number of PhD Examinations, **(B)** number of publications.

Members of the Institute received Honours and Awards during the Period of this Report
The following list incompletely reports on recognitions that were obtained.

Serena DeBeer	Guest-Editor of 'Chemistry of Materials' - virtual issue on 'Applications of Modern X-ray Spectroscopy in Chemistry' (2017) Associate Editor 'Chemical Science' (2018) European Research Council Synergy Grant Awardee (2019)
Manuel v. Gemmeren	Thieme Chemistry Journal Award (2017) ADUC Award of the Gesellschaft Deutscher Chemiker (2019)
Walter Leitner	Casey Lecture of the University of Wisconsin, Madison, USA (2018) Evonik Lecture, 31st Congress of Chinese Chemical Society (2018) International Organic Chemistry Foundation Lecture, Kyoto/Osaka, Japan (2019) Finalist for the "Deutscher Zukunftspreis 2019" together with Dr. Christoph Gürtler and Dr. Berit Stange (Covestro AG)
Wolfgang Lubitz	Robert Bunsen Lecture of the German Bunsen Society for Physical Chemistry (2017) Luigi Sacconi Memorial Lecture in Chemistry, University of Florence (2018) Harden McConnell Lecture, Caltech, Pasadena, CA, USA
Robert Schlögl	ENI Award - Energy Transition (2018) Eduard Rhein Award - science communication (2019) Ipatjeff Lecture, CCSS Northwestern University, Evanston, USA (2019)
Andreas Vorholt	Professor Young talent award, DECHEMA (2017) Jochen Block Prize of the Gecats (2018)
Christophe Werlé	Guest-Editor of 'Organometallics' - special issue on 'Organometallic Electrochemistry: Redox Catalysis Going the Smart Way'

The Institute develops into a valued participant of larger projects and coordinated activities. During the reporting period members of the Institute participated in the following activities. The list * reports ongoing (with starting year) and new activities.

Title	Start	Type	PI
Spectroscopic Studies of N_2 Reduction: From Biological to Heterogeneous Catalysis	2014-2019	EU / ERC	DeBeer
Carbon2Chem - reducing CO_2 emissions from industrial plants	2016-2020	BMBF	Schlögl
REDIFUEL - Robust and Efficient processes and technologies for Drop In renewable Fuels for road transport	2018-2020	EU	Leitner
SFB TRR 247 - Heterogeneous Oxidation Catalysis in the Liquid Phase	2018-2022	DFG	DeBeer/Schlögl
e-conversion - Fundamentals of Energy Conversion Processes	2019-2025	Center of excellence	Schlögl
Fuel science center - Adaptive Conversion Systems for Renewable Energy and Carbon Sources	2019-2025	Center of excellence	Leitner
CatVIC - Catalytic Valorization of Industrial Carbon	2019-2022	BMBF	Schlögl
CUBE - Unravelling the secrets of CU-based catalysts for C-H activation	2020-2026	EU / ERC	DeBeer
Kopernikus Project of the Energy Transition – Power-to-X (P2X)	2016-2020	BMBF	Leitner

New Departments

In the present status of the development of the Institute it is adequate to prepare for the creation of the two additional departments completing the Institute. The collegium started this process in 2018 with planning to provide the necessary additional resources (positions) for new departments. With the permission of the President to start an appointment process for 2 more Departments arriving in late 2019 this pre-condition is ascertained. The institute wishes to thank the President for generously supporting its completion.

The scientific deliberations started in 2018 with a nomination procedure involving a list of suggestions from the collegium plus additional suggestions from members of the Fachbeirat and from directors from the scientifically related institutes. According to the mission of the institute, the subject area considered was interfacial catalysis and activities to bridge molecular and interfacial catalysis. Suggestions to consider engineering and life cycle analysis as relevant subject areas were discarded by the collegium for the argument that the mission of the institute is not to contribute to the implementation of the energy transition but rather to generate versatile and reliable "tools" for the applied sciences who may create practical solutions. Consequently, it is critical that the scientifically excellent new colleagues are interested in fundamental catalysis science and dedicated to team up with the existing two departments dealing largely with molecular systems in the ambition to understand creation and operation of active sites beyond the traditional simplified models.

The search process ended in a list of 6 candidates with whom the Institute conducted a 2-day symposium. Invited were the collegium, the group leaders, external advisors, the section chair, our appointment mentor and the interested public in Berlin. Critical deliberations immediately after the symposium produced two potential names. The initial plan to go for a double appointment procedure was discarded following a discussion with CPT section perspective commission. The institute rather decided to split up the process. Meanwhile another potential candidate who was identified in the initial nomination process but not considered to be moveable expressed interest and is being invited to discuss matters at the time where this report is being completed.

The collegium decided to go forward now with an appointment process for Dr. Yogesh Surendranath (MIT). This decision came after several intense deliberations with the candidate. In addition, the candidate and his wife visited for a week the institute and explored the option to live and work in the area. A possible position of the wife of the candidate at Cologne university was opened that needs to be supported by the MPG. The collegium expects that at the time of meeting of the Fachbeirat the appointment process is accepted by the section of CPT and an appointment commission has been installed.

Summary

The MPI CEC accommodated during the last 3 years its first phase of creation following an intermediate phase after its implementation in 2012. The multiple challenges were met by all involved with great enthusiasm and professionalism. The Institute is now at the onset of the second phase of its creation. In this phase the collegium has the task to complete the collaborative competence that is required by its mission. Catalysis science needs now an integrated and systemic approach going beyond simplifying model concepts. These have laid out foundations of a theoretical and quantitative concept. Their evolution into application is hampered, however by the gaps created by simplifying assumptions. The most important element in the systemic approach that can cure the over-simplification is to find a robust description of active sites and their true structural and functional analysis. The application of chemical energy conversion is a sufficiently large challenge justifying such an endeavour. The dimension of energy applications requires scalable solutions in processes and materials. They can only be found if theory and experiment cooperate on the basis of a stable and comprehensive understanding of catalysis. It is the vision of the institute to contribute to its methodical and conceptual evolution.

SCIENTIFIC ADVISORY BOARD OF THE INSTITUTE (FACHBEIRAT)

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Prof. Dr. Nils Metzler-Nolte	Ruhr University Bochum Bioinorganic Chemistry Universitätsstraße 150, 44801 Bochum, Germany
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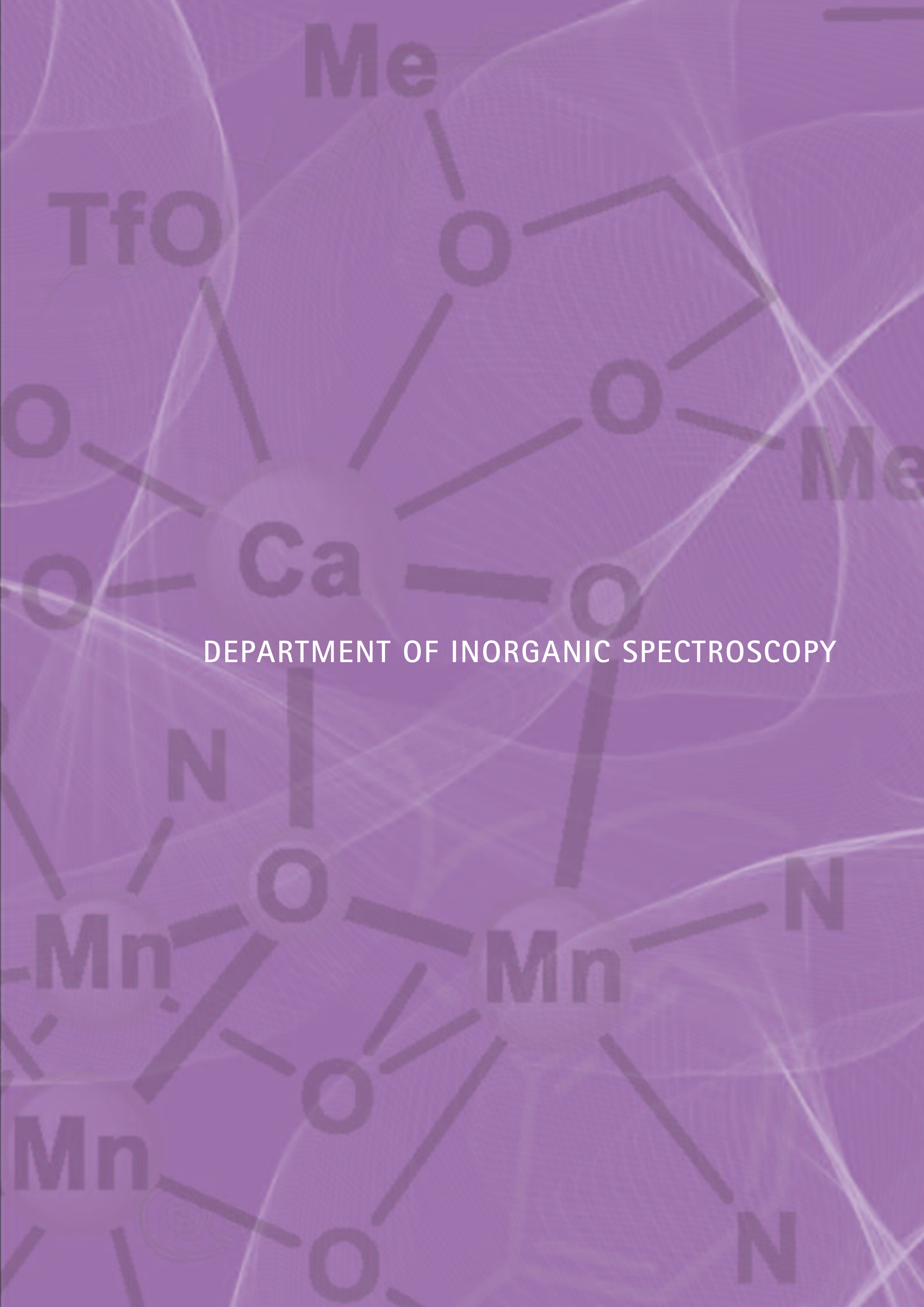
Prof. Dr. Joost Reek	University of Amsterdam Homogeneous, Supramolecular and Bio-Inspired Catalysis Postbus 94720, 1090 GS Amsterdam, The Netherlands
Prof. Dr. Bert M. Weckhuysen	Universiteit Utrecht Department of Chemistry Universiteitsweg 99, 3584 CG Utrecht, The Netherlands
Prof. Dr. Charlotte Williams	University of Oxford Inorganic Chemistry South Parks Road, Oxford OX1 3QR, U.K.

BOARD OF TRUSTEES OF THE INSTITUTE (KURATORIUM)



DEPARTMENT OF INORGANIC SPECTROSCOPY

DEPARTMENT OF INORGANIC SPECTROSCOPY

PROF. DR. SERENA DE BEER

Ph.D.: SLAC Stanford University, CA, USA (2002)
Beam Line Scientist: SLAC Stanford University, CA, USA (2001-2003)
Staff Scientist: Stanford University, CA, USA (2003-2009)
Assistant Professor: Cornell University, NY, USA (2009-2012)
Research Group Leader: MPI for Bioinorganic Chemistry; today: MPI CEC (2011-2017)
Group Leader: PINK Beamline, Helmholtz-Zentrum Berlin (since 2012)
Adjunct Professor: Cornell University, NY, USA (since 2012)
Honorary Faculty: Ruhr University Bochum (since 2014)
Director: MPI CEC (since 2017)

The department of inorganic spectroscopy was started in March 2017, at the time of Prof. Serena DeBeer's appointment as an MPI CEC director. From 2011-2017 she was a W2 professor and research group leader at the institute. Her department focuses on the development and application of advanced spectroscopic tools for understanding processes in heterogeneous, molecular, and biological catalysis. Broadly speaking, her group is interested in addressing a very fundamental question in energy research – namely, how do we reversibly store and release energy from a chemical bond in the most efficient manner possible? Effecting these conversions in an efficient way requires a catalyst – be it heterogeneous, a small molecule homogeneous catalyst or the biological catalysts found in enzymes. In all cases, the job of the catalyst is to lower the kinetic barrier in order to enable challenging chemical conversions. The DeBeer group is interested in identifying the unifying principles that enable fundamental energy conversion reactions. At present, the department focuses primarily on the key reactions shown in Figure 1 below.

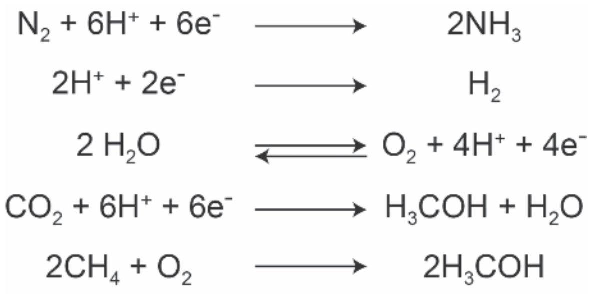


Figure1. Key small molecule activation reactions.

In particular, the department seeks to obtain an atomic level understanding of the changes that occur in the geometric and electronic structure of the catalyst over the course of the reaction. Ultimately, the detailed knowledge of reaction mechanisms at the homogeneous, heterogeneous and biological limit will provide the basis to guide rational catalytic design. As catalysts must ultimately be sustainable, the department primarily concentrates on earth abundant transitions metals.

The department of inorganic spectroscopy has a strong focus on the development and application of X-ray spectroscopic methods for understanding the geometric and electronic structure of transition metals. The utilized methods include, X-ray absorption spectroscopy (XAS), X-ray emission spectroscopy, resonant X-ray emission/ inelastic X-ray scattering (RXES/ RIXS), X-ray magnetic circular dichroism (XMCD), nuclear resonant vibrational spectroscopy (NRVS), and scanning transmission X-ray microscopy (STXM). The department is actively involved in the development of synchrotron beamlines to enable such experiments (e.g. PINK at BESSY and a new MPG beamline in planning at PETRA), as well as the development of in-house setups to allow such methods to become more routinely accessible tools in catalysis. In all studies, X-ray spectroscopic data are complemented by more standard spectroscopies (including EPR, UV-vis, IR, MCD, Raman and Mössbauer) and correlated with theoretical calculations. These efforts involve strong synergy with the department of Prof. Frank Neese in the context of the joint work space. Through the strong correlation between theory and experiment, the chemical information content of the spectroscopic data can be greatly advanced, thus providing more quantitative insights into the changes in geometric and electronic structure.

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. Since 2017, the department has published nearly 100 papers in top journals, including JACS, Angewandte Chemie, PNAS, and Nature Chemistry. In the sections that follow, the department structure is first briefly described followed by recent highlights in development and applications.

Department Structure

Presently, there are seven group leaders in the department of inorganic spectroscopy. The group leaders' expertise span biological catalysis (Drs. Birrell and Decamps), homogeneous catalysis and molecular syn-

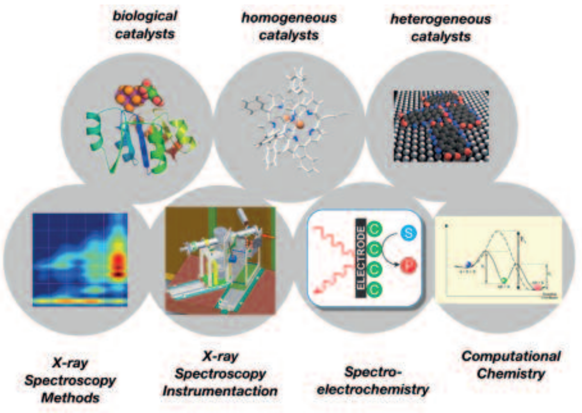


Figure 2. Key competencies and research areas in the department of inorganic spectroscopy.

thesis (Drs. Roemelt and Weyhermüller), X-ray spectroscopy instrumentation (Dr. Peredkov), spectroelectrochemistry (Dr. Rüdiger) and computational chemistry (Dr. Björnsson). Figure 2 highlights the key competencies and research areas spanned by the department. In total, the department is comprised of a total ~30 scientific (group leaders, PhD students and postdoctoral fellows) and technical staff members.

Presently Prof. DeBeer serves as the group leader for X-ray spectroscopy method development and directly supervises the Ph.D. and postdoctoral fellows in this research area. The group of Dr. Rüdiger takes the lead in applications of spectroelectrochemistry to heterogeneous catalysis in collaboration with Dr. Harun Tuysuz (MPI KoFo). Additional collaborations in the area of heterogeneous catalysis also exist between the department of inorganic spectroscopy and the departments of both Prof. Schlögl and Prof. Leitner, as well as with Max Planck Fellow, Prof. Martin Muhler.

Despite the broad efforts of the department of inorganic spectroscopy, the common energy relevant reactions (Figure 1) serve as a bridge between the various groups within the department and also in collaborative projects between CEC and KoFo. Within the DeBeer department, X-ray spectroscopy serves as a common tool, such that the instrumentation and method developers, have strong synergies with the catalysis groups.

The molecular synthesis group of Weyhermüller and Roemelt play an important role in providing well-defined molecular complexes that allow for the information content of various spectroscopic methods to be rigorously tested and quantitatively assessed. They also play an active role in the synthesis of molecular catalysts for small molecule activation. In addition, Weyhermüller provides a service role as the institute crystallographer and NMR spectroscopist, with support from two technical staff members. The biocatalysis groups of Birrell and Decamps are utilizing microbiology and biochemical approaches to generate variants of a range of energy converting enzymes, thus enabling the role of both the active site and the protein matrix to be better understood.

The group of Rüdiger, together with DeBeer, have taken the lead in developing operando approaches for X-ray spectroscopic studies, these have included combined X-ray spectroscopy and electrochemistry in the soft and hard X-ray regime, the development of nanoreactors for STXM of operating catalysts, and microfluidic mixing setups for the study of liquid phase catalysts. The department also has designed, built and is now commissioning the PINK beamline at BESSY in Berlin led by Peredkov, with active involvement from group leaders, Ph.D. students and post-docs from the MPI CEC.

The methodologies and instrumentation developed by the department of inorganic spectroscopy are utilized in a range of collaborations at the Mülheim Chemistry Campus (MCC) and also in a wide range of international collaborations.[1-8]

X-ray spectroscopy methodology development

VtC XES as a probe of O-O bond cleavage

The DeBeer group has actively involved in developing the information content of valence to core X-ray emission spectroscopy (VtC XES) and applying it to questions of interest in chemical catalysis for nearly a decade. Highlights include the use of this method to detect single

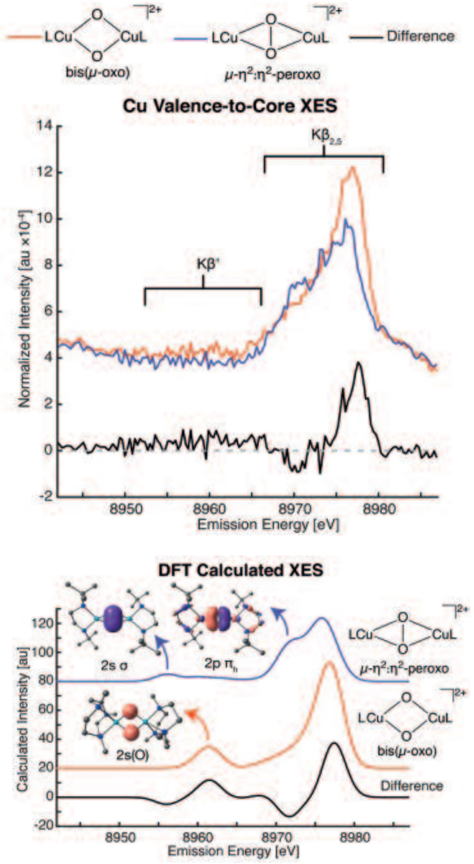


Figure 3. (top) Experimental Cu Valence-to-Core XES of a dicopper-peroxo and -oxo complexes with difference spectrum of the two plotted **(bottom).** Ground-state DFT calculated Cu Valence-to-Core XES of a dicopper-peroxo and -oxo complexes and select molecular orbitals plotted corresponding to unique transitions are plotted.

protonation events at metal active sites, as well as the identification of the central atom in the catalytic active site of both Mo- and V- nitrogenases. During the present review period, George Cutsail (an AvH postdoctoral fellow in the DeBeer group and now an independent research group leader at the MPI CEC) showed the ability to use VtC XES as a selective probe O-O bond activation in molecular copper complexes (Figure 3).[4] This work was featured as a "hot paper" in Angewandte Chemie, and also highlighted by the European Synchrotron Radiation Facility and ChemistryViews.org. By establishing spectroscopic features that are sensitive to the O-O bonding interactions, it was demonstrated that this method could serve as an experimental probe of small molecule activation by transition metals. This development is particularly promising for future time-resolved studies of O_2 activation.

2p3d RIXS as a probe of d-d transitions

The department of inorganic spectroscopy has made significant progress is utilizing 2p3d RIXS as a selective probe of the electronic structure of both molecular and heterogeneous materials.[9-11] Previously, applications of 2p3d RIXS were largely focused in condensed matter physics related research, and the efforts by the department represent some of the first applications of 2p3d RIXS to molecules. In brief, in a 2p3d RIXS experiment the transition metal active site being probed begins at a $2p^63d^n$ ground state, arrives at $2p^53d^{n+1}$ intermediate state, and subsequent decay results in a $2p^63d^{n'}$ final state (Figure 4). The difference between the initial $2p^63d^n$ ground state and the $2p^63d^{n'}$ final state is the equivalent of a d-to-d transition. However, it has been arrived at via two dipole allowed processes. Further due to 2p spin orbit coupling in the intermediate state, formally spin-forbidden transitions may gain intensity. This provides access to the full manifold of low-lying excited states, which is typically inaccessible by optical methods. This is particularly important in catalysis research as the low-lying states ultimately dictate the reactivity.

Further the elemental specificity of X-ray core spectroscopy provides additional selectivity. Recently, the DeBeer group has systematically applied this approach to a series of molecular ferrous and ferric sites in both O_h and T_d geometries.[10,12] Clear 2p3d RIXS signatures have been established for oxidation state and local site symmetry and indicate that the method can be utilized to selectively probe sites of a specific oxidation state and/or symmetry. The utility of this technique was highlighted for a Ni/Mn based water oxidation catalysts.[9] The study by Al Samarai, Rüdiger, DeBeer and coworker challenges the notion that the β-NiOOH phase is the active phase in OER and provides further evidence that the γ-NiOOH phase is cata-lytically active. 2p3d RIXS is presently being extended to spinel-based materials in the context of SFB/TRR 247.

1s2p, 1s3p, and 1sValence RIXS

The department has also been very active in exploring the information content of 1s2p, 1s3p and 1sValence RIXS. In general, 1s2p RIXS provides a means to access higher resolution XAS data, and is often referred to as high-energy resolution fluorescence detected (HERFD) XAS. Highlights of the HERFD technique include recent applications to the N_2 reducing enzyme nitrogenase and the CH_4 oxidizing enzyme, soluble methane monooxygenase, which will be highlighted in a later section. 1s3p RIXS provides a means to obtain oxidation and multiplet selective XAS, while 1s valence RIXS provides a means to obtain ligand selective XAS. During the present review period the information content of 1sValence RIXS was greatly enhanced by experimental and theoretical studies, which demonstrated that this method could be utilized to obtain polarization dependent information from isotropic samples.[13] This study was carried out in close collaboration with the Neese group.

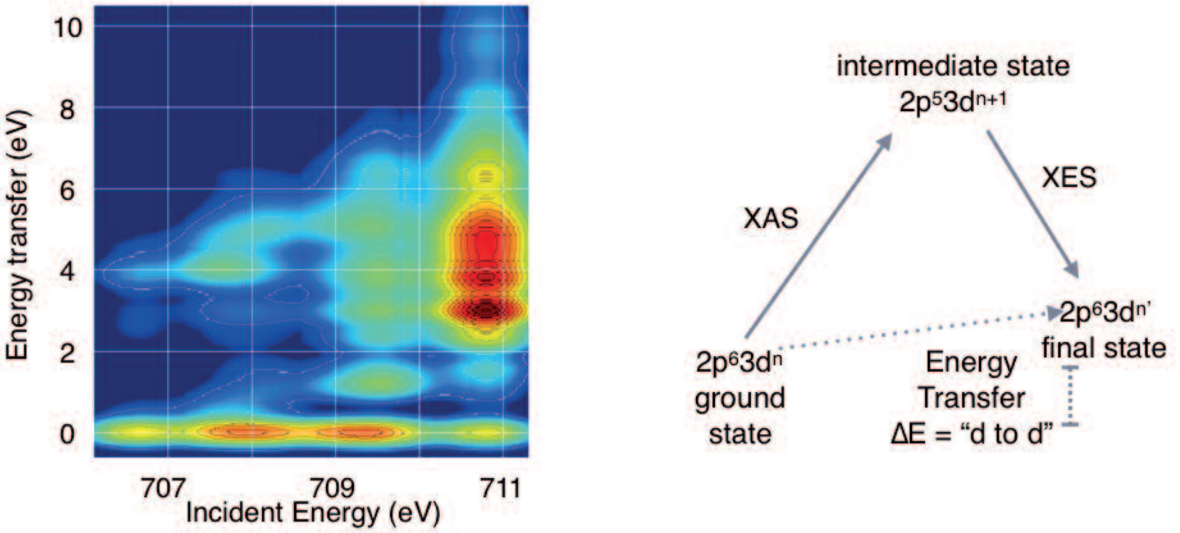


Figure 4. (left) A 2p3d RIXS plane at the Fe L-edge. The x-axis shows the XAS direction and the y-axis show the energy transfer axis, corresponding to d-d transitions **(right)**. The states involved in a 2p3d RIXS process.

XMCD

Another important area of development in the department has been establishing the information content of X-ray magnetic circular dichroism for applications in molecular and enzymatic systems. XMCD utilizes left and right circularly polarized X-rays and in a simple picture provides access to alpha and beta spin excitation channels. During the 2017-2019 timeframe, initial studies were carried out on molecular iron model complexes in order to establish the trends for both oxidation states and changes in covalency.[14] These studies were then extended to nitrogenase and related model complexes, providing experimental evidence for an unusual non-Hund configuration in a model for the FeMoco active site for N_2 reduction.[15] This work was featured by Angewandte Chemie (Figure 5).

Figure 5. A recent feature of the departments XMCD work on nitrogenase and related models, featured by ACIE. Adapted from reference 15.

X-ray spectroscopy instrumentation developments

Developments at synchrotron facilities.

In order to study catalytic systems by X-ray spectroscopy (under ex situ, in situ or operando conditions), one requires access to dedicated instrumentation to enable these experiments. Historically this has occurred at synchrotron facilities. However, recently there has become an increasing interest in the development of in-house X-ray spectroscopy setups to enable more facile access to routine measurements, and to use synchrotron beamline for more demanding experiments. In the department of inorganic spectroscopy, there are active efforts in the development of synchrotron beamlines, setups for in situ/operando studies and in-house instrumentation developments.

During the 2017-2019 period the department has been very active in the design and construction of the PINK beamline at BESSY in Berlin, with efforts led by Dr. Peredkov. The beamline is designed to span the ~2-10 keV energy range and will allow for a range of XAS, XES and RIXS experiments with dedicated sample environments for studies of catalytic systems (including low temperature cryostats, electrochemical cells, liquid flow cells and reactors). The CEC has been responsible for all beamline elements downstream of the last optical element, while the upstream portion of the beamline, including the undulator insertion device, are the responsibility of HZB. Due to delays in installing the hard X-ray undulator at PINK, the CEC team instead transported their instrument to the PETRA synchrotron at Hamburg for initial commissioning. The CEC team was responsible for all mechanical design, engineering, construction and control software for the PINK spectrometer, and was able to have the setup fully installed at beamline P64 at PETRA, commissioned and have initial data with only two weeks of beamtime. Beginning in October of 2019, the actual commissioning at BESSY was then able to begin. Presently, the multilayer monochromator is installed, and experiments with ~100 eV band width "pink beam" are possible, enabling non-resonant XES experiments. It is expected that commissioning of the double crystal monochromator, which will enable XAS and RIXS experiments, should begin early in 2020.

In collaboration with the FHI, the CEC team is also actively involved in planning for an MPG hard X-ray beamline at PETRA. The planned beamline will have an accessible energy range up to ~55 keV and will enable combined spectroscopy and scattering based techniques, allowing both local and long-range changes in catalytic materials to be monitored simultaneously.

In situ/Operando Set-ups
for Synchrotron Spectroscopy

During this evaluation period, the department has been actively developing new setups for both in-situ and operando X-ray spectroscopy experiments. This has included a nanoreactor for STXM experiments under high pressures (up to 8 bar) and temperatures (up to 800 °C) The nanoreactors are made of either silicon nitride or silicon carbide, thus enabling studies at the C and N K-edges, respectively without interference from the reactor window material. The nanoreactor has 41 circular windows with a diameter of 6 µm and ~18 nm thickness, which are etched between the windings of the micro-heater spiral. The presence of the windows on these locations allows for sufficient transmission of X-ray signal. The nanoreactor also contains inlet/outlet which is used to load the nanoparticles into the channel and for the pressurization of the microchannel by flowing the gasses. This setup (shown in Figure 6) has been utilized for in situ STXM studies of iron-based ammonia synthesis and decomposition (in collaboration with Prof. Schlögl and Prof. Behrens), as well as for studies of dry methane reforming by Ni, Co and Fe based catalysts (in collaboration with Prof. M. Muhler).[16]

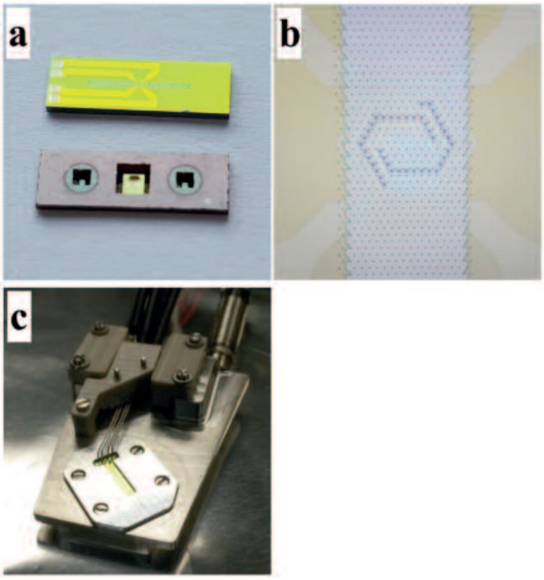


Figure 6. a) Image of a silicon nitride nanoreactor **b)** microscopic image of the microchannel located in the nanoreactor. **c)** Image of the mounted nanoreactor on the gas-phase holder.

Another major area of development has been the extension of spectroelectrochemical (SEC) capabilities from UV-Vis, EPR and FT-IR, to advanced X-ray spectroscopies. The group of Rüdiger has developed a range of SEC cells that are compatible with soft, tender and hard X-ray setups. The designs include cells for studies of homogeneous catalysts in solution and a cell to study immobilized catalysts. These setups have already been used for studies of molecular catalysts, proteins and heterogeneous catalysts.

In addition, in collaboration with the group of Prof. Lois Pollack (Cornell University), the DeBeer group is developing microfluidic setups for studies of molecular and biological catalysts under transient conditions. In December 2019, the first successful experiments on a dilute metalloprotein were carried out by the group, demonstrating the viability of this setup for studies of enzymatic intermediates.

In-house X-ray spectroscopy developments

Funded by an ERC Consolidator grant the DeBeer group, in collaboration with B. Kanngießer (TU Berlin), constructed an in-house X-ray emission spectrometer which began commissioning at the end of 2016. During the present evaluation period, the commissioning was completed and a publication describing the instruments capabilities for catalysis research was published in the Review of Scientific Instruments.[17] In addition, the first scientific application papers using this instrument were published.[18,19] A particular highlight was a calcium XES study, which systematically showed the information content of calcium VtC XES and how this method could be used to distinguish different proposed core confirmations in the Mn_4CaO_5 oxygen evolving complex of photosystem II. This research was selected as the cover for Inorganic Chemistry and was the master's project of Zac Mathe, for which he won the German Chemical Society (GDCh) Master Prize.

In addition to the in-house XES instrument, the department of inorganic spectroscopy also purchased a combined XAS/XES instrument from EasyXAFS for operations in the 5-12 keV range. The instrument was installed in late 2018 and is now in routine use in the department for measurements on concentrated solids. Presently, we are also working on a combined electrochemistry setup for this instrument. The first publications using this instrument are presently in preparation.

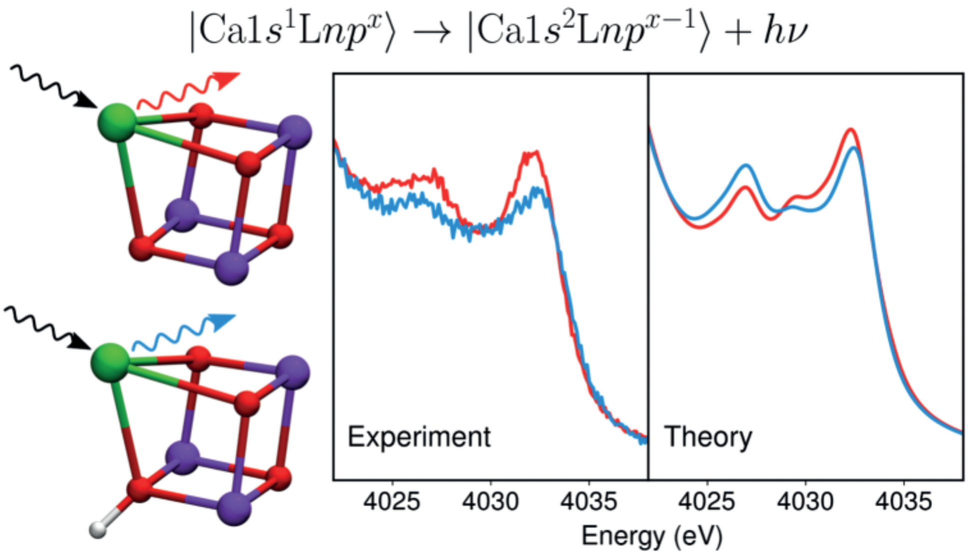


Figure 7. (left) Models of the oxygen evolving complex of photosystem II studies by VtC XES. The experimental and calculated spectra are shown. Data were measured using the MPI CEC in-house XES spectrometer. Figure adapted from reference 19.

Selected Research Highlights

Studies of biological methane oxidation.

The catalytic oxidation of methane to methanol is considered one of chemistry's grand challenges. However, despite decades of research, synthetic chemists have yet to realize this goal. The ability to affect this conversion in a controlled and selective manner would greatly enhance the ability to utilize natural gas via the conversion to liquid fuels. Present industrial processes to enable methane oxidation invole costly mutli-step processes that are inefficient and not readily scalable. In contrast, methanotrophs are able to catalytically oxidize methane at ambient temperatures and pressures utilizing the enzyme methane monooxygenase (MMO). The soluble form of MMO contains a dinuclear iron active site, which is known to be the site of O_2 activation and subsequent methane oxidation. However, the exact nature of the active intermediate that is responsible for abstracting a proton from methane, the so-called intermediate Q, has remained a subject of controversy for more than twenty years. Yet understanding exactly what intermediate Q is, is absolutely essential for a complete understanding of the mechanism and ultimately for guiding rational catalytic design. Both so-called "closed" and "open" core models of Q have been proposed (Figure 8).

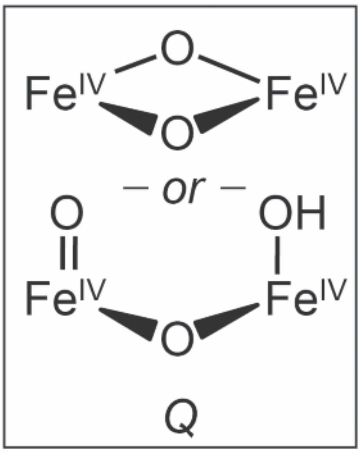


Figure 8. Proposed core structures for intermediate Q. Closed core **(top)** and open core **(bottom)**.

The closed core model was most strongly supported by the observation of a short Fe-Fe vector from EXAFS data. However, studies of molecular catalysts for C-H activation showed open core structures to have much higher reactivity. Recently the department of inorganic spectroscopy revisited this important question by applying advanced X-ray spectroscopic approaches.[2,3] Specifically, high energy resolution fluorescence detected XAS was utilized at the Fe K-alpha line in order to obtain higher resolution Fe K-edge data. The analysis of the Fe K- pre-edge region in combination with time-dependent DFT calculations strongly favor an open core. Further the HERFD detected EXAFS show no evidence for the short Fe-Fe vector observed in previous publications. In a detailed and systematic study, Cutsail and coworkers showed that the previously reported short 2.5 Å Fe-Fe vector observed in the EXAFS most plausibly arises from background iron contamination in the experimental setup, which is eliminated in HERFD EXAFS due to the increased selectivity (Figure 9). These studies were published in two separate publications in JACS,[2,3] and have important implications for our understanding of biological methane oxidation and also for studies of dilute iron-containing catalytic systems in general.

Selenium HERFD XAS reveals localized electronic structure in the FeMoco active site of nitrogenase

During the present evaluation period the department has made great progress toward deepening our understanding of biological nitrogen reduction through both experimental and computational efforts. This has resulted in 11 publications in this area from the department.[5,14,15,20-28] In addition, the department also authored a Chemical Review article on this subject, which is due to be published in summer 2020.

Here a recent JACS paper from the department is highlighted in which selective selenium substitution is utilized to probe the local electronic structure of the catalytic FeMoco active site of molybdenum nitrogenase.[26]

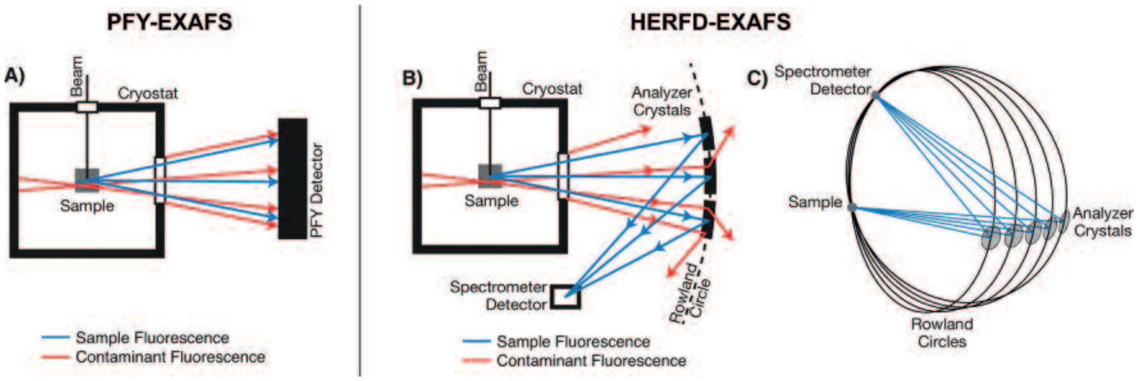


Figure 9. (left) standard partial fluorescence yield EXAFS setup showing how both signal from the sample and contaminating fluorescence from the background can reach the detector. **(right)** HERFD-EXAFS setup showing how the use of a Bragg-optic-based spectrometer eliminates unwanted contaminating fluorescence. Adapted from reference 3.

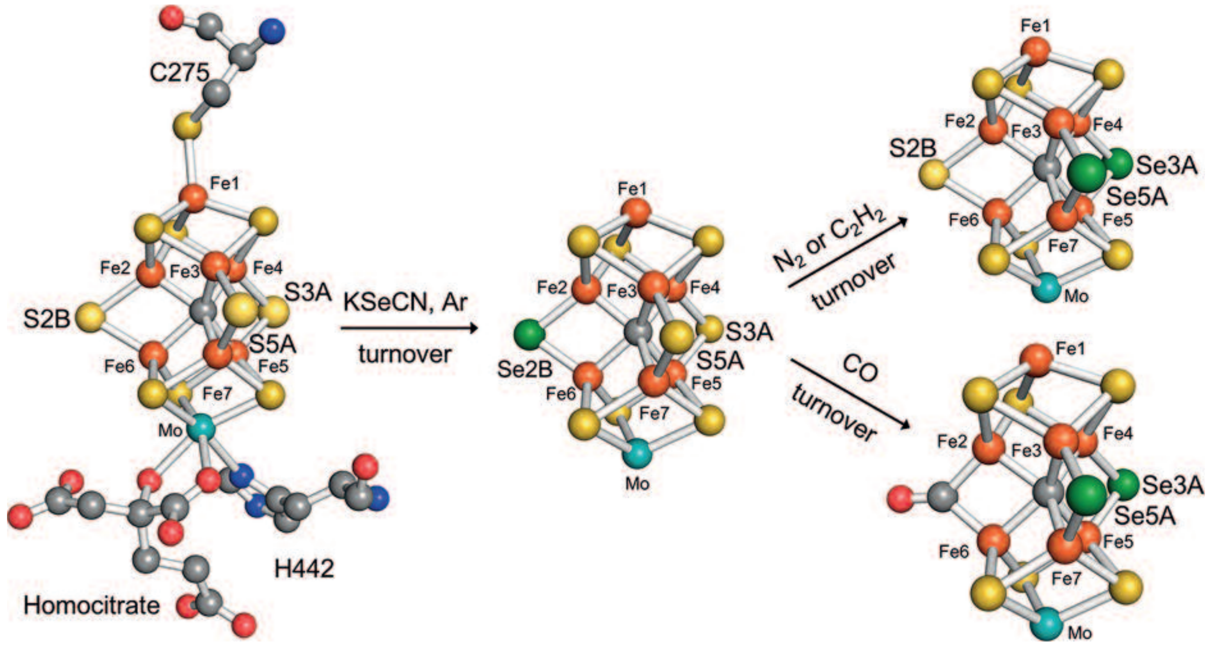


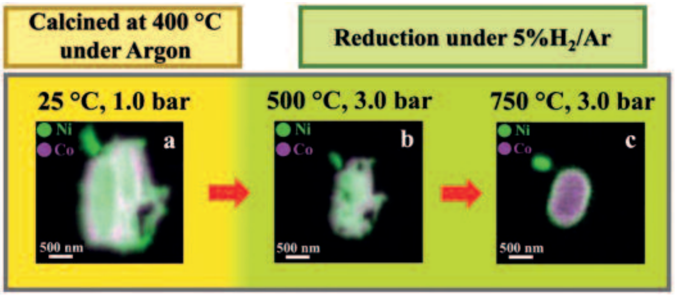
Figure 10. Se incorporation and migration reactions in FeMoco from A. vinelandii (PDB-IDs 3U7Q, 5BVG, 5BVH). Nitrogen atoms are shown in blue, oxygen atoms in red, and carbon atoms in gray. Adapted from reference 26.

Figure 10 (far left) shows the $MoFe_7S_9C$-containing FeMoco active site of nitrogenase. The presence of seven iron sites at FeMoco, with an additional 8 irons in the electron transfer P-cluster site, makes selectively probing the FeMoco active site very challenging. Further sulfur cannot readily be utilized as a probe due to the presence of 72 total sulfurs in MoFe protein. One way to obtain selectivity is to utilize selenium substitution, which can be achieved by utilizing KSeCN under turnover with protons. Interestingly, selenium substitutes selectively into the 2B position of FeMoco, allowing the Se to be utilized as a spectator to probe the irons 2 and 6 (Figure 10, middle panel). By turning the protein over with N_2 or C_2H_2 migration of the Se to the 3A and 5A positions is seen with roughly equal proportions. This suggest that the active site is much more dynamic than conventional static pictures suggest. Further the migration of the selenium allows the irons at the 3, 4, 5 and 7 positions to be studied relative to those at the 2 and 6 position. The results of the Se HERFD XAS shows that the electronic structure is much more asymmetric than our conventional pictures of iron-sulfur electronic structure. These results suggest that the protein may utilize the electronic asymmetry to tune a specific site for interaction with substrate. Figure 10 bottom right shows the selective binding of CO at the 2B position, further highlighting nature's engineered selectivity.

STXM studies of a Dry Methane Reforming Catalyst.

Presently, there is great interest in the DMR reaction, as it provides a means to convert harmful greenhouse gases (CO_2 and CH_4) into industrially useful syngas (CO and H_2). Nobel metal catalysts are particularly efficient at effecting this conversion, however, they are costly and not sustainable. It is for this reason that interest has grown in earth abundant Ni-based catalysts for DMR. Unfortunately, the Ni-based catalysts suffer coking and readily become deactivated. It has been found that the addition of cobalt improves the stability of Ni DMR catalysts and inhibits coking. There have been many reports as to why this may be the case, and the prevailing hypothesis in the present literature is that this may be due to the formation of a Ni/Co alloy. Recently Askari et al. have shown how a Ni/Co catalyst transforms under operating conditions during the reductive activation step and the subsequent DMR reaction (Figure 11).[16] Interestingly, the particles start out as Ni/Co alloy materials. However, upon reduction clear elemental segregation occurs in which all the Co migrates to the center of the nanoparticles. This has been demonstrated in multiple STXM experiments and suggests strongly that the particles undergo a "self-assembly" process in order to optimize catalytic activity.

Figure 11. a) STXM elemental composition maps showing the distribution of Ni (in green) and Co (in violet) for: **a)** the freshly calcined particles, **b)** following the reduction step at 500 °C under 5% H_2 in Ar, where the Ni and Co oxides are reduced, and **c)** at 750 °C and under 5%H_2/Ar flow where the Ni and Co Al_2O_4 are fully reduced.



These results thus provide the first clues as to how particle dynamics and morphology optimize catalytic activity. Importantly, these results provide experimental evidence against the commonly accepted notion that Ni/Co alloys form the active sites for catalysis. In our studies, it is clear that the surface of the catalyst is in fact entirely Ni-based. Further, under in situ DMR conditions, the formation of Ni-rich branches is observed, which suggest a pathway for the eventual deactivation of the catalyst. These studies highlight the ability of in situ STXM to monitor the evolution of particle morphology and electronic structure under operating conditions. Hence, from a methodological perspective, STXM of catalyst under operating conditions has great promise for guiding rational catalytic design.

Future studies of copper-based C-H activation.

Looking forward, the department will also engage in systematic studies of copper-based C-H bond activation at the biological, homogeneous and heterogeneous limits. Specifically, this will involve taking inspiration from copper-based enzymes that are able to activate strong C-H bonds (e.g. lytic polysaccharide monooxygenase and particulate methane monooxygenases enzymes) and copper zeolites which can oxidize methane, and engineering the key design principles into metal organic frameworks (MOFs). This is part of a collaborative effort between the CEC and groups in Norway and Italy. Recently, S. DeBeer, together with S. Bordiga, U. Olsbye and V. Eijsink, received an ERC Synergy Grant to fund this new research direction (Figure 12).

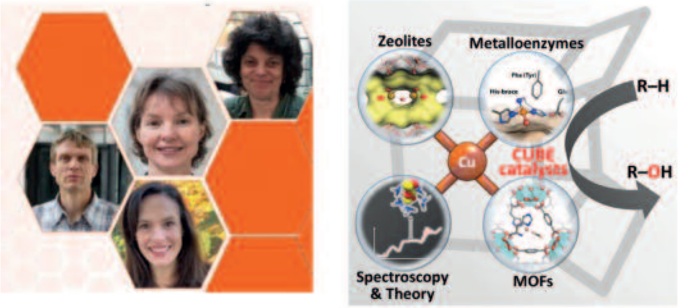


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Figure 12. (left) The PIs for the ERC funded Synergy project "CUBE". Bordiga, Olsbye, Eijsink and DeBeer. **(right)** An overview of the approach that will be utilized to understand Cu-based C-H activation.

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DEPARTMENT OF INORGANIC SPECTROSCOPY

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Mechanisms of catalysis in energy converting metalloenzymes

Metalloenzymes such as hydrogenases (H_2ase), CO dehydrogenase (CODH), formate dehydrogenase (FDH) and methane monooxygenase (MMO) (**Figure 1**) carry out some of the most fundamental energy converting reactions in nature at very high rates and with very high efficiency using earth abundant metals in their active sites. Despite the importance of these reactions in energy conversion, the mechanisms by which these enzymes carry out their reactions are poorly understood. Using a combination of biochemical, electrochemical and spectroscopic techniques (Figure 1) my group is trying to learn how the active site structure and surrounding coordination spheres guide the mechanism of small molecule transformations in these enzymes. In particular, multiple spectroscopic techniques (UV-Vis, IR, Raman, EPR, MCD, Mössbauer, X-ray and NRVS) are combined to provide a complete picture of the active site and interactions with the surrounding ligands.

Recombinant production of complex metalloproteins

A severe hurdle in studying many metalloproteins is often the low yield and lengthy procedure associated with purification from native host organisms. The enhanced yields, coupled with the simplicity of genetic manipulation, makes over-expression in recombinant hosts such as *Escherichia coli* an attractive alternative (Figure 2). However, many metalloproteins cannot be easily produced in traditional *E. coli* systems and so the methods of expression or the hosts used must be further developed. Our group is developing stable recombinant expression systems for high yield production of metalloproteins to facilitate sample intensive spectroscopic investigations.

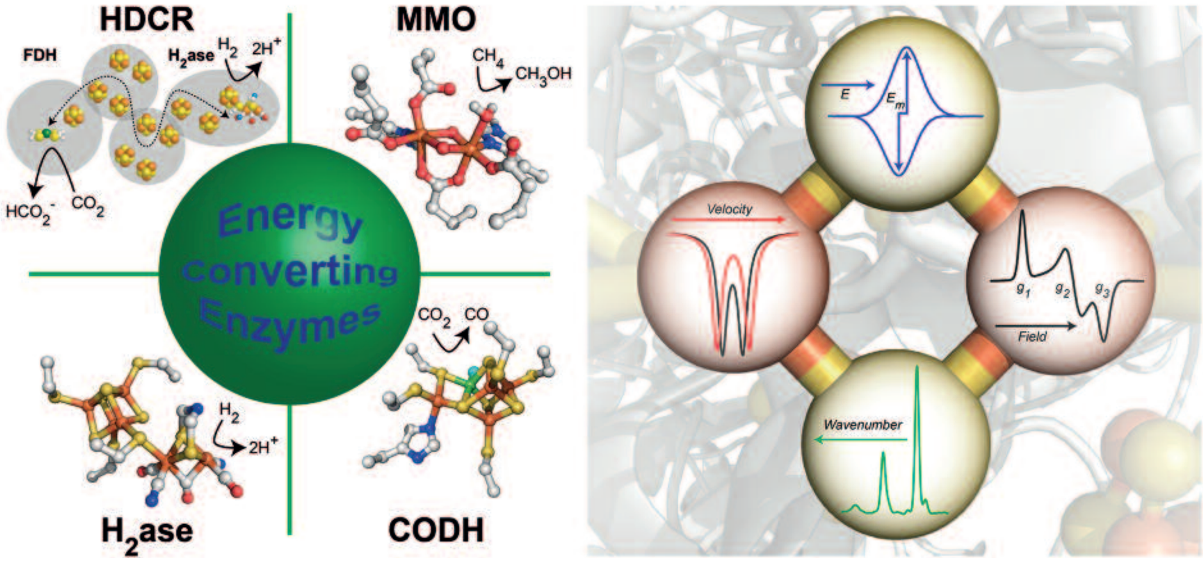

Figure 1. Enzymes studied in the group and techniques used. Left: the arrangement of cofactors in the hydrogen dependent CO_2 reductase (HDCR) and the structures of the active site cofactors of hydrogenase (H_2ase), methane monooxygenase (MMO) and CO dehydrogenase (CODH). Right: metallocofactors in proteins (background image) can be studied by a number of different techniques including electrochemistry (top), Mössbauer spectroscopy (left), infrared (IR) spectroscopy (bottom) and electron paramagnetic resonance (EPR) spectroscopy (right).

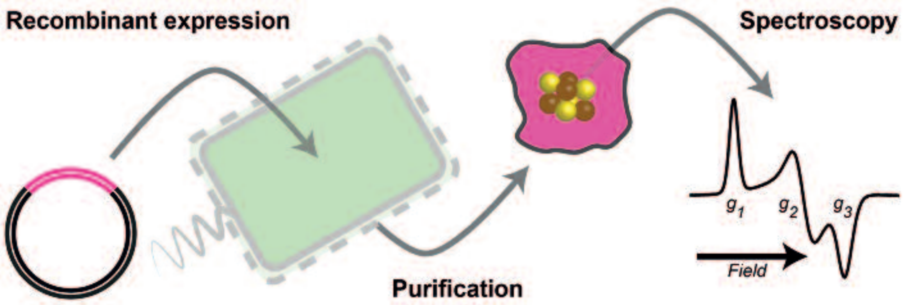

Figure 2. Recombinant production of metalloproteins. Scheme illustrating the workflow for recombinant production of a metalloprotein in *E. coli*. Plasmid DNA vectors encodingproteins of interest are introduced into *E. coli*. Cells are grown and protein production is induced. Proteins are purified and characterized (an EPR spectrum is shown).

[FeFe] hydrogenase

[FeFe] hydrogenases are highly active and efficient H_2 converting enzymes, achieving turnover frequencies of (at least) 10,000 s^{-1} for H_2 production and (at least) 150,000 s^{-1} for H_2 oxidation, with essentially no overpotential requirement. Their mechanism of catalysis remains elusive, in spite of intensive efforts from a number of research groups. During my time working with Prof. Wolfgang Lubitz, I helped to contribute substantially to the group's research efforts in this area. Notable achievements were the observations of proton-coupled electronic rearrangement between the two parts of the active site H-cluster (Figure 1) [1], redox anticooperativity between the H-cluster and accessory F-clusters [2], spectroscopic characterization of the crucial terminal hydride bound intermediate [3], and observation of disrupted proton-coupled electronic rearrangement in a sensory hydrogenase [4] and a cysteine to histidine variant [5]. Together this work has led to the development of an elegant catalytic mechanism for these enzymes (Figure 3). This successful work is now being followed up in collaboration with both Prof. Serena DeBeer and Prof. Wolfgang Lubitz, and with independent funding from the Deutsche Forschungsgemeinschaft Priority Program 1927 "Iron-Sulfur for Life: Cooperative Function of Iron-Sulfur Centers in Assembly, Biosynthesis, Catalysis and Disease". An important recent discovery was how to reversibly convert a highly oxygen sensitive [FeFe] hydrogenase into an oxygen stable inactive state [6]. In collaboration with Jun-Prof. Ingrid Span at Heinrich Heine Universität in Düsseldorf, we were able to obtain crystals of this hydrogenase and solve the structure (manuscript submitted). The structure, together with anomalous diffraction data show a sulfur ligand bound to the formerly open co-ordination site. X-ray absorption, infra-red, nuclear resonance vibrational and resonance Raman spectroscopies, together with quantum mechanics molecular mechanics calculations, in collaboration with Dr. Ragnar Bjornsson, confirm the nature of the ligand as SH^-. Currently running [FeFe] hydrogenase projects aim to tackle a wide range of open questions, using a vast number of techniques, in collaboration with numerous national and international partners.

Ni-dependent carbon monoxide dehydrogenase

In nature, CO_2 conversion into biomolecules in achieved by a number of different biochemical pathways. One of these is the Wood-Ljungdahl pathway of the acetogenic bacteria. This pathway starts with the reduction of CO_2 to CO by enzymes called carbon monoxide dehydrogenases (CODH). The CODH from anaerobic organisms contains a fascinating active site structure known as the C-cluster in which a canonical [4Fe-4S] cluster is pulled apart and a Ni ion inserted to give a [Ni-4Fe-4S] cluster (Figure 1). How these enzymes operate is still not well understood but is thought to occur by binding of the carbon of CO_2 to an open coordination site on Ni, while the unique "dangler" Fe interacts with one of the two oxygen atoms. Electrons are then transferred to the CO_2 molecule giving CO bound to Ni and OH^- bound to Fe. However, these ligand-bound intermediates have not been observed spectroscopically, and the proposed catalytic cycle remains rather primitive (Figure 4). We are currently producing the Ni-CODH enzymes from the hyperthermophilic bacterium *Carboxydothermus hydrogenoformans* recombinantly in *E. coli* and characterizing them using spectroscopic methods. Another project is to produce CODH in the absence of Ni and study the process of Ni-insertion in detail. A key component for this process is thought to be the metal-binding ATPase CooC3. We are also producing this enzyme and studying its metal binding properties and catalytic activity, and attempting *in vitro* reconstitution of Ni into a Ni-deficient form of CODH.

Formate dehydrogenase and the hydrogen dependent CO_2 reductase

A second pathway for the acquisition of carbon in nature is the conversion of CO_2 to formate. This is carried out by Mo or W dependent enzymes called formate dehydrogenases (FDH). The active site of these enzymes is complex (the metal ion (Mo or W) is coordinated by the cis dithiolene group of two pyranopterin guanidine dinucleotides, a (seleno)cysteine residue and a sulfide group) and their mechanism of catalysis remains highly controversial (Figure 5).

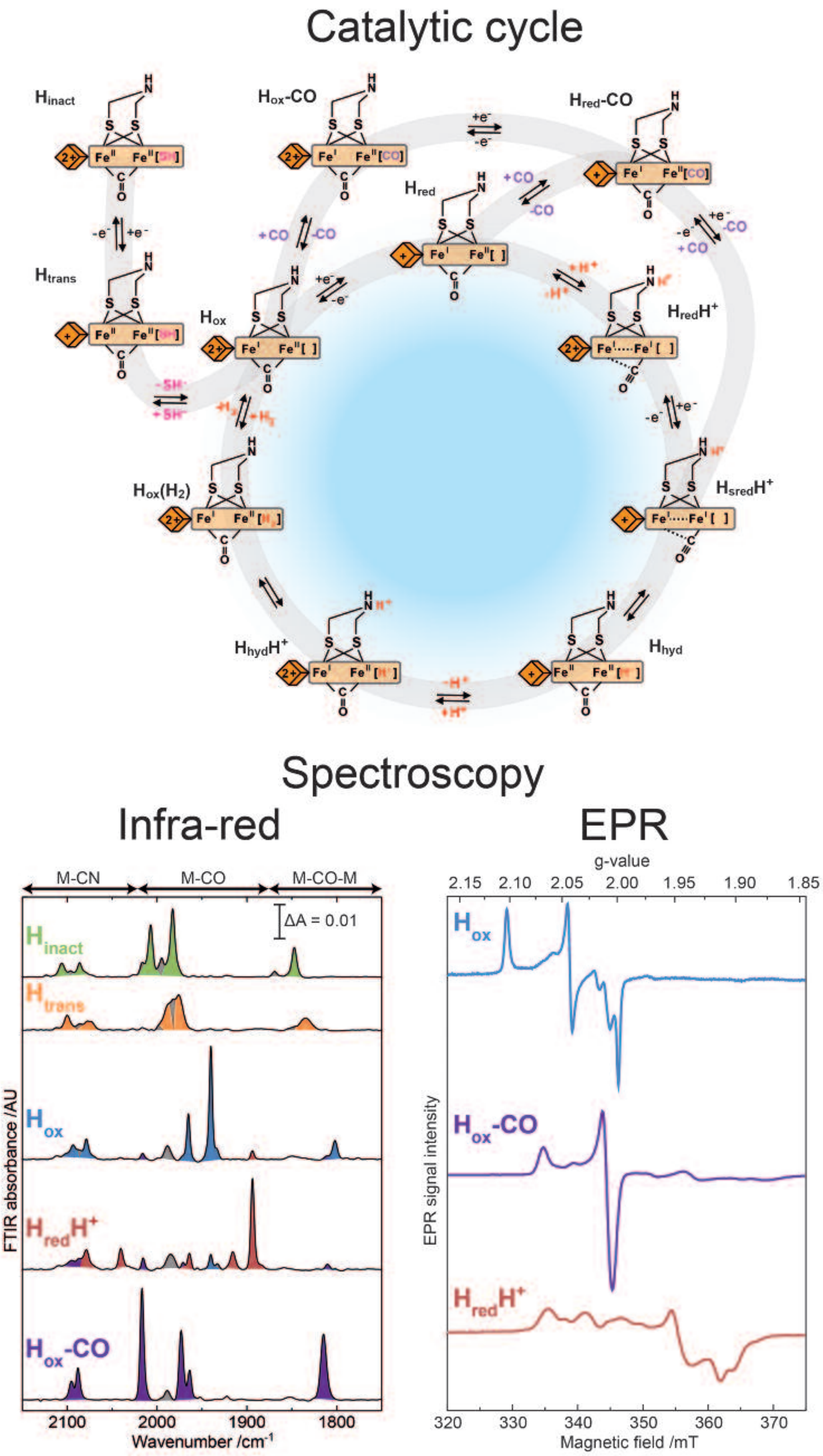

Figure 3. Catalytic cycle and spectroscopy on [FeFe] hydrogenase. **Left:** putative catalytic cycle for the [FeFe] hydrogenase including active states, CO-inhibited states and sulfide inhibited states. The [4Fe-4S] sub-cluster of the H-cluster is represented by an orange cube and the [2Fe] subcluster is represented by a light orange rectangle. The bridging aminopropane dithiolate ligand and the bridging CO are shown but the terminal CO and CN^- ligands are omitted for clarity. **On the right,** infra-red and EPR spectra are shown for several key states of the enzyme from *Desulfovibrio desulfuricans*. H_{ox} and H_{ox}-CO EPR spectra originate from the low spin Fe(I) ion of the [2Fe] subcluster. For the $H_{red}H^+$ state, the H-cluster is EPR silent and the EPR spectrum originates from the accessory clusters.

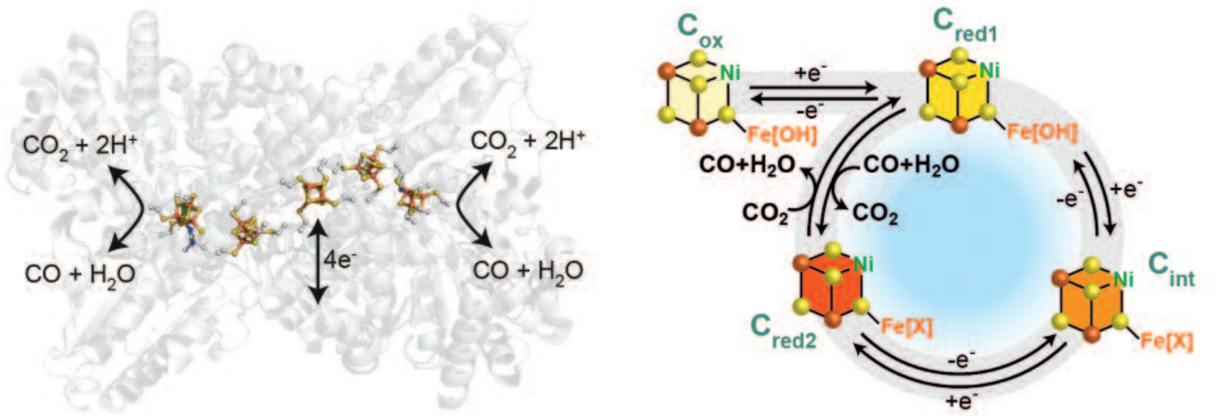

Figure 4. Structure and catalytic cycle of Ni-CODH. **Left:** crystal structure of Ni-CODH from *Rhodospirillum rubrum* (PDB code 1JQK, Drennan, *et al.* (2001) *PNAS* **98** 11973). The protein backbone is shown in the cartoon representation and the metallocofactors are shown as balls and sticks. The site of electron exchange with external electron carriers (e.g. ferredoxin) and the site of CO$_2$/CO (the C-cluster) binding are shown. **Right:** scheme showing the catalytic cycle occurring at the C-cluster. The [3Fe-4S] portion of the C-cluster is represented by brown and yellow spheres while Ni is shown in green and the unique "dangler" Fe is shown in orange. The exogenous ligand bound to the C-cluster in C$_{int}$ and C$_{red2}$ is not known, while for C$_{ox}$ and C$_{red1}$ it is proposed to be OH$^-$.

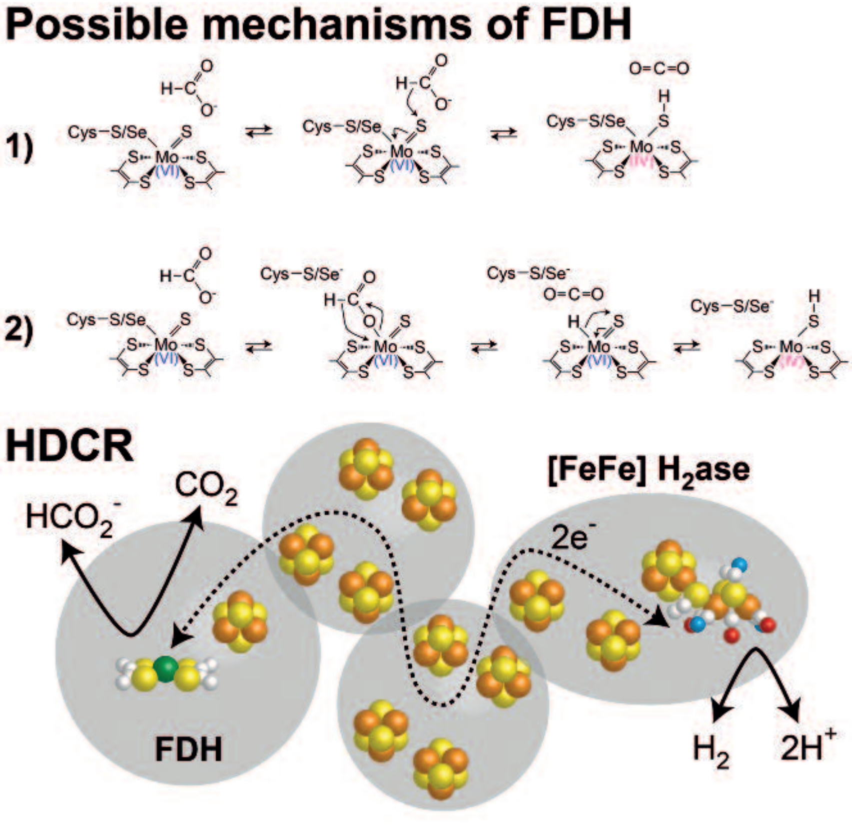

Figure 5. Possible mechanisms of FDH and arrangement of cofactors in HDCR. **Top:** two possible mechanisms for the oxidation of formate to CO$_2$ by the molybdopterin site in FDH. Mechanism 1 (Niks et al. (2016) *JBC* **291** 1162, Maia et al. (2016) *JACS* **138** 8834) involves hydride transfer to the crucial sulfide ligand, while mechanism 2 (Tiberti et al. (2012) *IC 51* 8331) involves displacement of the Cys (or Sec) residue, binding of formate, hydride transfer to Mo and electron transfer to Mo. Other mechanisms exist in which displacement of ligands invariably occurs with formation of hydrides or direct electron transfer to Mo. **Bottom:** arrangement of cofactors in the HDCR from *Clostridium beijerinckii* is shown with the FDH subunit on the left, the [FeFe] hydrogenase subunit on the right and electron transferring ferredoxin subunits connecting the two catalytic subunits.

We are producing both the FDH from *E. coli* and also the hydrogen dependent CO$_2$ reductase (HDCR) from *Clostridium beijerinckii*, which contains both an [FeFe] hydrogenase subunit and an FDH subunit (Figure 5).

By performing spectroscopic studies on trapped intermediates, we hope to be able to provide some additional insight on the catalytic mechanism of these enzymes.

Soluble methane monooxygenase

In nature, methane is used as a source of carbon and energy by methanotrophic bacteria. The first stage of methane metabolism is hydroxylation to methanol, an extremely important industrial process, which is carried out in a controlled fashion under ambient conditions by methanotrophs. The organism *Methylosinus trichosporium* possesses two enzymes for hydroxylating methane, the Cu-dependent particulate methane monooxygenase (pMMO) and the Fe-dependent soluble methane monooxygenase (sMMO). The latter, produced only in the absence of Cu, contains an interesting bimetallic iron site where each iron is coordinated by His and Glu amino acids. The catalytic hydroxylase component (MMOH) is composed of three subunits (MMOX, Y and Z), and requires additional reductase (MMOR), and regulatory (MMOB and D) component proteins for activity. While the reductase and regulatory proteins can be easily produced recombinantly, so far there are no reports of successful recombinant production of the hydroxylase component proteins. Thus, a focus of our work is to develop a recombinant system for producing the hydroxylase with high yield and purity, as well as facilitating site-directed mutagenesis to probe the role of the protein surrounding on catalysis.

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DEPARTMENT OF INORGANIC SPECTROSCOPY

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Computational chemistry of complex systems

The Björnsson group (established in April 2018) uses multiscale modelling methods to gain insight into complex chemical systems related to biocatalysis and molecular catalysis. The primary research focus is to gain fundamental insight into biological nitrogen reduction, catalyzed by the nitrogenase enzymes via detailed theoretical modelling and calculations of spectroscopic parameters, working in close collaboration with experimentalists.

1. Biological nitrogen reduction

Nitrogenases

A strategy for pursuing the goal of creating efficient and affordable small-molecule-activating catalysts is to learn directly from the biocatalysts of nature. Nature has through millions of years of evolution created complex metalloenzymes that are fine-tuned to catalyzing the reactions of small molecules to various products. These enzymes utilize inorganic coordination chemistry without precious heavy metals to achieve such difficult reactions as the reduction of N_2 to NH_3. This electrochemical reduction of N_2 to NH_3 is catalyzed by a complex iron-molybdenum-sulfur cluster (FeMoco) in the nitrogenase enzymes. While molecular catalyst design for N_2 reduction is inspired by nitrogenases, the biological system still remains poorly understood, hindering progress in the important area of bioinspired catalyst design for N_2 reduction. These bacterial nitrogenase enzymes are responsible for all biological reduction of dinitrogen to ammonia on Earth. They are essential for all life as the ammonia produced is incorporated into nitrogen-containing biomolecules such as proteins and DNA. Different nitrogenase enzymes have been characterized and are named by the presence, or absence, of a single heterometal ion in the enzyme cofactor. The most studied nitrogenase is the molybdenum nitrogenase, a multiprotein system that under turnover conditions consists of the catalytically active molybdenum-iron protein (MoFe protein) and a reductase, the iron protein (Fe protein). Similarly, the vanadium nitrogenase consists of the vanadium-iron protein (VFe protein). These enzymes utilize complex metal-sulfide cofactors, an iron-molybdenum-sulfur cofactor, FeMoco, in the case of molybdenum nitrogenase and an iron-vanadium-sulfur cofactor, FeVco, in the case of vanadium nitrogenase. The mode of action of these intriguing cofactors remains poorly understood. Considerable efforts from the CEC have for the past few years been devoted to improve our understanding of the resting redox state (E_0) of these cofactors via experiments and computations. We now have better insights into the electronic structure such as the charge state, metal oxidation states, electronic delocalization and local spin states. Less information, however, is available on the reduced states of FeMoco and FeVco (E_1-E_8) and how dinitrogen binds. According to the Thorneley-Lowe model, dinitrogen does not bind until after 3 or 4 reduction events with the E_4 state being argued to be the primary state involved. FeMoco and FeVco are unique among iron-sulfur clusters to bind and reduce dinitrogen (related $[MoFe_3S_4]$ model cubanes will, however, catalyse reduction of hydrazine and dimethyldiazene in a Mo-centric mechanism as discussed in DFT study from our group[1]).

Computational models of reduced states of FeMoco

We have been modelling the early redox states of Fe Moco by QM/MM modelling. This involves systematically exploring the large chemical phase space available as multiple electron/proton pairs are added to the cofactor, while keeping in mind the constraints available from experimental observations, such as spin-state information, magnetic hyperfine coupling, presence/absence of hydrides etc. Multiple protonation states, spin states and broken-symmetry states have to be considered in these efforts. The singly reduced E_1 redox state has been studied in detail and, together with experimental X-ray absorption measurements have now led to a joint EXAFS-QM/MM characterization (Figure 1) of this state that is probably the most detailed characterization of this state to date.[2]

Recently we have devoted considerable effort into an attempt to characterize the E_4 state by QM/MM computations and this has to led a new computational model for the E_4 state, not previously discussed in the literature.

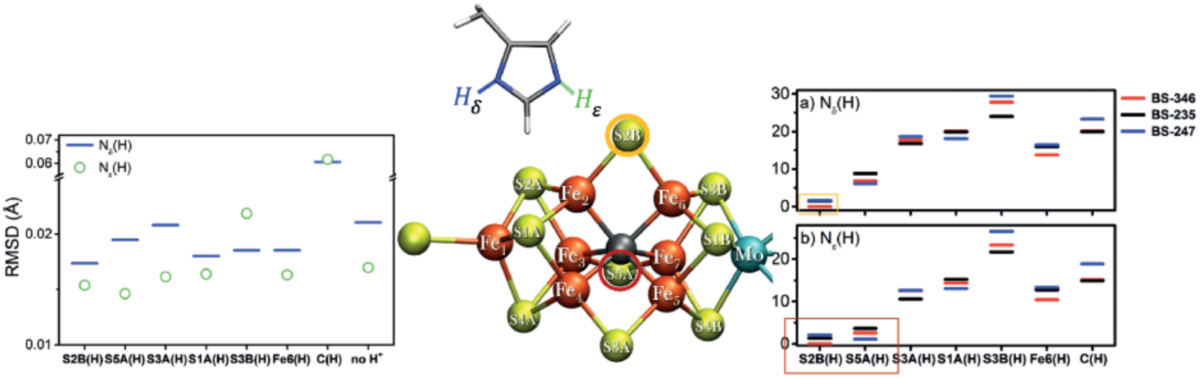

Figure 1. The geometric comparison of different pronation site QM/MM models of E_1 to the the new Mo and Fe EXAFS data (left) and the relative energies between models (right). Different protonation sites, broken-symmetry solutions and His195 protonation states were considered.

Interestingly this new model for the E_4 state appears consistent with experimental hyperfine coupling data, shows favorable N_2 binding (unlike most previous models) and offers a chemically intuitive explanation for why N_2 binding occurs in this state and not others (hydrides invoke spin-pairing at one Fe that increases backbonding to a π-accepting ligand, like N_2) Furthermore, the geometry of the N_2-bound state hints at how the reductive elimination step (H_2 elimination via hydrides) could occur, leading to a reduced FeMoco state that partially activates N_2 for protonation (Figure 2). These results have very recently been published.[3] These results may be a step towards a mechanistic understanding of N_2 activation in nitrogenase. However, the next challenge will be to design an experiment to confirm or rule out this model.

Insights into FeVco redox states

Considerably less is known about vanadium nitrogenase and particularly the FeVco cofactor. Recently, new crystal structures of the resting state VFe protein and a state featuring a ligand-bound FeVco, became available. The latter structure, curiously, showed that a bridging sulfide had been replaced by a light atom ligand, either NH or OH. The presence of a bound NH group would suggest an interpretation of the state as a reaction intermediate, however, the resolution of the crystal structure did not allow one to distinguish between NH and OH groups. With the help of QM/MM calculations our group explored both scenarios (Figure 3) and found that a calculated structure with an OH ligand was in considerably better agreement with the crystal structure than an NH ligand, thus implying that this interesting state is not a reaction intermediate.[4]

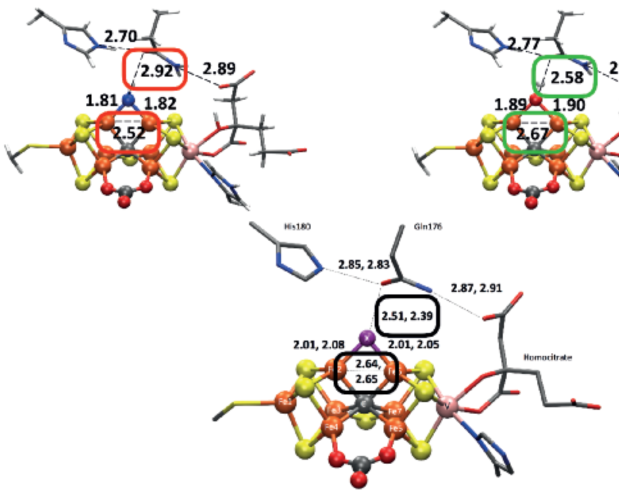

Figure 3. Comparison of QM/MM-computed FeVco structures with an NH ligand (top left), OH ligand (top right) with the crystal structure (bottom).

2. QM/MM methods for environmental effects in spectroscopy and redox chemistry

The objectives of this project are to develop black-box QM/MM protocols to model redox reactions and spectroscopic properties in essentially any molecular environment and use the established methodology for reliable modelling of interesting systems in the field of molecular, solid-state- and enzyme catalysis. Catalytic reactions of small-molecule activation often involves redox chemistry and proton-transfer reactions. Studying such chemistry by computational methods requires the reliable computation of redox potentials and p*K*a values, which is a challenge in computational chemistry, as it involves charged species and large solvent contributions.

Figure 2. Calculations show how dinitrogen binding, reductive elimination and protonation might occur at FeMoco.

Benchmarking studies for these properties have been carried out through the years, mostly focusing on varying the DFT method or the continuum solvation model, but the progress has been rather disappointing and it is our view that real progress in this area can only come from explicit solvation modelling as well as going beyond DFT methods to high-level wavefunction theory.

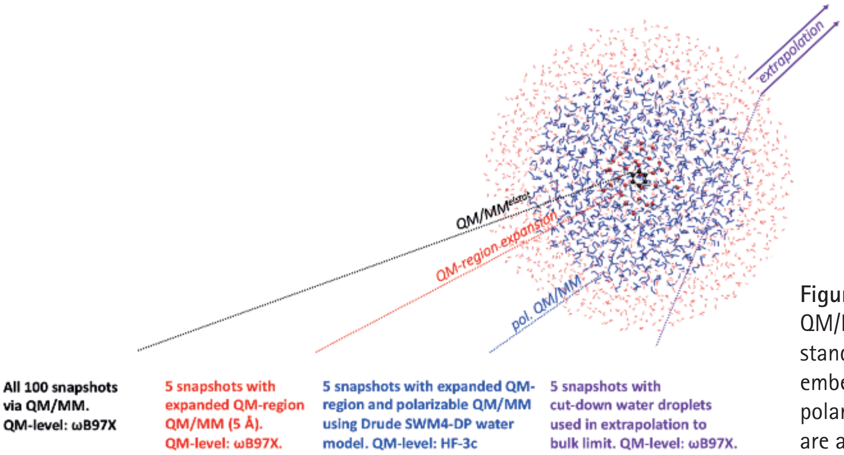

Figure 4. Scheme for the explicit solvation QM/MM-based protocol. Together with standard electrostatic QM/ MM embedding, short-range and long-range polarization effects as well as bulk effects are accounted for via additive corrections.

QM/MM methodology offers the ability to go beyond continuum solvation, but an explicit account of the environment requires solvent sampling, challenging black-box usage and computational cost. We have been working on a QM/MM-MD based protocol for modelling redox potentials in aqueous solution. There is now a black-box implementation of our approach available in a developmental version of the Chemshell code that features an automatic semi-empirical QM/MM-MD step and a polarizable QM/MM single-point ionization step over multiple snapshots that calculates the adiabatic free energy of oxidation/reduction via the linear response approximation and accounts for bulk effects, short-range and long-range polarization via additive corrections (Figure 4). This work was recently published where we showed that our protocol can calculate experimental aqueous redox potentials of organic molecules with ~0.1 V accuracy, outperforming DFT-continuum protocols.[5] Our protocol thus shows considerable promise but there are challenges associated with going beyond organic molecules to transition metal coordination chemistry, to generalize the protocol to multiple solvents and to reduce the computational cost. Such a protocol is also being explored in the context of spectroscopic properties in solution.

We have also been working on methodology as a modelling approach in the solid-state. This is based on earlier work and is a QM/MM-based method for modelling local geometries and molecular properties of molecular crystals[6]. The initial version had some severe limitations on the systems that could be modelled but the code has now been rewritten from scratch and now allows the black-box modelling of any molecular crystal and is currently being used to study solid-state effects on ^{57}Fe NRVS spectra of Fe complexes in molecular crystals. A QM/MM modelling approach offers an attractive alternative to periodic approaches and truncated cluster models, as our protocol directly allows the use of wavefunction theory approaches (unlike most periodic approaches) for higher accuracy of geometries and molecular properties, yet is able to capture the solid-state effects present in the crystal. This approach will be developed further so that it becomes a useful tool for calculating spectroscopic properties of molecules in the solid state to high accuracy.

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DEPARTMENT OF INORGANIC SPECTROSCOPY

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Biochemistry of Metalloproteins – a focus on nitrogen fixation

Our group studies iron-sulfur cluster enzymes involved in nitrogen fixation and their biosynthesis, with a particular focus on nitrogenases, the only enzymes that catalyze the reduction of dinitrogen (N_2) into ammonium (NH_4^+). This reaction occurs at a complex metallocofactor, termed FeMco, after multiple electron transfers from a [8Fe:7S] P-cluster.[1] Bearing in mind the importance of the protein environment on the reaction, we are characterizing variants of well-studied nitrogenases substituted near the cofactor and studying nitrogenases from microbes belonging to distant families. To this purpose, we established optimized procedures for the diazotrophic growth of *Rhodobacter capsulatus*, *Chlorobium tepidum*, and *Methanococcus thermolithotrophicus* in the laboratory. We also follow the maturation of the P-cluster, using nitrogenase purified from mutant strains carrying deletions for maturation cofactors, in collaboration with the lab of Prof. Dennis Dean (Virginia Tech, USA). Our group combines microbiology, biotechnology and biochemistry techniques to study biological nitrogen fixation and produce nitrogenases, and biophysical methods for spectroscopical characterization, in particular EPR and X-ray absorption spectroscopy.

Nitrogenase variants

The molybdenum nitrogenase of *Azotobacter vinelandii* is one of the most studied and best characterized nitrogenases. Therefore, variants of this protein constitute a great resource to understand the roles held by certain protein residues in the reaction, from cofactor insertion to proton transfer. We have generated single and double mutants of *A. vinelandii* carrying mutations on the chromosome, following the procedure shown in Fig. 1.

The degree of conservation of residues throughout nitrogenases correlates with their importance in the enzyme. Our group is particularly interested in positions at which a residue is strictly conserved in a specific phylogenetic group. Therefore, we have generated mutant *A. vinelandii* strains to produce Mo nitrogenase carrying substitutions Y276Q and/or Q440N in NifD (see Fig. 2, A), which are characteristic of group C nitrogenases.[2] Those strains were shown to grow slower and be less efficient at acetylene (C_2H_2) reduction. Likewise, isolated variant nitrogenases were less performant for C_2H_2 reduction and hydrogen evolution. Their EPR characterization showed a considerable modification in the $S = 3/2$ signal, implying a different electronic structure of FeMo-co in those variants (Fig. 2, B). XANES and EXAFS studies will provide more insights into the role of those residues in tuning the cofactor.[3] Characterization of Mo nitrogenase with a deleted Y446 as well as a triple variant (currently in construction) will complete this study on group C nitrogenases key residues.

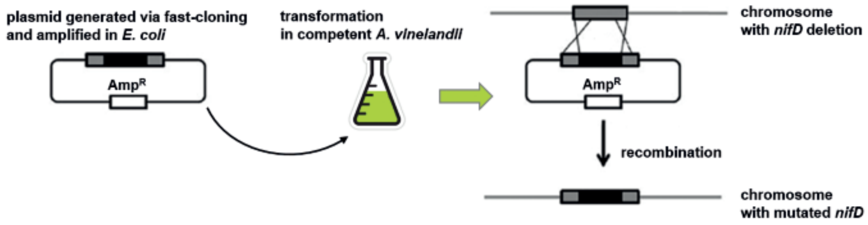

Figure 1. Generation of a mutated strain of *A. vinelandii* to produce a variant of Mo nitrogenase. First, a plasmid carrying the mutated *nifD* gene is generated and amplified in *Escherichia coli*. This plasmid is then transformed in competent *A. vinelandii* in which the *nifD* gene had been deleted. Bacterial recombination finally yields an *A. vinelandii* strain carrying the mutated *nifD* gene, therefore producing a substituted Mo nitrogenase.

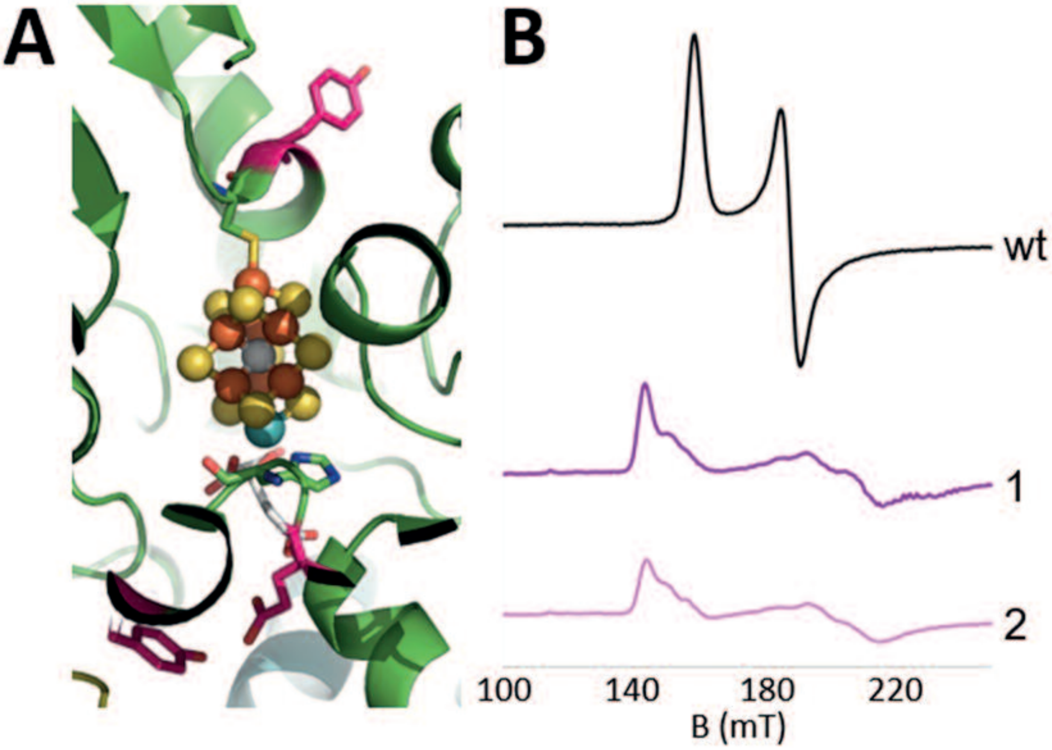

Figure 2. Influence of Y276Q and Q440N substitutions in NifD on FeMo-co. A: View of FeMo-co and surrounding residues in *A. vinelandii* Mo nitrogenase (PDB ID: 3U7Q). Residues of interest (Y276, Q440, Y446) are highlighted in magenta. B: EPR spectra (X-band) of Mo nitrogenase variants. wt: no substitution, 1: single variant Y276Q, 2: double variant Y276Q-Q440N.

Influence of tungsten on the model diazotroph Azotobacter vinelandii

It was previously reported that tungsten inhibits nitrogen fixation and can replace molybdenum in Mo nitrogenase, leading to the synthesis of a FeWco-containing nitrogenase unable to catalyze N_2 or C_2H_2 reduction. To understand the electronic differences in the cofactor due to the Mo → W substitution, we characterized MFe_3S_4 clusters using X-ray absorption spectroscopy combined with DFT calculations (Fig. 3).

Cultivation of *A. vinelandii* with a large excess of W and no Mo led to the expression of the *nif* system, but no FeWco-containing nitrogenase could be detected. Instead, EPR and W L-edge revealed a tetra-oxo coordination reminiscent of catechol siderophores, which should be further characterized via mass spectrometry and HPLC.[4] New W-resistant strains of *A. vinelandii* have been isolated and will be selected upon their ability to produce a W-containing nitrogenase.

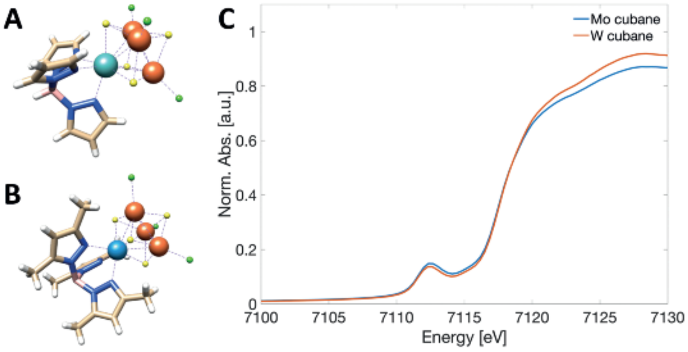

Figure 3. Influence of the Mo → W substitution on Fe in MFe_3S_4 clusters. **A:** $MoFe_3S_4$ cluster compound, **B:** WFe_3S_4 cluster compound, **C:** Fe K-edge XANES of both compounds.

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DEPARTMENT OF INORGANIC SPECTROSCOPY

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A tender x-ray beamline for an x-ray emission spectroscopy at BESSY II

X-ray emission spectroscopy (XES) can reveal the ligand identity, the ligand ionization potential and the metal-ligand distance, etc. in metalloproteins and chemical catalysts. Valence-to-core (VtC) x-ray emission spectroscopy in combination with DFT offers an alternative approach to the structural characterization of organometallic species that overcomes 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 group of the X-ray Instrumentation was organized in 2017. The research of our group is focused on development of new instruments and methods for x-ray emission and absorption (XAS) spectroscopies. VtC XES is a "photon hungry" technique that presents a real challenge to studies using laboratory-based sources [5]. Necessity in fast high resolution VtC experiments and arose demand for studies low Z elements requires using tunable high brilliance synchrotron sources. The PINK project is devoted to establishing a high-resolution XES setup at the BESSY II synchrotron ring, opening up "two-color" and time-resolved VtC XES studies of catalytic systems at an unprecedented level.

PINK beamline and beam diagnostic

The PINK branch at the EMIL beamline 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 (Kα, Kβ lines) and Zr to Ag (Lα, Lβ), as well as light elements P, S, Cl, K, Ca (Kα, Kβ. The beamline is operated in two modes. In the high flux mode, a multilayer (ML) monochromator ($E/\Delta E \approx 30 \div 80$) focuses beam in a 30µmx500µm (VxH) spot and provide the high photon flux (10^{15} ph/s @ 2.3 keV and 10^{14} ph/s @ 6 keV) allowing non-resonant XES measurements of very dilute substances. XANES and XERFD techniques are available in the second-high monochromatic mode ($E/\Delta E \approx 10000 \div 40000$) with the help of DCM monochromator, but a price must be paid in a loss of incoming photon flux intensity.

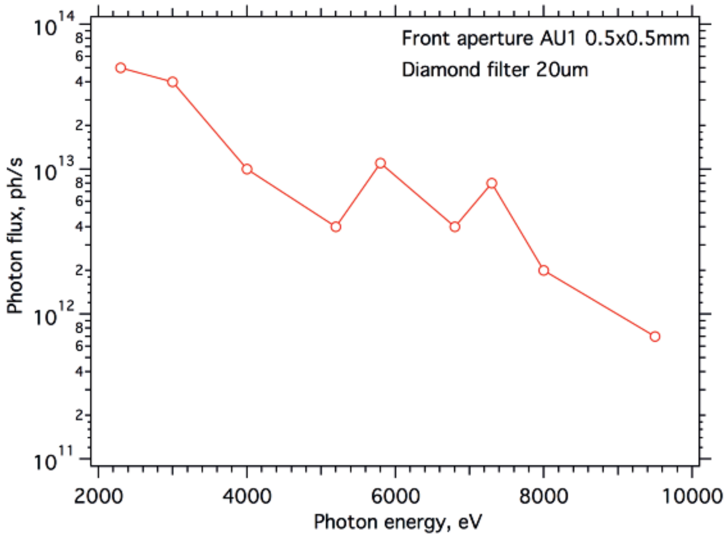

Figure 1. High flux mode. Measured photon flux at a sample position as a function of incident energy. ML monochromator has 9 stripes providing x-ray beam at 9 fixed energies. Front aperture size is 0.5x0.5 mm. By opening the front apertures, we should be able to increase the photon flux at least by order of magnitude.

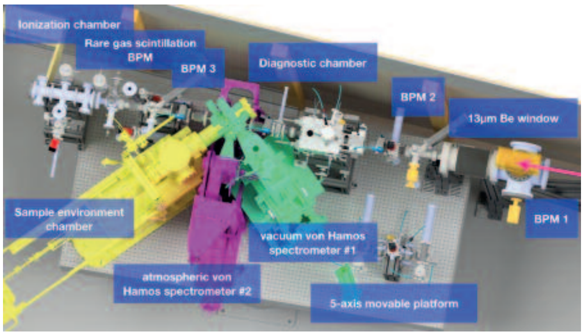

Figure 2. Scheme of the PINK setup

Much attention was given to development of a beam diagnostic for careful beam forming and positioning, and measurement of incoming beam intensity. The beamline incorporates 3 optical beam position monitors (BPM), a quadrant intensity monitor, a set of attenuators and a fast x-ray shutter providing careful dosing of radiation on a sample.

Commissioning of the multilayer monochromator has been started in October 2019 (Figure 1). Unfortunately, due to technical problems commissioning of DCM monochromator was postponed to January 2020.

Experimental setup

The main infrastructure works were done by our group during 2017-2018. They included cabling and network wiring, design of the gas supply system, provision of necessary amenities at the experimental hutch and the control room.

Sample environment

Increasing photon flux we generate radiation damages of the irradiated specimens. Our latest measurements of Ru complexes showed radiation damages already after 0.2-0.4 s under incoming photon flux of 10^{13} ph/s. There are two ways allow to decrease radiation damages of the specimens: using high flow rate liquid cells and putting samples under 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 set-up. The first chamber operated under room temperature can carry up to 4 solid samples and a liquid cell. This chamber was extensively used since March 2019 for the PINK set-up commissioning and studies of ruthenium and phosphorus complexes in solid and liquid states [6]. The second - cryogenic chamber - designed in collaboration with the Sample Environment Group (HZB) will drive up to 8 samples under low temperatures down to 15K (Figure 2). Presently the cryogenic chamber is under commissioning. The first successful cryo-tests were done during spring 2019 and now we are testing a fast sample exchange system. Another currently running project is using of graphenic carbon as an alternative to highly toxic beryllium as material for vacuum windows at cryo-SEC offered benefit of nonhazardousness [7].

Von Hamos spectrometer

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 diced Si, Ge and quartz crystals optimized for

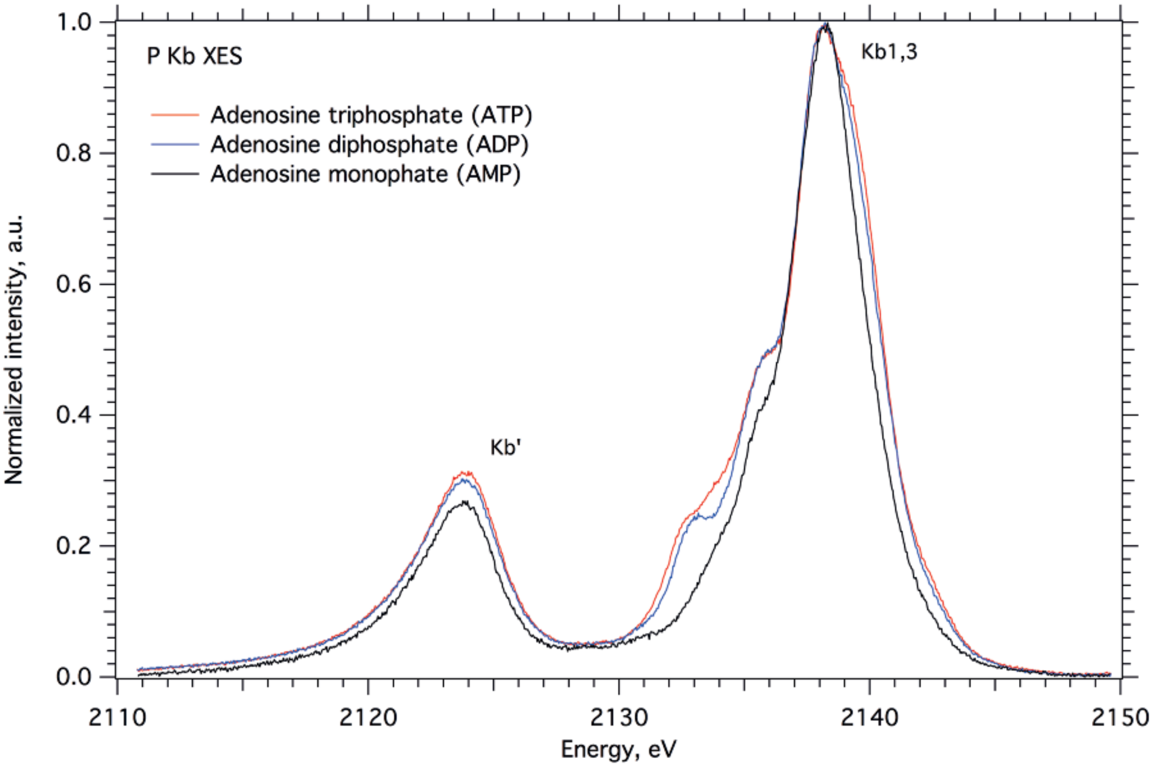

Figure 3. XES spectra of P complexes using Si(111) analyser crystal.

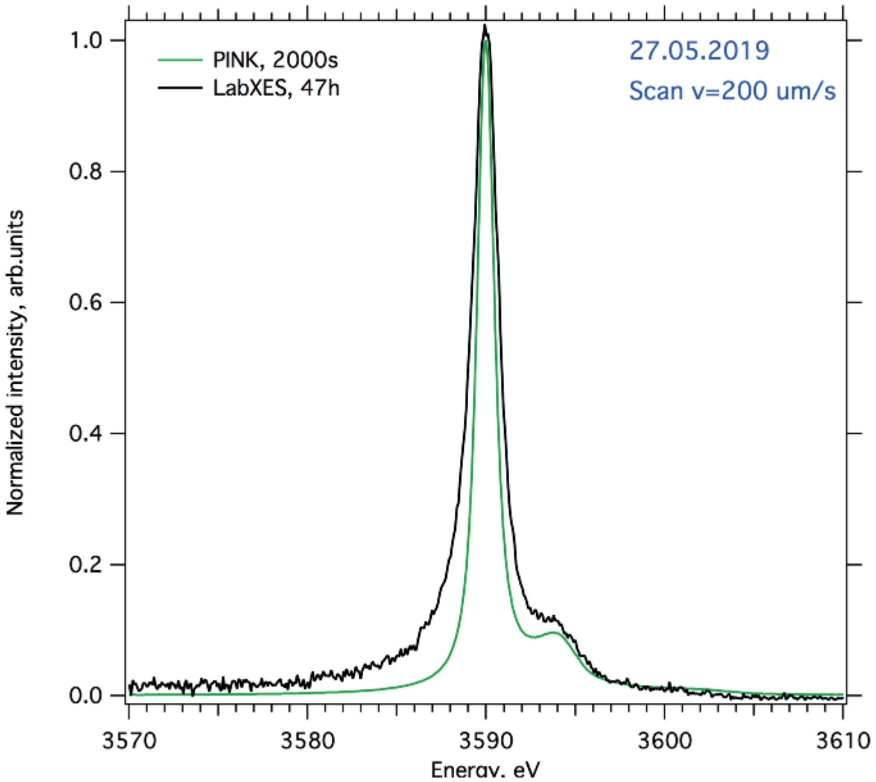

Figure 4. Iron catalyst with 2% K doping. Comparison of XES Kß spectra recorded at the PINK beamline and at the LabXES setup.

operation at large 82°-55° bragg angles, and manufactured in collaboration with Paul-Scherrer-Institute. Taking advantage of a wavelength-dispersive analyzer to record the entire spectrum simultaneously, we will be able to provide very attractive time resolved (2ms - 10s) XES measurements. Both spectrometers can be run independently, thus we will be able to record non-resonant XES spectra for two elements simultaneously, so called "two-color" experiments.

A vacuum von Hamos spectrometer is intended for measurements at low photon energies from 2 to 5 keV. It was built on a classical von Hamos scheme (a bragg angle defined by a linear shift of a crystal and a detector) and placed inside a vacuum volume. Studying capabilities of a vacuum von Hamos spectrometer we recorded Kß emission lines of phosphorus (2120-2140 eV) – a lightest element the spectrometer was designed for (Figure 3). At high energy side we could reach potassium Kß emission lines around 3590eV using Si(110) analyser crystal. Comparing potassium emission spectra (Figure 4) recorded at the PINK beamline and at a lab-based setup LabXES (CEC MPI) we can clearly see advantages of using of synchrotron-radiation – more than two times better energy resolution combined with 80 times shorter acquisition time.

Based on the collected data we elaborated an energy calibration procedure for the spectrometer. We also completed Ru Lß2 XES measurements on solid samples for a project devoted studies of a Ru based water oxidation catalyst [6].

The second, atmospheric von Hamos spectrometer with fixed exit direction (5-10 keV working energy range) has another optical scheme making the spectrometer insensitive to a large horizontal beam size and a sample thickness effect that sacrifice the energy resolution of classical von Hamos spectrometers. A price we pay is more complicated positioning of a crystal and a detector. Commissioning of the atmospheric spectrometer has been started in November 2019 when the U17 undulator source reached the designed parameters [8].

Vacuum system

Availability of measurements at low energies below 5 keV were made possible by incorporation of the sample environment and the spectrometers in to the beamline vacuum system. A set of 6 vacuum windows separates the experimental station and the beamline in to sections operated under different working pressures: ultra-high vacuum, high vacuum, low vacuum up to 100 mbar and atmospheric pressure. Demands for different sample environment conditions require from one side a fast and fail resistant vacuum control system and high flexibility from the other side. Design, assembling and logic programming of the vacuum control were made by our group on the base of programmable logic controller (PLC) that provided 5ms reaction time and high level of configurability.

Control system

The control software has to manage more than 16 stepper motors, 12 piezostages, 9 current channels, thermocouples, cryocontroller, vacuum equipment, video cameras and 3 x-ray detectors from different manufactures. Development of the control system has been started in the beginning of 2017 and the following principles formed the basis:

- Open Source: with an established community and available support (free and open source software and operating systems, no proprietary drivers)
- Developer friendly: to reduce the amount of system administration
- Staff autonomy: the PINK staff and users with programming skills should be able to write their own control system components for their domain, reconfigure and upgrade the control and acquisition systems on demand
- Integration with Python as widely used scripting language and HDF5 data format

After extended series of tests a combination of EPICS control system as a base [9], CS-Studio [10] as a GUI interface and PShell [11] as an acquisition framework were chosen. The last 9 months of the PINK setup commissioning showed high stability and easy adaptation of the chosen framework. We hope that this experience can be in future extended to other experimental setups currently have been built at the Department of Inorganic Spectroscopy.

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DEPARTMENT OF INORGANIC SPECTROSCOPY

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Design and Synthesis of Transition Metal Catalysts for Small Molecule Activation

Due to their extremely high stability, activation and conversion of small molecules like CO_2 and CH_4 presents one of the main challenges in chemistry and catalytic energy conversion. CO_2, being the main product of all combustion processes, contributes significantly to the greenhouse effect. Its abundance and negative effect to the environment make it an attractive precursor for conversion into C1 building blocks for fuels and chemicals. Proton coupled electrochemical CO_2 reduction requires electrocatalysts to lower kinetic barriers as well as influence the selectivity of a reaction.[1]

Research in my group focuses on the spectroscopic and theoretical investigation of known catalysts as well as the design and synthesis of novel catalysts for the transformation of highly stable small molecules into reusable materials. Ligand design and variation as well as the incorporation of different earth abundant metals are followed by spectroscopic characterization (XAS, Mössbauer, Resonance Raman, EPR, etc.) of the electronic features of the complexes. Their catalytic properties are then evaluated with the help of CV (cyclic voltammetry).

Resonance Raman as a tool to analyze the electronic structure of reduced iron porphyrins

In order to rationally design novel catalysts, it is very important to understand the electronic features of the active forms of catalysts and their role within the catalytic cycle. Earlier, we reported the determination of the electronic structure of reduced iron porphyrins by employing a combinatorial study of theory and spectros-

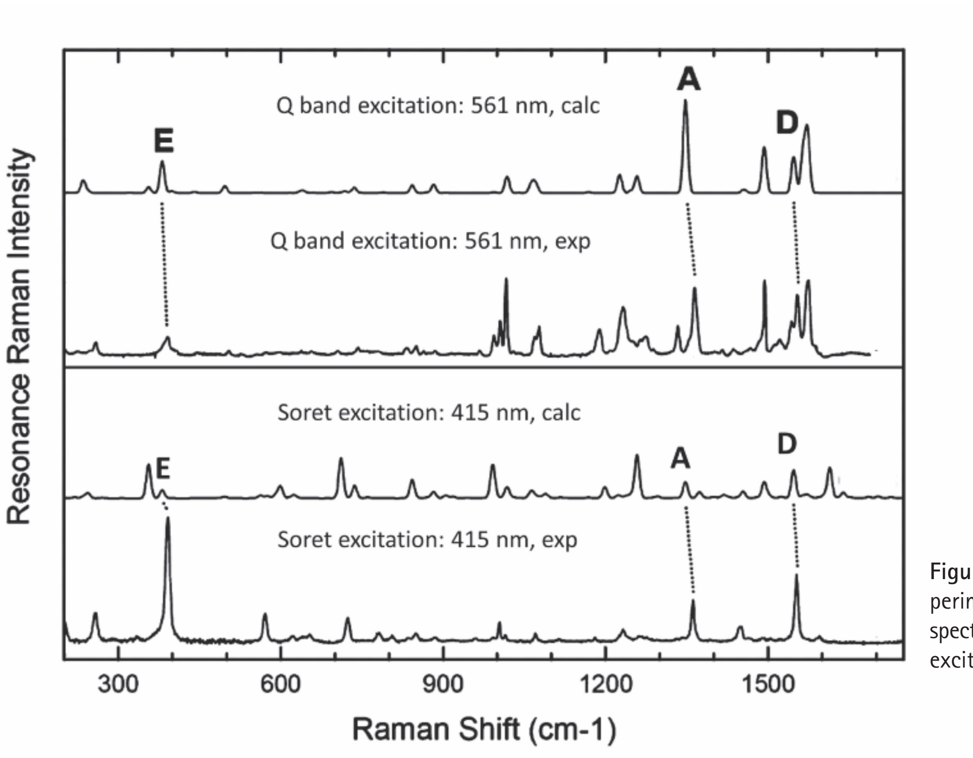

Figure 1. Calculated and experimental Resonance Raman spectra upon Q-band and Soret excitation.

copy,[2] a topic which was highly debated over four decades. With the help of Resonance Raman Spectroscopy, we were able to further corroborate our assigned electronic structures.[3] Raman and Resonance Raman spectra were recorded for all reduced iron porphyrins as well as the starting compound Fe(III)ClTPP. The experimental Resonance Raman spectra for Soret and Q band excitation were then compared to the calculated spectra. Numerical frequency calculations, giving the non-Resonance Raman spectra, as well as normal mode gradient calculations were carried out. Based on the therein obtained absorption spectrum, the possible excitation wavenumbers for calculating a Resonance Raman profile were determined. A detailed iron porphyrin study of *Lehnert et al.*[4] covers the assignment and characterization of experimental vibrational frequencies with the help of calculated Resonance Raman spectra. We compared our experimental and theoretical work and identified various bands, including the most important oxidation and spin state marker bands **A – E**[5] (Figure 1).

For each reduction step (FeClTPP → [FeTPP] → $[FeTPP]^-$ → $[FeTPP]^{2-}$), the marker bands were determined. Careful consideration of reported trends of the identified (marker) bands as well as comparison of these trends with zinc porphyrins (experimental values) and H_2TPP (calculated values) leads to the unambiguous assignment of ligand centered reductions. It allowed the identification of a diradical tetraanionic ligand in $[Fe(II)TPP]^{2-}$ being the key intermediate in the catalytic CO_2 reduction cycle.

Towards new catalysts for CO_2 activation

Decades of research[6] on CO_2 reduction catalysis have shown that a few trends and considerations should be taken in account when designing novel catalysts. First, transition metals surrounded by a (non-innocent) ligand environment which offers three or four nitrogen atoms as bonding sites are promising moieties. These complexes have to be able to store at least two electrons which are required during the catalytic cycle. Second, it was found that functional groups which are able to stabilize the $[CO_2$—complex] adduct have considerable influence on the reactivity of the complexes. Thus, the introduction of hydrogen bonding donors or positively charged groups on the periphery of the ligands is a key element in our synthetic strategy. We are currently investigating pyridine imine (PI) ligands as promising candidates to form catalytically active complexes of the type $[ML_2]$ (Figure 2, left).

Early results show that the introduction of NMe_2 functional groups ("FG") leads to $[MLX_2]$ complexes in which iron, cobalt or nickel are coordinated to all three nitrogen atoms of the ligand. Since one PI ligand is only able to store a single electron, which was verified by CV measurements, these complexes are not active in electrocatalytic CO_2 reduction. We then methylated the NMe_2 functional groups to form $NMe_3^+I^-$ substituents, assuming that breaking of one of the N—M bonds leads to the coordination of a second ligand. So far, formation of a $[MLX_3]$ complex (Figure 2, middle) was observed in the case of iron. Current research employing PI ligands focuses on the exchange of the NMe_3^+ counter anion by weaker binding anions like PF_6^- or OTf^- and subsequent introduction of a second non-innocent ligand, which can either be another PI or a bi- or terpyridine moiety. When switching to pyridine diimine (PDI) ligands bearing NHTs (Ts = tosyl) functional groups, the formation of the desired iron, cobalt and nickel complexes was observed. Based on MS spectroscopic results, however, it was found that keeping the protonation status of the NHTs groups intact upon complex formation is highly challenging. Cleavage of HX from these complexes leads to formation of two NTs—M bonds, rendering a $[MN_5]$ environment and thus blocking access of CO_2 to the metal center. After careful adjustment of the reaction conditions, we were able to isolate a $[FeBr_2(MeCN)(NHTs\text{-}PDI)]$ complex (Figure 2, right) which will now be subject to cyclic voltammetry studies in order to evaluate its catalytic properties in CO_2 reduction.

Monomeric model Cu complexes in C,H activation

Selective C,H activation, transforming hydrocarbons to (bio)fuels like methanol, presents one of the challenges of homogeneous catalysis. The proteins LMPO and pMMO catalyze the O_2 oxidation of strong C-H bonds, as found in polysaccharides (LPMO) and CH_4 (pMMO). Both contain the so-called *His-brace* as active site where one copper atom is surrounded by histidines in a T-shape geometry (Figure 3, left).[7]

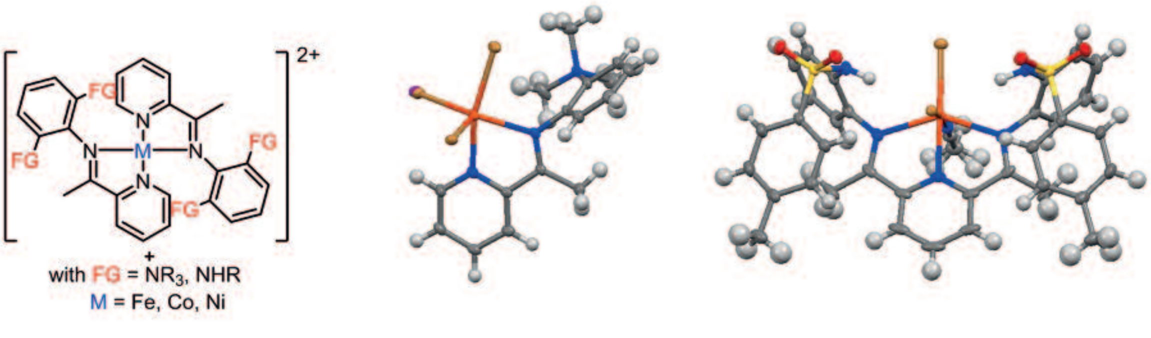

Figure 2. Envisioned (left) as well as obtained PI (middle) and PDI (right) complexes.

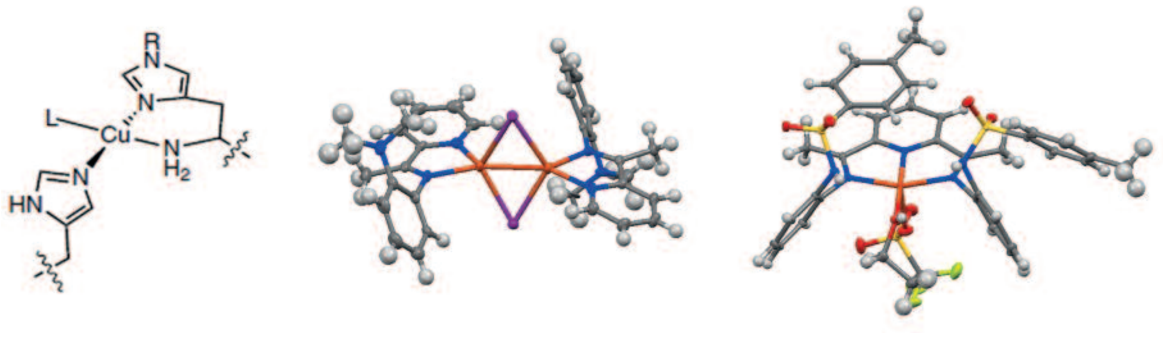

Figure 3. His-brace (left) as well as first experimentally obtained PI (middle) and PDI (right) complexes.

There are, however, several questions which are subject to intense research and have not been answered satisfyingly so far. These include, amongst others, the unknown structural as well as electronic features of the active species in the catalytic cycle, the possible influence of the 2nd coordination sphere and the proposed mechanism of C,H activation. Our aim in this new project is to synthesize model copper complexes which resemble this T-shape geometry and, with the help of spectroscopy and theory, try to answer these questions. Preliminary experiments with pyridine imine (PI) ligands yield dimeric $[Cu_2I_2PI_2]$ moieties (Figure 3, middle) which do not exhibit the desired geometry. However, upon employing sterically more demanding pyridine diimine (PDI) ligands (Figure 3, right), we were able to obtain a Cu center which is surrounded by three nitrogen atoms in a T-shape geometry. Evaluating the behavior of this PDI complex under aerobic conditions is topic of our current research. UV-Vis spectroscopic studies will show if this complex is able to interact with molecular oxygen since the formation of a $[Cu{-}O_2]$ feature leads to the formation of characteristic peaks within the spectrum. Further, modification of the PDI side chains, specifically the introduction of positively charged anchoring groups, is currently being investigated.

Our current synthetic approach also includes the synthesis of complexes which incorporate histidine moieties in their ligands (Figure 4). These complexes exhibit a high structural similarity to the actual His-brace which makes them highly promising candidates for evaluating their behavior under aerobic and C,H activating conditions.

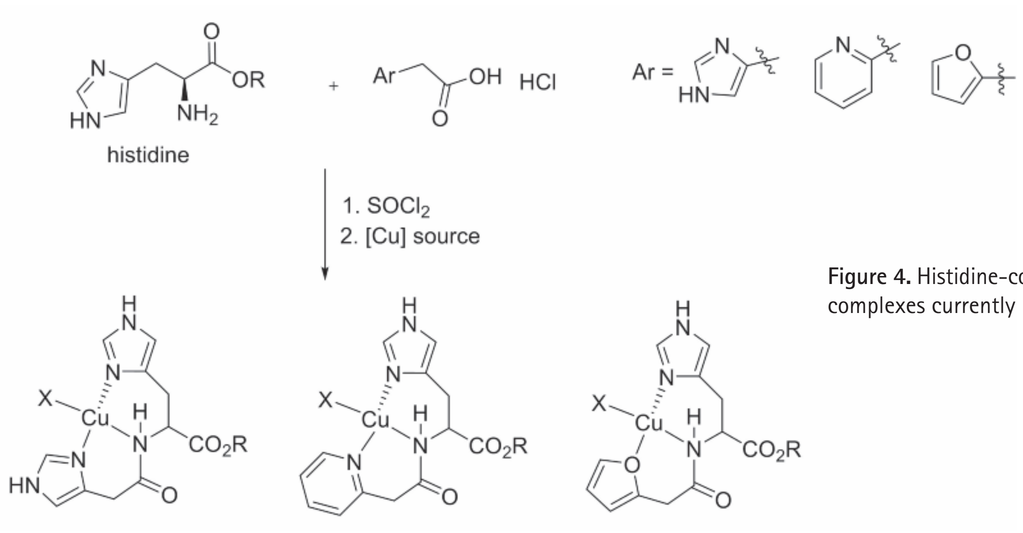

Figure 4. Histidine-containing model [Cu] complexes currently under investigation.

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DEPARTMENT OF INORGANIC SPECTROSCOPY

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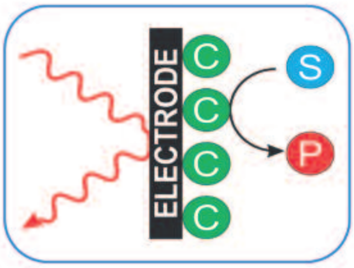
Spectroelectrochemistry

Electrochemistry is a useful technique to characterize energy converting catalytic systems. It is the basic tool to study catalysts involved in water oxidation reactions, since the electric current is a direct measurement of the activity of the catalyst. Nevertheless, if we want to elucidate complex reaction mechanisms or understand why a catalyst is better than another one, the combination of electrochemistry with different spectroscopies can be extremely informative. This is specially the case if the spectroscopy is measured simultaneously with the electrochemistry using *in situ* or *operando* conditions. This has been the main effort of our group during the last three years. Our integration in the Inorganic Spectroscopy group has open the opportunity to extend our **spectroelectrochemistry** (SEC) capabilities from UV-Vis, FTIR and EPR to advanced X-ray spectroscopies both in the soft and hard regime. In addition, we have expanded our spectroelectrochemical studies from protein and bio-inspired electrocatalysis to heterogeneous materials for water oxidation.

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). Over the last years hydrogenase research has focused on the study of [FeFe] hydrogenases since there is controversy about the catalytic mechanism of this enzyme (Haumann, Stripp, *Acc. Chem. Res.* 2018). While some authors assign the redox states $H_{red}H^+$ and $H_{sred}H^+$ to *slow* states containing a bridging hydride, we favor a proton coupled electron transfer (PCET) cycle including these states (see J. Birrell report).[1-2] In a work in collaboration with the group of Thomas Happe at the Ruhr Universität in Bochum we explored alterations of the coordinating cysteine residues of the [4Fe4S] cluster of the *Chlamydomonas reinhardtii* hydrogenase (*Cr*HydA1). **Protein film electrochemistry** (PFE) showed how the different mutations alter the bias of the enzyme[3] with the extreme example of the C362H variant. Using a combination of PFE and IR-SEC we demonstrated that exchanging a cysteine by a histidine shifts the potential of the [4Fe-4S] cluster by almost +200 mV. This shift disrupts the internal PCET of the enzyme. As a result the C362H variant is not capable of H^+ reduction and requires 200 mV overpotential for H_2 oxidation.[4] More subtle were the changes observed when altering some residues hydrogen-bonded to the CO and CN^- ligands of the active site of *Cr*HydA1. In this work we could assign for the first time the CN^- IR bands to the CN^- located on the proximal or the distal Fe atoms of the [2Fe] site. Modeling of the electrocatalytic currents obtained by PFE from the individual enzyme variants shows that small shifts on the potential of the H-cluster can be used to tune the catalytic bias of the enzyme.[5]



Scheme 1.

In collaboration with the group of James Birrell we have investigated the more complex *Desulfovibrio desulfuricans* hydrogenase (*Dd*H). This enzyme has the highest activity rates among all known [FeFe] hydrogenases. Using FTIR-SEC we could show that the active site of this enzyme breaks down at negative potentials releasing the [2Fe] cluster when the enzyme is in its CO-inhibited state, in a process that would be the inverse of the artificial maturation. Subsequent increase of the potential on the SEC cell, reassembles the H-cluster, demonstrating that the [2Fe]-[4Fe-4S] bond stability depends on potential.[6]

The other peculiarity is that this enzyme was originally isolated in an air-stable inactive state (H_{inact}). Irreversible reduction of this state brings the enzyme to the extreme O_2-sensitive active states. Artificial maturation of this enzyme produces the enzyme in the reduced active states (Birrell, J. et al. *Isr. J. Chem.* 2016). PFE shows that exposure of the enzyme to sulfide at precise oxidizing potentials brings the enzyme to an air stable inactive state that is different to the already known high-potential inactivated state. The reactivation potential of this sulfide inhibited state occurs at the same potential as the activation of the air-stable as-isolated native enzyme. This could be reproduced with the protein in solution and FTIR demonstrates that the H_{inact} state can be produced by exposing the artificially maturated hydrogenase to a mixture of hexaamineruthenium (III) chloride as an oxidant and sodium sulfide.[7]

As mentioned above, [FeFe] hydrogenases are active only at moderately low potentials. Exposure of the enzyme to oxidizing potentials reversibly inactivates the enzyme, which is a limitation to the use of these enzymes in biofuel cells. We have overcome this limitation by modifying the electrodes covalently with viologen groups. This viologen layer results in a mixed direct and mediated electron transfer between enzyme and electrode, depending on the applied potential. As a result the film acts as a redox buffer, preventing enzyme inactivation at high potentials. This protection methods eliminates the requirement of employing cathode-limiting conditions in hydrogenase-based fuel cells.[8]

Bio-inspired catalysts

Continuing with our collaboration with the group of Wendy Shaw at Pacific Northwest National Laboratory we have designed polymer/catalyst film to protect and stabilize the $Ni[P_2N_2]_2$ catalysts against O_2 damage. These Ni bio-inspired catalysts that use a pending amine base analogous to that found in [FeFe] hydrogenases, to facilitate proton transfer to and from the Ni have excellent catalytic properties. We demonstrated that the complexes are irreversibly inactivated under turnover conditions during H_2 oxidation (Rodriguez-Maciá, P. *et al. Angew. Chem. Int. Ed.* 2015). On the other hand it was described that when these complexes are H_2 reduced in solution, they can catalytically reduce O_2 to H_2O (Yang, Y.Y. *et al. Dalton Trans.* 2009). We used this feature to protect the catalyst. To this end we used a non-conductive polymer to support the catalyst and obtain a layered polymer containing two discrete phases: (i) a phase close to the electrode surface where the catalyst can directly exchange electrons with the carbon electrode. This layer is responsible for the H_2 oxidation catalysis. (ii) A solvent exposed phase, where the catalyst cannot exchange electrons with the electrode, but can be reduced by H_2 and thus constitutes the protection layer. This type of electrode shows enhanced stability for the H_2 oxidation currents, but more importantly it avoids O_2 damage during catalysis.[9] During these experiments I realized that for systems where FTIR could not be used, we were lacking a tool to identify the electronic structure of the catalysts we were studying. This motivated the development of X-ray and EPR SEC techniques.

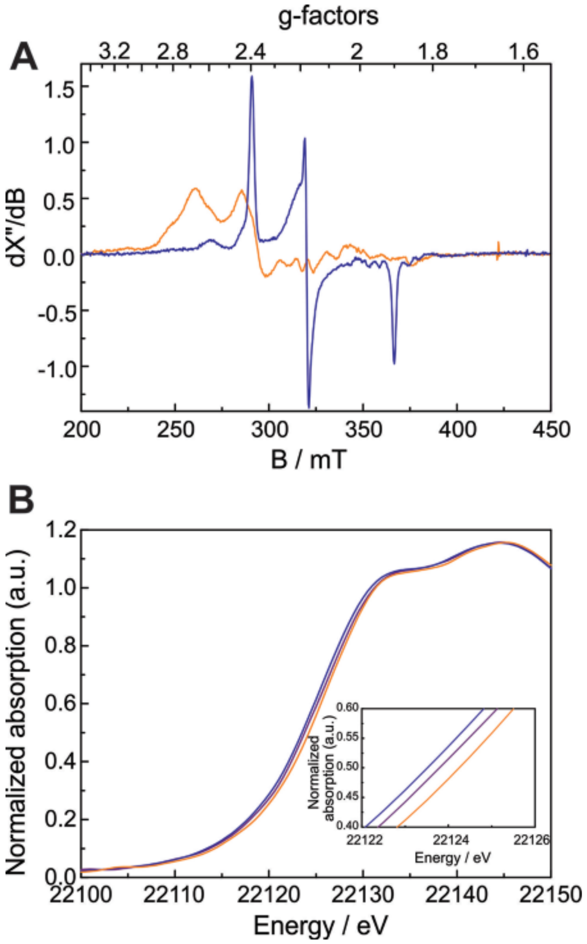


Figure 1. A) X-band CW EPR (at 25 K)of Py_2^{Me}tacn Ru in aqueous electrolyte at E=0.4 V (green) and in butyronitrile at E=2 V, vs SHE (purple). Dry organic solvent stops the catalysis trapping the complex at its Ru(V) state. **B)** Ru K-edge XANES spectra of Py_2^{Me}tacn Ru in acetonitrile at 100 K. The potential on the spectro-electrochemical cell before freezing the solution was 1.2 (blue), 1.9 (purple) and 2.2 (orange) V, vs SHE. The figure inset shows detail on the edge shift.

EPR spectroelectrochemistry

We have designed two EPR spectroelectrochemical cells, one for freely diffusing molecular systems (homogeneous cell) and another one to study catalysts immobilized on electrode surfaces (heterogeneous cell). The homogeneous cell was used to study a pentadentate Py_2^{Me}tacn Ru water oxidation complex. We showed the formation of a new paramagnetic species when oxidizing a Ru(IV)=O complex, consistent with the formation of a Ru(V) species and in agreement with the X-ray observations (see below).

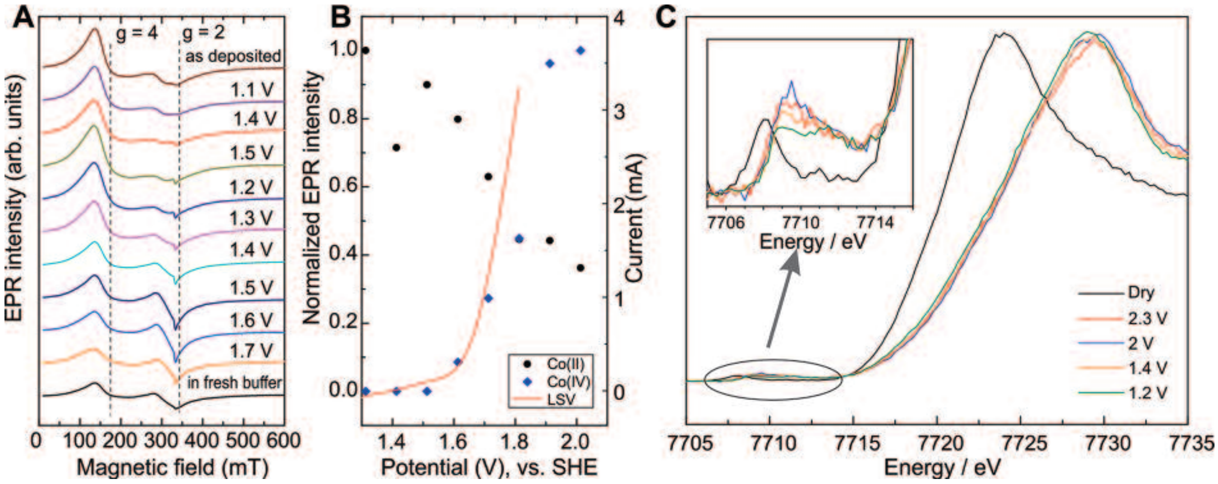


Figure 2. (A) X-band CW EPR spectra of a Co-Pi modified working Au electrode electrolyzed at increasing potentials; P_{MW} = 63 mW, T = 5K. **(B)** The loss of the Co(II) species (black circles) and the increase in the Co(IV) intensity (blue diamonds) as a function of applied potential are shown. The increase in the Co(IV) population in the film coincides with the water oxidation red line; linear scan voltammetry at 1 mV/s measured in the EPR spectroelectrochemical cell). **(C)** Co Kβ HERFD spectra of a film modified with $Co(NO_2)_3$ in nafion (black trace) and after it is oxidized to form an amorphous Co oxide phase at different electrode potentials. The inset shows the pre-edge region in detail.

We used the heterogeneous cell to analyze the Nocera CoPi catalyst (Kanaan *et al. Science*, 2008), a self-healing inexpensive material that has been proposed as a good candidate for larger scale water oxidation catalysis. Our measurements could be used to follow the deposition process from a $Co(NO_3)_2$ solution. As deposited the film is predominantly Co(II), which converts to Co(IV) at potentials commensurate with electrocatalytic O_2 evolution (Figure 2). The EPR resonance position of the Co(IV) shifts to higher fields as the potential is increased above 1.2 V, which may be indicative of a more distorted ligand field or more radical ligand character, supporting its assignment to the catalytically active species.[10]

X-ray Spectroelectrochemistry of Molecular Catalysts

In the recent years o*perando* X-ray spectroelectrochemistry is becoming more commonly used to analyze heterogeneous catalysts and batteries (van Oversteeg C. H. M. *et al. Chem. Soc. Rev.* 2017), nevertheless to our best knowledge, so far this technique has been only applied to one molecular system (Lebedev D. *et al. J. Am. Chem. Soc.* 2017). We have designed two different cells: i) An homogeneous cell to measure molecular complexes freely diffusing in a thin-layer, ii) Heterogeneous cells to study immobilized catalysts (these cells can be used for both homogeneous and heterogeneous catalysts). With the homogeneous cell we could see a shift on the Ru K-edge when increasing the electrode potential in aqueous solution. Additionally, using quick scanning XAS, we could observe a shift of the edge to higher energy, when starting from a Ru(IV)=O complex in dry organic solvent, which in combination with the EPR-SEC experiments suggest the formation of a Ru(V)=O. For the $Ni[P_2N_2]_2$ complexes, we observed very minimal shifts of the edge with the electrode potential. This observation, in combination with TD-DFT calculations has changed our idea of the catalytic mechanism, suggesting that the complex rarely stays in a Ni(0)-H$^-$ state, but rather on a Ni(I) state. Additionally, using quick scanning XAS, we could observe a shift of the edge to higher energy, when starting from a Ru(IV)=O complex in dry organic solvent (Figure 1B), which in combination with the EPR-SEC experiments suggest the formation of a Ru(V)=O. For the $Ni[P_2N_2]_2$ complexes, we observed very minimal shifts of the edge with the electrode potential.

X-ray Spectroelectrochemistry of Heterogeneous Catalysts

We have investigated a Ni_3MnO_4 catalyst for water oxidation by *operando* Ni L-edge X-ray absorption spectroscopy and 2p3d resonant inelastic X-ray scattering (RIXS) in the frame of the MANGAN project. Electrochemical measurements showed that the mixed Ni/Mn oxide had lower catalytic activity than NiO. Using XAS L-edge we could show that under alkaline conditions Ni_3MnO_4 converts to hydroxides and at catalytic potentials forms predominantly the γ-NiOOH phase, similarly to what has been described for NiO.[11]

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 techniques to investigate the synergistic effect of these metals in catalysis. For example, Kβ detected high energy resolution fluorescence detected (HERFD) can provide information about the oxidation state and geometry changes with the potential. On figure 2C, we can observe a drastic shift on the Co K-edge upon oxidation of the film, and while once oxidized the edge barely shifts, on the pre-edge region there are more pronounced changes that could be related to the Co(IV) line-shift with applied potential observed on the EPR experiments.

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DEPARTMENT OF INORGANIC SPECTROSCOPY

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Small Molecular Model Systems to Learn About Electronic Structure and Function

Chemical activation of inert small molecules like CO_2, CH_4, N_2 is a key problem in energy research. In the future, energy from renewable sources will be used on a big scale to transform these abundant materials to chemicals for industry and agriculture. Metal catalysts are needed to make such transformations energetically and chemically efficient and selective. We strongly believe that a deep understanding of mechanistic functionality and electronic structure of catalytic systems vastly supports the process of developing better catalysts. It is our approach to combine in-house spectroscopic methods (EPR, MCD, Mössbauer, Resonance Raman, X-Ray methods, etc.) with quantum theory to shine light on the chemical and electronic structure of catalytically active centers. The combination of spectroscopy and theory allows to interpret even very complicated spectroscopic data and to extract the desired chemical information.

Research in my group focuses on the synthesis of small molecular metal complexes for spectroscopic investigations. Directed variation of structural and electronic parameters in a series of compounds allows to systematically studying their spectroscopic response. Our samples are typically analyzed by standard methods (elemental analysis, IR, UV/vis, NMR, XRD) before they are further investigated as mentioned above. Such compounds with known molecular structure provide a reliable basis to collect high quality spectroscopic data. In the following, two examples of recent projects are given.

Attempts to Model the Interstitial Carbon Atom in Nitrogenase

Nitrogenase is a bacterial enzyme which catalyzes the conversion of nitrogen from air to ammonia, an essential source for the biosynthesis of nitrogen containing compounds like peptides or nucleobases. The activation of nitrogen is very challenging since it is probably 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, the catalytic mechanism and the function of an interstitial carbon atom[1] in the molybdenum cofactor remains extremely challenging.

One of the two metal containing cofactors in nitrogenase, namely FeMoco, 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 **I** in Figure 1).

After we have recently worked on model complexes of FeMoco to shine light on the oxidation state of the Mo ion in the resting state[2] we started a project to synthesize iron clusters with bridging carbon ligands to model the central carbon atom in FeMoco. Very few examples of such complexes have been reported in literature and synthetic strategies allowing the introduction of C-based ligands bonded to more than one Fe atom (μ_{2-6}-C-based ligands) are very rare, explaining the lack of suitable model systems.

We felt that ylides could be suitable ligands to build up carbon bridged complexes and investigated the reaction of ylides with Fe(II) diamido species $[Fe(N(SiMe_3)_2)_2]$ which, in a first step, formed mononuclear higly reactive three coordinate iron(II) complexes[3] of type **A** or more general **E** (Figure 1).

Further experiments showed that **E** can undergo a self-protolysis reaction at elevated temperatures since a carbon bound proton of the ylid is in close proximity to a strong base L which allows formation of doubly yldiide-bridged diiron(II) complexes of type F and HL.

Complexes **1** and **2** represent the first examples of dinuclear ylid-supported Fe_2C_2 iron diamond cores (Figure 2). Fe-C-Fe angles are found to be very acute at about 78.5° and the Fe…Fe distances are very short at ~2.58 Å. Mössbauer and x-ray absorption spectra in combination with magnetic susceptibility studies showed that the complexes are strongly antiferromagnetically coupled high-spin iron(II) dimers. Density functional calculations (DFT)

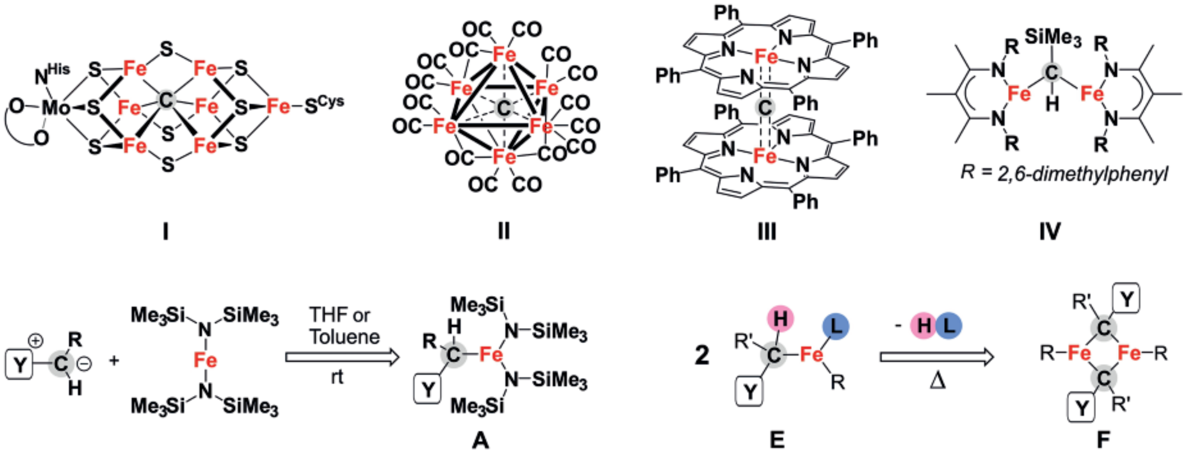

Figure 1. Top: FeMoco structure (I) and other published nitrogenase relevant iron clusters containing C-based ligands (II-IV); **Bottom:** Synthetic strategy to form doubly yldiide bridged iron(II) high-spin dimers via self-protolysis (Y = electron withdrawing group).

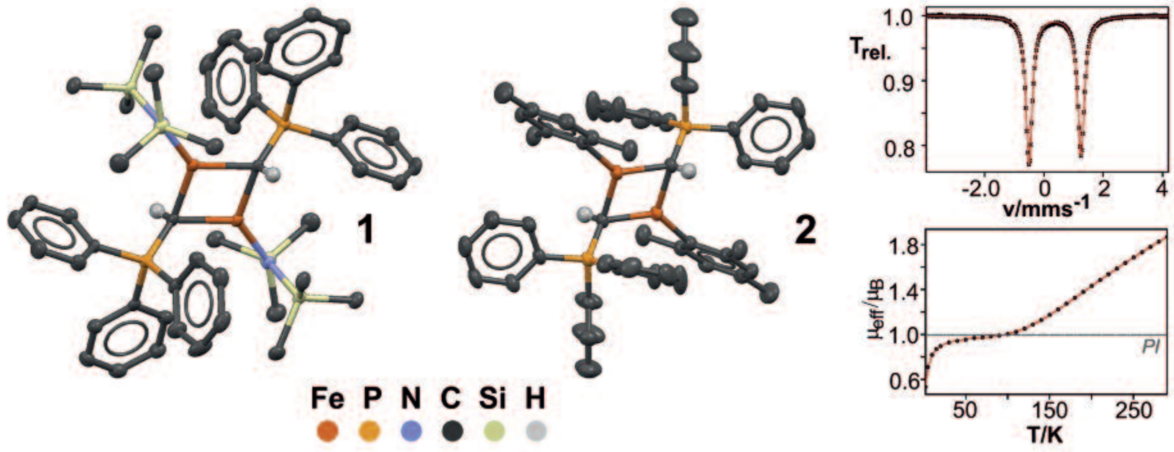

Figure 2. Left: Molecular structures of **1** and **2**. **Right:** 80 K zero field ^{57}Fe Mösbbauer spectrum and simulation of **1** (top; $\delta = 0.35$ mms^{-1} and $\Delta E_Q = 1.75$ mms^{-1}) and magnetic susceptibility measurement and simulation (1T, fit: $J = -214$ cm^{-1} , $g1 = g2 = 2.2$, PI = 2.9 %) revealing the antiferromagnetically coupled diiron(II) high-spin nature of **1** (values for **2** are similar and not shown).

reproduce the experimental data well and exclude a direct metal-metal bond.

We are continuing this project with sulfur containing ligands of a similar type which better model the sulfur-carbon ligation environment of the iron centers in FeMoco and have successfully isolated diiron complexes containing a distorted tetrahedral C_2S_2 environment and trigonal bipyramidal C_2S_2N coordination shell. All full spectroscopic characterization and DFT study is on the way.

X-Ray Structure Determination

In close collaboration with the x-ray diffraction facility of the MPI für Kohlenforschung, my group provides service for the x-ray determination of compounds produced in the MPI CEC. Research on molecular transition metal compounds for catalysis or spectroscopic investigations heavily relies on single crystal structure determinations since self-assembly often dominates in coordination chemistry and directed synthesis to obtain target compounds is in many cases limited. X-ray structure analysis delivers highly precise information about the three-dimensional arrangement of atoms, thereby providing bond length and bond angles, which are of enormous importance in understanding chemical properties. Since it is our aim to correlate experimental features and functional properties with structure, X-ray structure analysis is vital to this area of research.

As an example, Figure 3 displays two crystal structures from a recent paper of the department of Molecular Catalysis (Prof. Leitner) in which a precatalyst **1** forms a reaction intermediate **2** upon addition of pinacol borane in KO^{t}Bu/THF solution.[4] The system is highly active and catalyses the reductive hydroboration of various aliphatic and aromatic carboxylic acids and even CO_2.

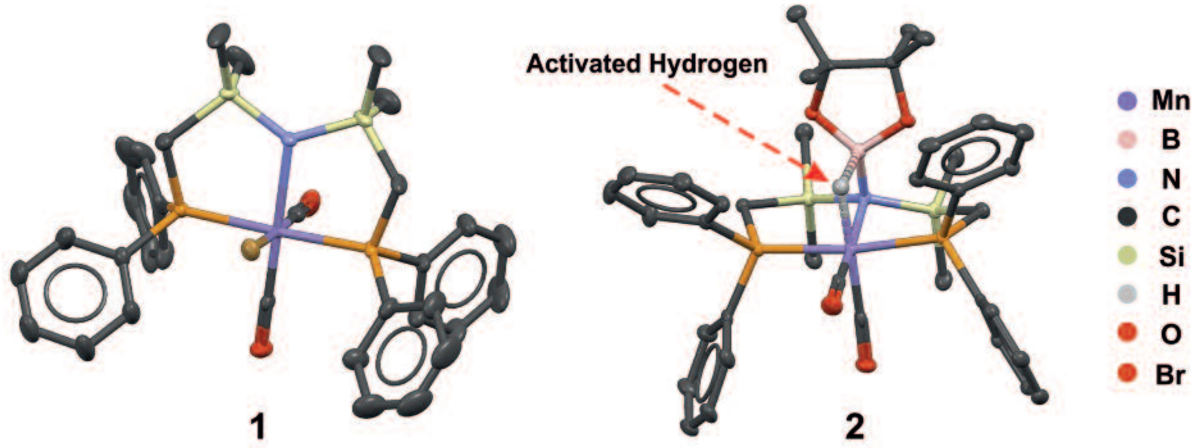

Figure 3. X-ray structures of precatalyst **1** and reaction intermediate **2** catalysing the hydroboration of carbonic acids, esters and CO_2.

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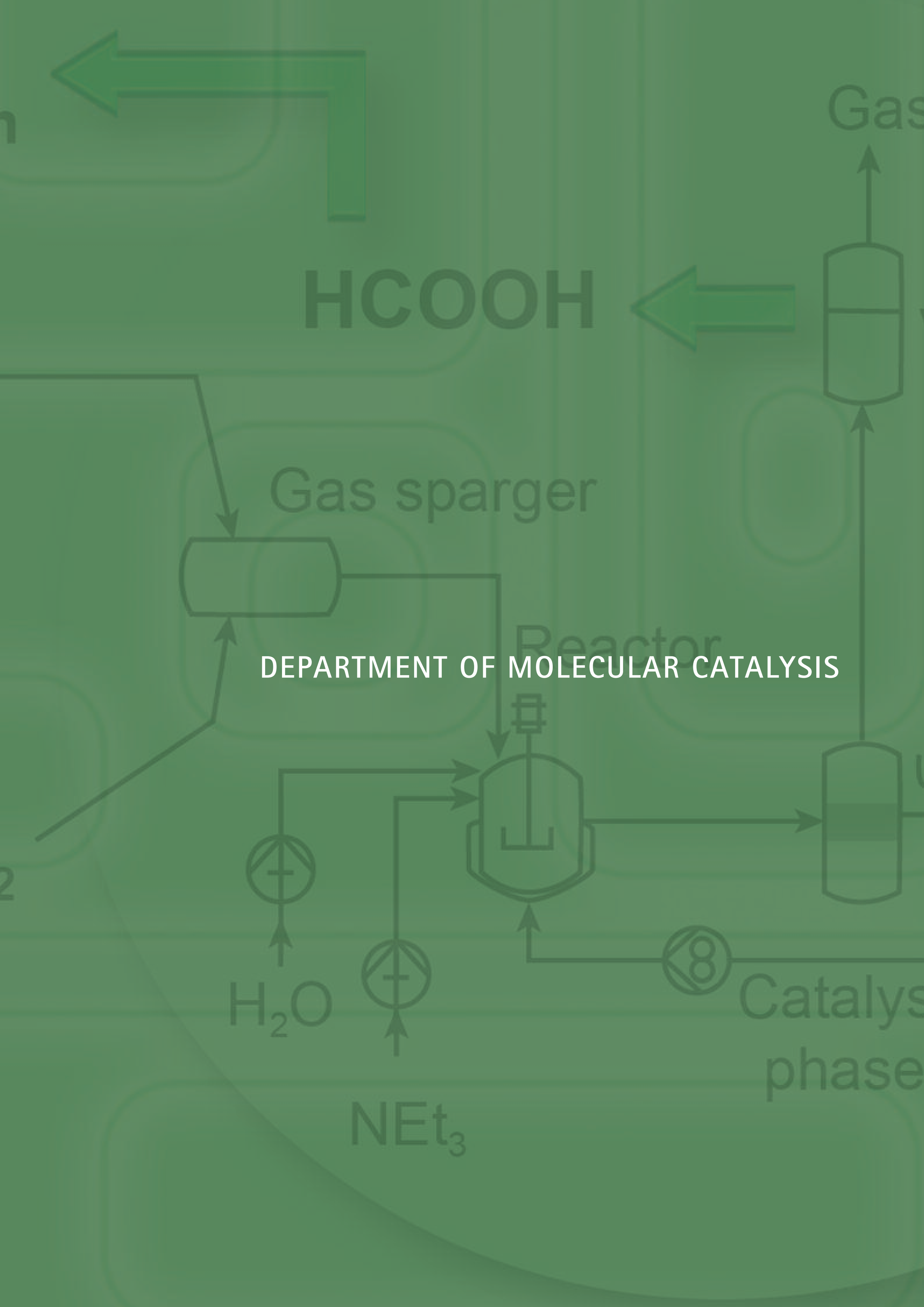

DEPARTMENT OF MOLECULAR CATALYSIS

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. Two major areas of potential application motivate our basic research targets:

- *Catalysis as the key enabling technology for a sustainable transformation of the energy sector*
- *Catalytic technologies for chemical production exploiting the increasing availability of renewable energy*

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 [1]. Potential synthetic targets range from liquid fuels as energy carriers, through large volume base chemicals, to high-value products of the chemical industry [2,3,4].

Within the integrated approach to catalysis at MPI CEC, our research activities are bridging molecular, material, and engineering aspects, firmly rooted in organometallic chemistry. As schematically depicted in Figure 1, our scientific approach involves the four areas of (i) design and preparation of *catalysts and catalytically active materials*; (ii) the search for new or improved *synthetic methods and chemical transformations* based primarily on the renewable resources CO_2 and biomass; (iii) the exploitation of *reaction media and support materials* to strategically influence and control catalytic performance; and (iv) new concepts for *reaction engineering* of molecular catalysis. As evidenced by the examples discussed below, these sectors are not isolated but are strongly

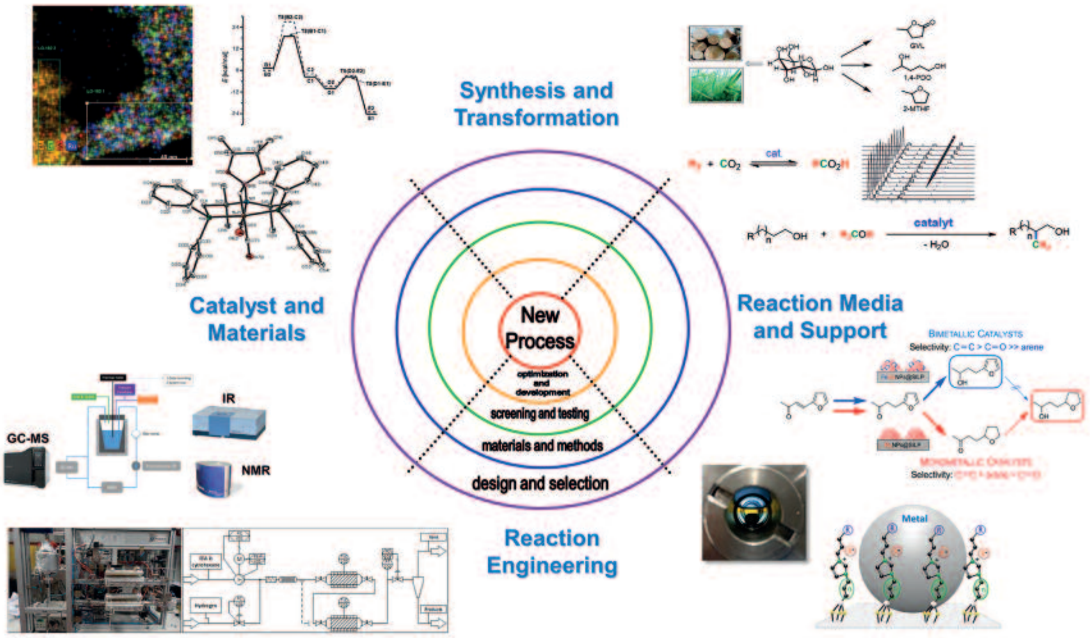


Figure 1. The "Green Chemistry" research target of the Leitner team.

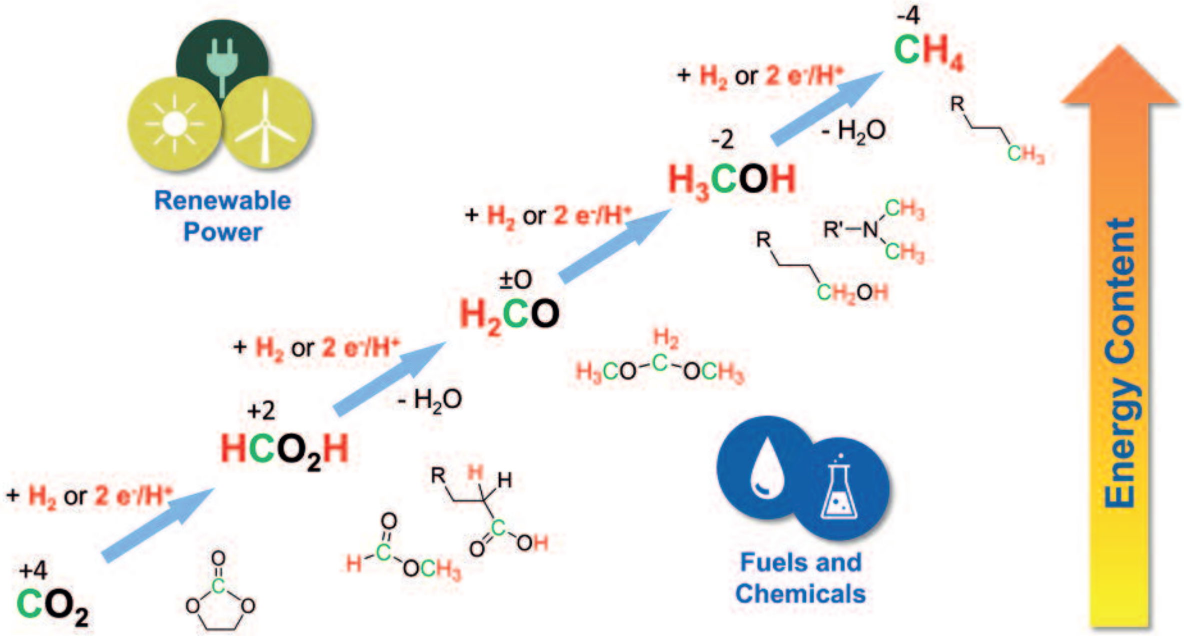


Figure 2. Catalytic hydrogenation of CO_2 as a central manifold for chemical energy conversion.

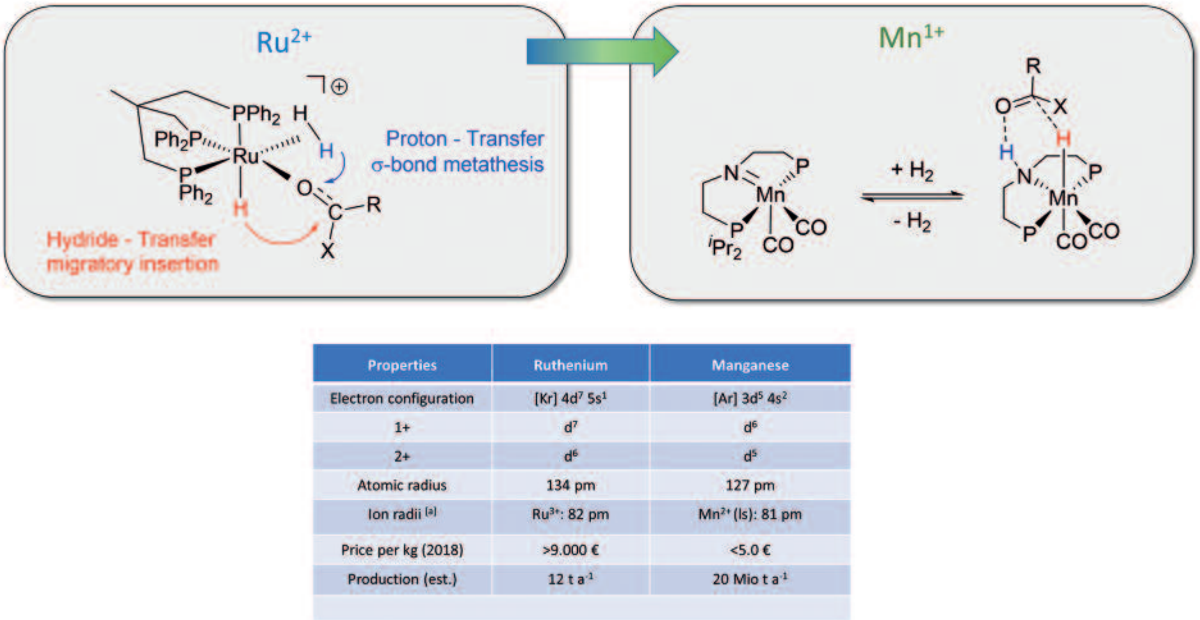
linked through common research goals and experimental techniques. Individual projects are typically ranging across more than one sector and are often addressed in a flexible team approach.

Recent Developments and Trends

Catalyst and Materials

Activities in this sector comprise the design, synthesis, characterization, and evaluation of molecular and nanoparticle catalysts. Novel ligands and complexes are targeted specifically for certain transformations using a rational approach based on mechanistic knowledge. Also, catalysts with a specific solubility profile for multiphase systems are developed. Recently, non-noble metals and redox-active complexes are gaining increasing attention. Our organometallic approach to catalytically active metal nanoparticles on molecularly defined supports is growing into a strategic new research field capitalizing on the research environment at CEC as described under section 2.3.

A significant driver for catalyst development in our team is the quest for selective CO_2 hydrogenation. As depicted schematically in Figure 2, the stepwise hydrogenation of CO_2 opens access to a broad space of chemical diversity targeting functional groups corresponding to the reduction level of the C1 compounds, respectively.



Properties	Ruthenium	Manganese
Electron configuration	[Kr] $4d^7\ 5s^1$	[Ar] $3d^5\ 4s^2$
1+	d^7	d^6
2+	d^6	d^5
Atomic radius	134 pm	127 pm
Ion radii [a]	Ru^{3+}: 82 pm	Mn^{2+} (ls): 81 pm
Price per kg (2018)	>9.000 €	<5.0 €
Production (est.)	12 t a^{-1}	20 Mio t a^{-1}

Figure 3. The "diagonal relationship" of Ru(II) and Mn(I) in the periodic table as a guiding principle for catalyst development.

As part of a longstanding research program, we are investigating the elementary steps comprising catalytic cycles for CO_2 hydrogenation with a combination of experimental and computational techniques. In the evaluation period of this report, a detailed study has been conducted on the insertion of CO_2 in the M-H bond of ruthenium phosphine catalysts, a major catalyst class for CO_2 hydrogenation to formic acid [5]. While the challenge of CO_2 conversion is generalized often with the term "CO_2 activation", the results of this study demonstrate that the energy span of the catalytic cycle is determined mainly by the stability of the formate intermediates and the barrier for formic acid liberation.

While complexes based on 3d metals mark the pioneering time of organometallic catalysis and its early large scale industrial applications (e.g., Co for carbonylation, Ni for olefin oligomerisation, Ti and Cr for polymerisation), complexes of the platinum group metals later have been found to outperform them often in terms of activity and selectivity. Therefore, fundamental science and application in organometallic catalysis have been focussing on noble metal complexes largely since the 1980s. In the last decade, catalysis with 3d metal complexes has seen a dynamic renaissance motivated by arguments such as lower costs, natural abundance, and reduced environmental impact. At the CEC, the role of 3d metals in biological energy conversion systems is a major line of research with a long tradition. The accessibility of more oxidation states, the broad involvement of open shell systems, and the higher kinetic lability make 3d metal complexes significantly distinct from the platinum group metals. In this context, manganese has caught much attention recently.

Initial studies addressing manganese complexes in our group were motivated by a BMBF funded initiative to explore their behaviour under the conditions of the oxygen evolution reaction [6,7]. Recognizing the potential of this metal in organometallic catalysis, we extended our interest to the use of Mn-complexes for hydrogenation and related reactions. Our concept is based on the straightforward assumption that the "diagonal relationship" between Ru(II) and Mn(I) in the periodic table can be exploited to identify lead structures for catalyst development using the 3d metal. In particular, the ligand-assisted heterolytic cleavage of H-H or E-H bonds appeared an attractive reaction principle to be translated in a first approximation from the noble to the non-noble metal (Figure 3).

Based on literature precedence, we focus on multidentate ligands containing amino groups as "non-innocent" units for cooperativity with the metal center. Various PNP pincer [8,9] and triazol-based [10,11] ligands were found to form readily accessible and very versatile Mn(I)-catalysts for a range of hydrogenation and related reduction reactions (Figure 4). Simultaneously with independent efforts by the groups of Milstein and Rueping, we reported that cyclic carbonates can be converted to methanol and diols under hydrogen atmosphere using a Mn-MACHO complex as the catalyst [8]. The hydrogenolysis of the carbonate linkage to methanol corresponds formally to the hydrogenation of CO_2. While the direct hydrogenation of CO_2 to methanol with Mn-catalysts remains as yet elusive, we were able to demonstrate their catalytic activity for the hydroboration of carbon dioxide to the methanol level [9]. Current mechanistic insight from stoichiometric model reactions, isotopic labelling, multinuclear NMR studies, and isolation and characterization of potential intermediates are consistent with the presumed basic analogy of ligand-assisted bond activation at Ru(II) and Mn(I) (see Section XXX for details). Further studies to elucidate the similarities and differences in much more detail are under way. We are confident that this will allow not only a translation of ruthenium catalysis to manganese complexes but will also open access to novel unprecedented pathways based on CO_2/H_2 activation (*vide infra*).

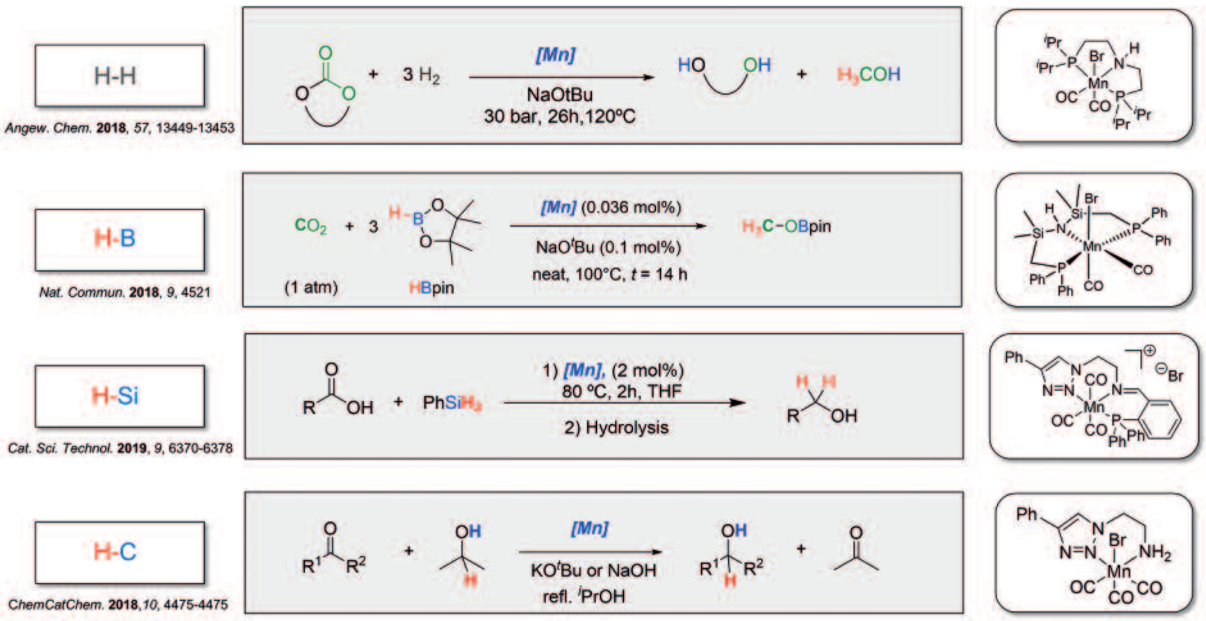


Figure 4. Catalytic reduction reactions using Mn(I) complexes.

The exploration and evaluation of new synthetic methodologies, which are not yet in the toolbox of organic and in particular industrial chemistry, is the main focus of this area. A longstanding program focusses on the use of CO_2 as raw material as an attractive way to harness renewable energy into chemical energy carriers and value-added products (cf Figure 2). The selective synthetic conversion of lignocellulosic raw materials and platform chemicals continues to be an active field of activities in particular as part of the Cluster of Excellence "The Fuel Science Center". We have developed the strategy of "catalytic pathway design" to identify possible synthetic routes based on these building blocks, in analogy to the concept of retrosynthetic analysis in organic synthesis. A generic scientific challenge in this area is the controlled de- and re-functionalization reducing the oxygen content of the starting materials (see also section 2.3).

During the reporting period, the use of "green" methanol as the reagent for catalytic methylation reactions was a particular focus. Methyl branches in the carbon chains of alcohols are a ubiquitous structural motif in chemical products, ranging from potential energy carriers (isobutanol) over commodity chemicals (e.g., 2-methyl-1,3-propandiol, MPO) to numerous biologically active compounds and APIs (e.g., naproxen alcohol). Catalytic methods to introduce methyl branches at a late synthetic stage are, however, largely elusive. In general, C-C bond forming reactions using alcohols as coupling partners are scarce, despite the broad synthetic potential in the framework of Green Chemistry. We have developed novel synthetic methods to achieve such transformations utilizing de-hydrogenation/aldol condensation/re-hydrogenation sequences. Such kind of reaction cascades are sometimes referred to as *"borrowing hydrogen"*, a term coined by the late Jonathan Williams.

Initially, ruthenium was studied as the active metal due to its well established performance in hydrogen transfer reactions [12]. A range of complexes was found to exhibit activity for the methylation of alcohols with the exclusive introduction of the methyl branch in β-position. The Ru-MACHO was found to be the most promising candidate and the method could be optimized to give synthetically useful conversion and selectivity. The procedure applies to a remarkable broad scope of substrates. A detailed experimental study comprising the analysis of conversion/time profiles, isotope labelling, and multinuclear NMR studies supported the assumption of a reaction network where the metal catalyst is responsible for the hydrogen transfer steps, whereas the aldol condensation is base catalysed (Figure 5). DFT calculations on plausible intermediates were used to map out a possible energetic hypersurface for the entire reaction network [13]. The structures and energies of the intermediates and transition states were fully consistent with the experimental data. Notably, the combined data indicate that the dehydrogenation of methanol, which is often assumed to be most critical due to the higher bond dissociation energy as compared to alcohols, is not a limiting factor in this case. The overall efficiency appears to be primarily defined by the high energy of the transition state of the aldol reaction (which does not involve the transition metal catalyst!) and the low energy of the Ru-alcoholate intermediates.

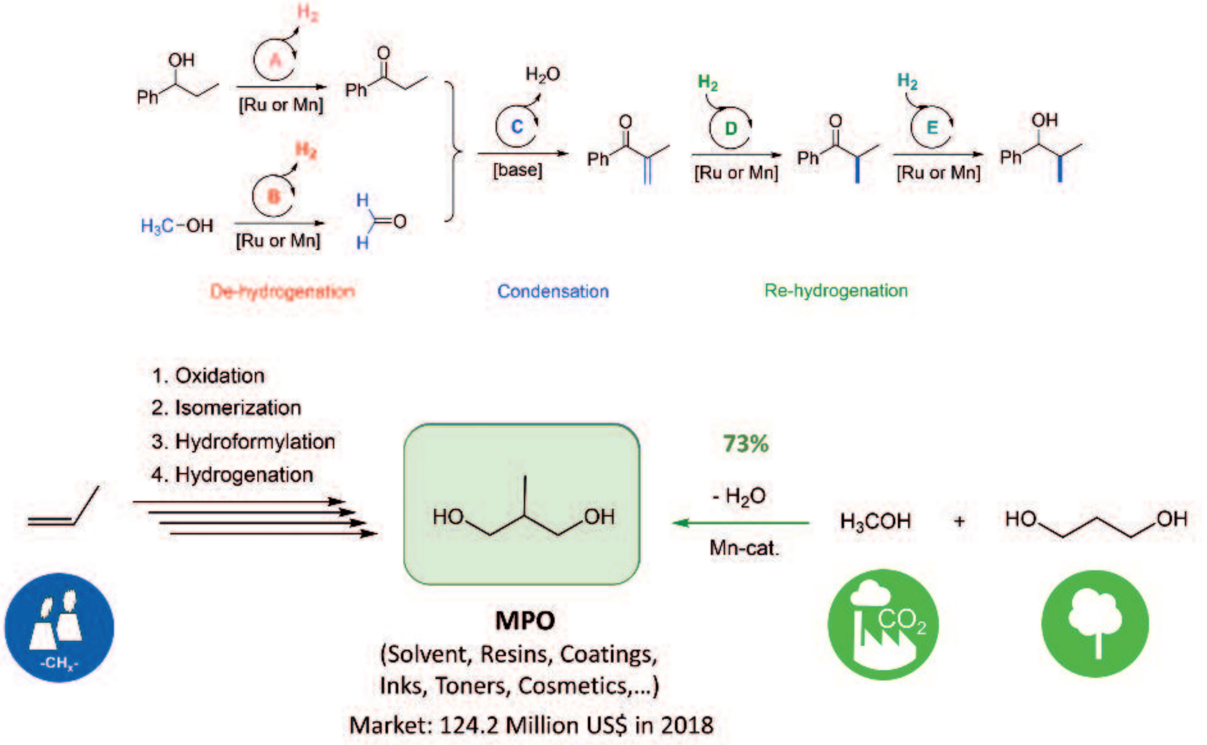


Figure 5. Schematic representation of the reaction network for β-methylation of alcohols using methanol as C1-building block and 2-methyl-1,3-propanediol (MPO) as synthetic example.

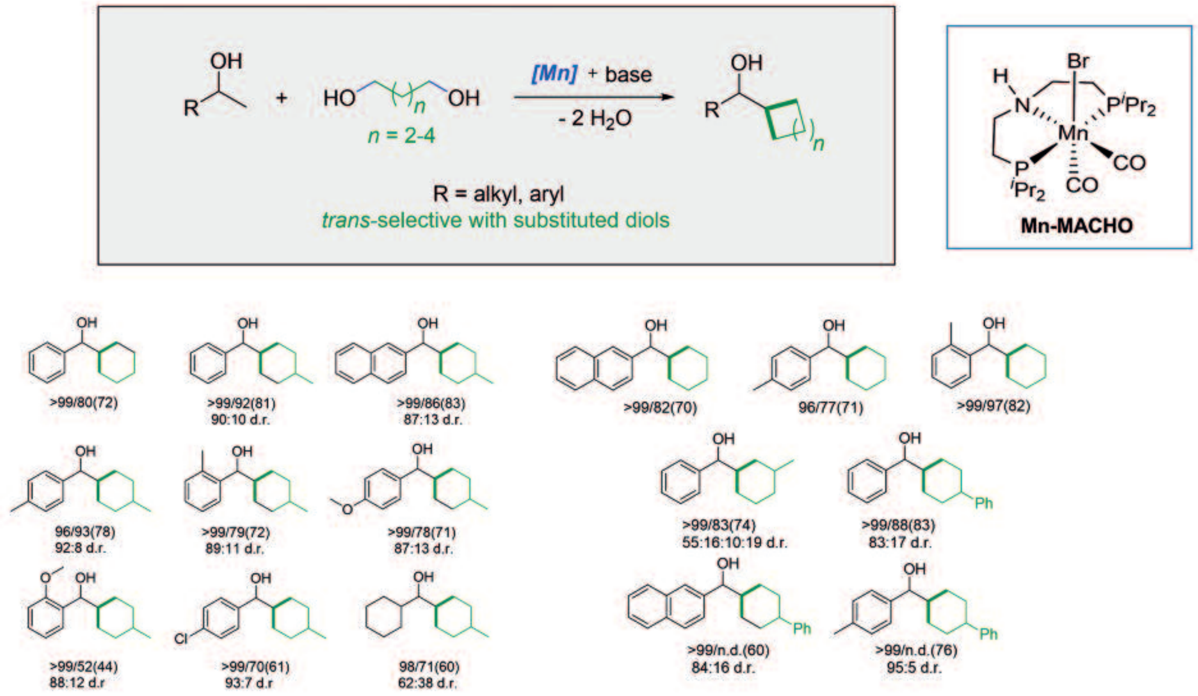


Figure 6. Mn(I) catalysed synthesis of cycloalkanes using the de-hydrogenation/aldol condensation/re-hydrogenation concept depicted in Figure 5.

Encouraged by this mechanistic insight, we turned to our concept of the Ru(II)/Mn(I) relationship. Indeed, the Mn(I)-MACHO catalyst proved not only fully capable of substituting its ruthenium congener but even allowed the extension of synthetic scope to methylation of various biogenic alcohols including diols [14]. Within the framework of the Fuel Science Center, such synthetic targets comprising biomass-derived building blocks, CO_2, and hydrogen as the only resources are referred to as "bio-hybrid products". A particularly illustrative example for the potential of this approach is 2-methyl-1,3-propanediol (MPO), a commodity chemical produced on large scale with a market volume of 124 Mio US$ in 2018. It was obtained in 73% yield under non-optimized standard reaction conditions in one step from methanol and propane diol, which is already industrially produced from biomass via fermentation today. This compares favourably with today's petrochemical production of MPO that comprises four process steps starting from propene as the refinery product.

Most recently, the "borrowing hydrogen" reaction principle has been developed further with the Mn(I) catalyst to double alkylate secondary alcohols or ketones with diols [15]. With these substrates, the reaction sequence leads to aliphatic carbocyles. It opens a novel synthetic approach to substitute cyclohexanes using readily available and cheap starting materials with the production of water as the only by-product (Figure 6). Seven- and five-membered rings were shown to be also accessible, albeit as yet with lower synthetic efficiency. Interestingly, the Mn(I) catalyst outperformed its Ru(II) congener under standard screening conditions in this case.

Reaction Media and Support

Chemical transformations involving organometallic catalysts typically are carried out in solution phase, and hence the solvent or reaction medium has a decisive influence on the molecular transformation as well as the overall process. In contrast to the electronic and steric influences of the ligand framework, interactions of the active metal centre with the reaction medium through coordination or via long-range interactions are far less understood and consequently are rarely used as rational control factors. This becomes even more critical in the case of catalytically active nanoparticles, for which the role of "ligands" or "stabilizers" continues to be a matter of much debate. At the same time, the intimate contact between nanoparticles and stabilizers opens the opportunity to generate multifunctional systems by a combination of reactivities enabled through the metal and its molecular environment, respectively. Such catalysts seem particularly attractive for transformations comprising hydrogenation and hydrogenolysis reaction sequences, offering the potential for novel de-oxygenation and de-functionalisation pathways as required for CO_2 and biomass conversion.

The research framework at the MPI CEC has motivated us to explore this opportunity systematically, capitalizing on experience from previous individual projects on metal nanoparticles in combination with advanced reaction media such as exemplified in ref. [16]. We currently focus on the use of ionic liquid-type structures to generate molecularly defined surfaces as functional supports for metal nanoparticles generated from organometallic precursors (Figure 7). Meanwhile, we have developed a toolbox of very robust synthetic methodologies and procedures to exploit the full flexibility of the surface modification and well as the nanoparticle assembly.

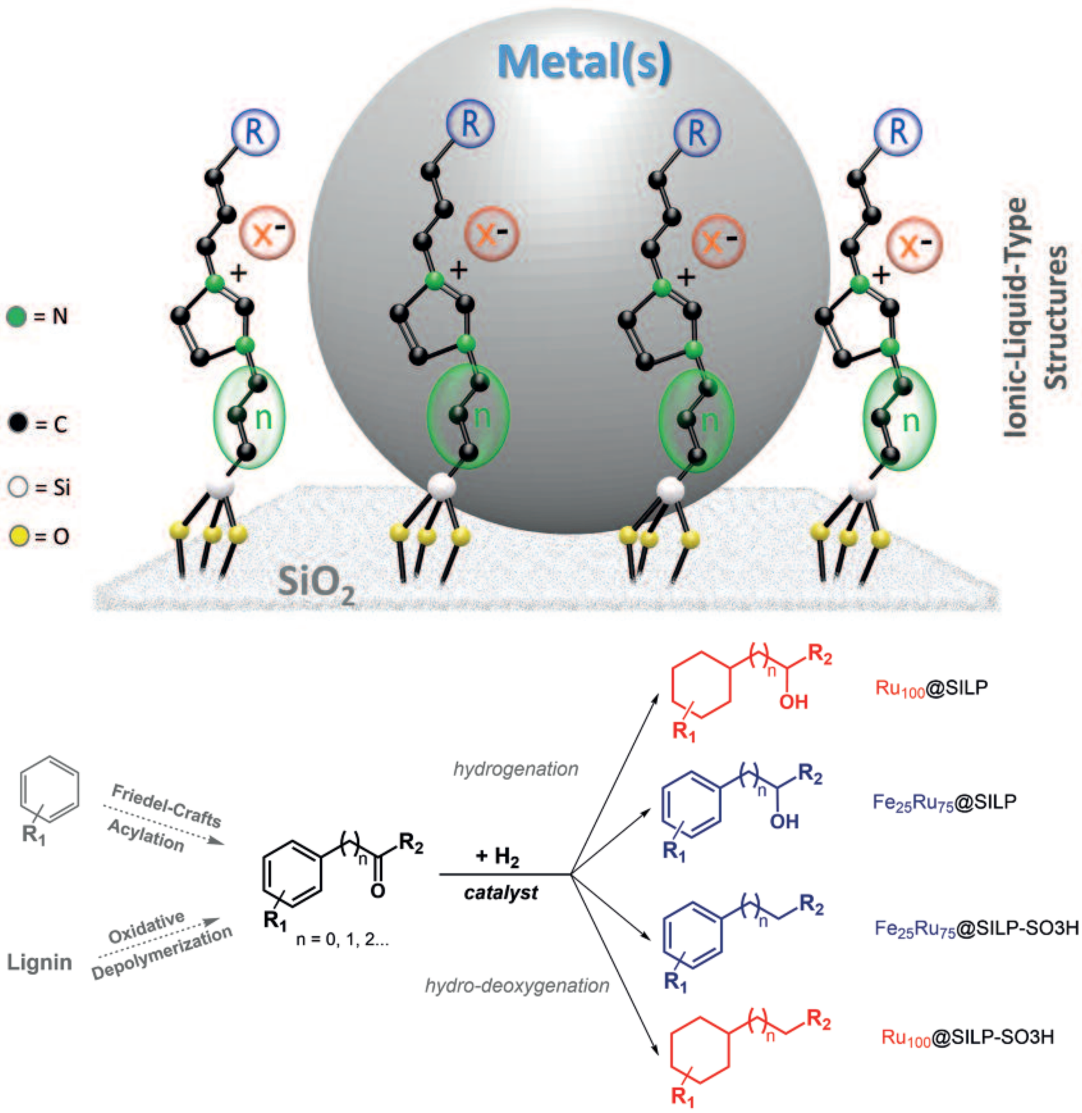


Figure 7. Multifunctional catalytic systems based on an organometallic approach to the flexible assembly of molecular stabilizers and catalytically active metal nanoparticles on solid supports and selected examples for synergistic catalytic performance.

Initial studies targeted the combination of ruthenium with Brønsted acidic stabilizers bearing SO_3H head groups. The proposed proximity and synergistic action of the two catalytic functions could be demonstrated by sophisticated electron microscopic studies (collaboration with the Schlögl group) and detailed reactivity studies. The selective catalytic hydrogenolysis of substituted diarly ethers provides an illustrative example for application [17]. This reaction type is discussed widely as an important step for the valorization of lignin and lignin derived feedstock streams. The cooperative functionality could be extended also to Lewis-acidic groups leading to selectivities in selective hydrogenation processes that could not be achieved with ruthenium on conventional supports [18]. Most recently, it has also been shown that the imidazolium-type stabilizing units can be replaced with phosphonium-based ionic liquids. In combination with rhodium nanoparticles, these hydrogenation catalysts show again unique and rather unexpected selectivities that were demonstrated to result from the specific combination of functionalities [19].

The formation of the nanoparticles from organometallic precursors allows the controlled formation of bimetallic systems. In particular, we are interested in combinations of noble and non-noble metals. The synthetic protocols are developed in collaboration with the group of Bruno Chaudret (LPCNO, Toulouse, France) and characterization by X-ray spectroscopy is done in collaboration with the DeBeer group at MPI CEC. As described in detail in the report by Dr. Alexis Bordet, promising results were obtained with the combination of ruthenium and iron in Fe_xRu_y@SILP-SO3H materials [20] for selective de-oxygenation of aromatic substrates. We are now extended this approach systematically to other combinations. Another current research line is to move from fixed functionalities to reactive head groups of the molecular units in order to generate switchable or even adaptive catalytic systems.

Reaction Engineering

We investigate multiphase systems for catalyst recycling and process integration utilizing in particular "green solvents" such as water, supercritical carbon dioxide, ionic liquids and combinations thereof. The exploitation of their potential requires a detailed understanding of the physico-chemical properties of these media and a profound knowledge about their interaction with catalysts and intermediates on a molecular level (for recent reviews, see: [21, 22, 23]. For supported organometallic [24,25] and nanoparticle catalysts [26,27], the continuous operation also offers additional control parameters such as spatial separation or residence time distribution. Implementing analogous systems on a laboratory piloting scale is an important asset to demonstrate the industrial relevance of fundamental research. At the same time, it allows the application of in operando techniques to analyse and ultimately control the fate of the catalytically relevant species under operating conditions (see report PD Dr. Andreas Vorholt). Thus, the results obtained from research with these units is coupled directly through a feedback loop with the catalyst development at the molecular level.

The hydrogenation of carbon dioxide to formic acid is the seemingly simplest reaction in the CO_2-based chemical energy scheme, as depicted in Figure 2. While myriads of catalysts have been developed over the years to overcome the kinetic barrier of the reaction, only very few studies are addressing the challenges of upstream and downstream integration which result from the unfavourable thermodynamics of the chemical equilibrium under standard conditions. They require the use of reaction media that minimize or compensate for the entropic loss associated with the transformation of H_2 (g) and CO_2 (g) into HCOOH (l). In order to achieve high formic acid concentrations, typical reaction require high gas pressures and reaction media that stabilize the product by solvation or acid/base equilibria.

Among the reaction media that allow formation of high concentrations of HCOOH in the absence of base, dimethylsulfoxide (DMSO) is particularly effective due to its effective solvation of protic substrates. While this reduces the number of components and hence seemingly simplifies the reaction mixture, it results in the formation of HCOOH/DMSO azeotropes that are very challenging for process development. In a collaborative team effort between catalysis and process systems engineering, the DMSO-based reaction system was fundamentally analysed using a combination of experimental and simulation tools [28]. While the catalyst could be effectively recycled in a biphasic reaction system and the azeotrope could be broken using an entrainer, the chemical stability of DMSO under the separation conditions was identified as a significant limitation.

Aqueous amine solutions are used industrially for carbon dioxide scrubbing from flue gases and are, at the same time, known to be effective reaction media for catalytic CO2 hydrogenation to formate. We have been able to design a catalytic system that allowed a combination of both processes in a biphasic reaction medium [29]. Thus, the deliberately chosen Ru-catalyst could be effectively recycled and the catalytic reaction could be carried out directly with scrubbing solutions without the need for CO_2 desorption and re-compression (Figure 8). While this approach achieves efficient upstream integration, the separation of the formic acid from the amine solution remains a challenge. A possible approach to overcome this problem is offered by the integrated derivatisation of the primary product formic acid into the esters. In particular, methyl formate appears as a highly attractive target as it is currently part of the petrochemical value chain towards formic acid and its derivatives and is also discussed as a potential fuel component or additive. The corresponding concept of an integrated process comprising multiphase catalysis with a tailored catalyst and reactive distillation was again validated by a team of chemists and engineers (Figure 8).

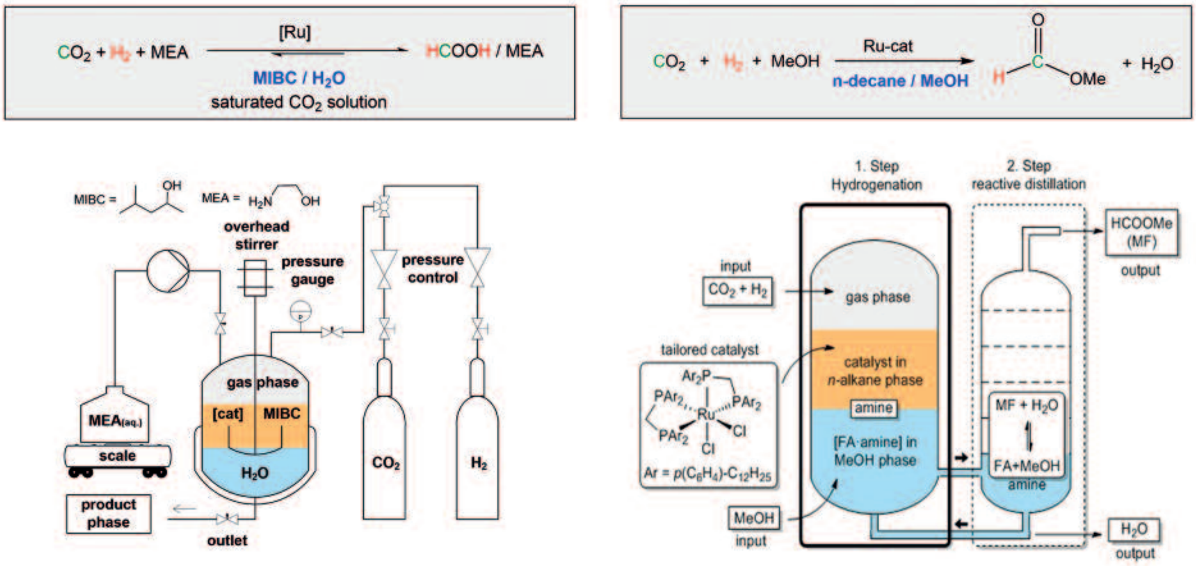


Figure 8. Multiphase approaches for catalytic hydrogenation of CO_2 to formic acid derivatives, demonstrating the potential for upstream and downstream integration.

Organisational Structure and Collaborations

Establishing the Department for Molecular Catalysis became effective with the appointment of the director on October 1, 2017. The most remarkable effort of the MPI CEC's workforce in the refurbishment of the laboratory building and the excellent team effort in setting up the necessary equipment and analytical techniques allowed starting of experimental work in nearly full operation by March 2018. The three thematic groups "Organometallic Electrocatalysis" (Dr. C. Werlé), "Multifunctional Catalytic Systems" (Dr. A. Bordet), and "Multiphase Catalysis" (PD Dr. A. Vorholt) could be installed and grew very quickly, mainly due to the recruitment of the respective group leaders. With Christophe Werlé successfully acquiring a Max-Planck-Research Group position starting in September 2019, a new group leader for the Organometallic Electrocatalysis team had to be recruited. Dr. Nicolas Kaeffer, currently Postdoc at ETH Zürich in the group of Christophe Coperet, will start in this position as of April 1, 2020. The interaction between the research groups within the department and across the departments at the MPI CEC has been highly prolific, resulting already in novel research lines and joint publications.

The joint affiliation of the Director of the Department with the Institute of Technical and Macromolecular Chemistry (ITMC) at RWTH Aachen University has been highly beneficial for the almost seamless build-up of the department without a noticeable induction period. The arrangement has proven very effective also for the integration of the MPI CEC in the Cluster of Excellence "The Fuel Science Center" and for the continuation of translational research efforts as part of the CAT Catalytic Center at RWTH Aachen. Thus, a valuable structural link between the MPI CEC and the Excellence Strategy of RWTH Aachen has been established.

The appointment of Prof. Regina Palkovits as MPG Fellow and the presently ongoing recruitment of a MPG Research group with tenure track (W3) at the ITMC are fostering the collaboration with RWTH additionally. Further links to neighbouring universities have been established through Christophe Werlé's MPG Research Group (RU Bochum) and the teaching affiliation (Privatdozent) of Andreas Vorholt at TU Dortmund.

The longstanding collaboration or Prof. Leitner as External Scientific Member at the MPI KoFo has been translated into the integration of infrastructure at the KoFo Technikum into the Joint Work Space between the two institutes. This has been essential for a quick start of high pressure experimentation for the Department and will continue to be highly beneficial for scientific collaborations and effective use of infrastructure at the Mülheim Chemistry Campus. The JWS framework also facilitates collaboration with the Neese group and two projects have been initiated on this basis within the IMPRS ReCharge Max-Planck-Research group.

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DEPARTMENT OF MOLECULAR CATALYSIS

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Objectives

With the depletion of fossil resources and the rise of alternative renewable energy sources and chemical feedstock, the permanent evolution and adaptation of catalysts is of critical importance. In this context, our work focuses on the design and development of multifunctional catalytic systems based on metal nanoparticles immobilized on functional supports, with a particular interest in supported ionic liquid phases (SILP). These so-called NPs@SILP systems are fully tunable, and a rational choice of the individual parameters (nature of the metal nanoparticles, ionic liquid, and support) provides control over the resulting catalysts' reactivity. This molecular approach allows producing innovative catalytic systems which can effectively address challenging chemical transformations. We especially focus on selective hydrogenation and hydrodeoxygenation reactions,[1-5] which are key transformations for the production of various value-added chemicals from renewable feedstock.

Results

Silica-based SILP are synthesized through the chemisorption of triethoxysilane-functionalized ionic liquids on amorphous SiO_2. The ionic liquid structures considered are based on imidazolium and phosphonium cations associated to a variety of anions (halides, triflates, acetates, NTf_2, etc.). In addition, the molecular structure of the ionic liquid can be easily modified to introduce functionalities, such as Brönsted and Lewis acids. Metal nanoparticles are synthesized *in-situ* in the SILP following a bottom-up approach involving the controlled decomposition of organometallic precursors under mild conditions. The characterization of the different components of NPs@SILP materials requires the use of several techniques such as ICP, BET, IR, solid state NMR, electron microscopy (TEM, STEM-HAADF/EDX, SEM-EDX), XPS, XAS.

1) Variation of metal NPs composition

In a first approach to multifunctional NPs@SILP catalysts we focused on the modification of the composition of metal NPs to produce catalytic systems with tailor-made reactivity. We worked in particular on the dilution of noble metal NPs (Ru, Rh) with 3d metals to obtain various bimetallic NPs immobilized on SILPs, such as Ru_xFe_{1-x}, Ru_xCo_{1-x}, Ru_xNi_{1-x} and Rh_xCo_{1-x}. The careful choice of the organometallic precursors allowed for the easy synthesis of nano-alloys with tunable metal ratios. The dilution of Ru and Rh with 3d metals induced changes in catalytic properties, and especially in the catalysts' ability to hydrogenate aromatics.

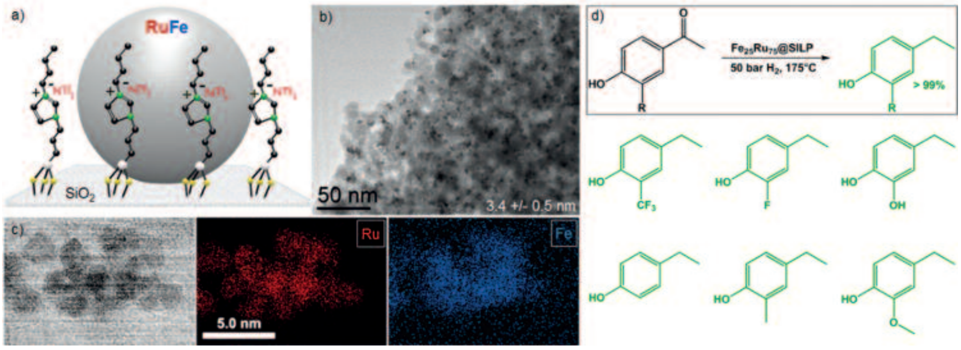

Figure 1. $Fe_{25}Ru_{75}$@SILP for the selective hydrodeoxygenation of hydroxyacetophenone derivatives.
a) Illustration of the $Fe_{25}Ru_{75}$@SILP catalyst; b) TEM; c) STEM-EDX; d) catalytic application.

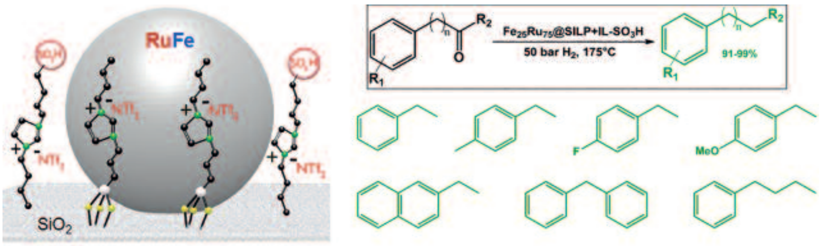

Figure 2. $Fe_{25}Ru_{75}$@SILP+IL-SO_3H for the selective hydrodeoxygenation of aromatic ketones.

We recently reported the synthesis of a bimetallic $Fe_{25}Ru_{75}$@SILP catalyst possessing excellent activity for the selective hydrogenation of aromatic ketones to aromatic alcohols. STEM-HAADF-EDX, XANES and EXAFS characterizations confirmed the formation of homogeneous $Fe_{25}Ru_{75}$ nano-alloys in which Fe and Ru are in the metallic state. Interestingly, the dilution of Ru with Fe resulted in synergistic effects and catalytic properties that are not accessible using the corresponding monometallic catalysts. In particular, the rate of ketone hydrogenation was significantly enhanced compared to pure Ru NPs while the hydrogenation of the aromatic ring was prevented.[1] We also discovered that the $Fe_{25}Ru_{75}$@SILP catalyst possesses excellent activity for the selective hydrodeoxygenation of hydroxyacetophenone derivatives (Figure 1). Substrates having electron-donating and withdrawing substituents could be effectively hydrodeoxygenated as long as an hydroxyl group was present on the aromatic ring. Interestingly, other acetophenone derivatives were only hydrogenated to the corresponding alcohols under these reaction conditions, evidencing the strong influence of the –OH group on the deoxygenation step. This opens the way to the selective hydrodeoxygenation of easily accessible hydroxyacetophenone derivatives (Friedel-Crafts acylation, lignin depolymerization) to produce of a wide range of valuable substituted phenols.

2) Introduction of additional functionalities, versatile approach to multifunctional catalysts

We then went one step further in the functionalization of our catalysts and focused on the combination of FeRu NPs with acid sites. The objective was to produce bimetallic bifunctional catalysts able to selectively hydrodeoxygenate aromatic ketones (other than hydroxyacetophenones) to aromatic alkanes. Unfortunately, the direct synthesis of bimetallic NPs on sulfonic-acid functionalized SILPs was unsuccessful due to the sensitivity of the metal precursors. However we found that the post-functionalization of $Fe_{25}Ru_{75}$@SILP with an acid functionalized ionic liquid is a convenient and versatile method for the production of bimetallic bifunctional catalytic systems. The resulting $Fe_{25}Ru_{75}$@SILP+IL-SO_3H catalyst was shown to be highly active, selective and stable for the hydrodeoxygenation of a large scope of benzylic and non-benzylic aromatic ketones (Figure 2). In contrast to previously reported catalysts, the activity of $Fe_{25}Ru_{75}$@SILP+IL-SO_3H was much higher for the hydrodeoxygenation of non-benzylic ketones as compared to benzylic ones.[3] $Fe_{25}Ru_{75}$@SILP+IL-SO_3H thus represents an attractive alternative to classical Clemmensen and Wolff-Kishner reductions and a promising catalyst for the hydrodeoxygenation of building-blocks from lignocellulosic biomass towards the production of value-added chemicals. In this context, we are currently collaborating with the group of Prof. S. Stahl (University of Wisconsin, USA) to achieve the selective hydrogenation and hydrodeoxygenation of lignin-derived diketones using $Fe_{25}Ru_{75}$@SILP and $Fe_{25}Ru_{75}$@SILP+IL-SO_3H and $Fe_{25}Ru_{75}$@SILP+IL-SO_3H catalysts.

Interestingly, the post-functionalization approach was not necessary for monometallic Ru NPs which could be easily synthesized directly on Brönsted acidic and Lewis acidic SILPs. Ru@SILP-SO_3H and Ru@SILP-$[ZnCl_4]^{2-}$ catalysts were found active for the selective hydrogenolysis of substituted diarylethers as lignin model compounds[4] and the selective hydrogenation of benzofuran derivatives,[5] respectively.

3) Towards switchable/adaptive catalytic systems

An important part of our work is also directed toward the development of switchable and adaptive multifunctional catalysts. The goal is to produce catalytic systems whose

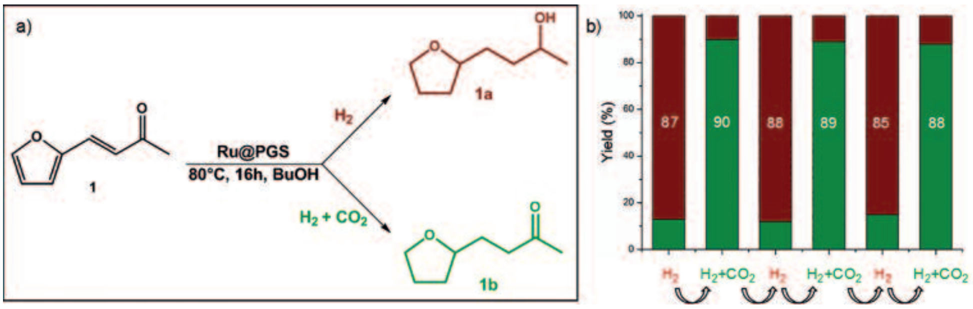

Figure 3. Ru@PGS for the selective and switchable hydrogenation of furfuralacetone. a) Reaction sequence; b) Selectivity switch in continuous flow reactor as a function of the atmosphere composition (red: **1a**; green: **1b**).

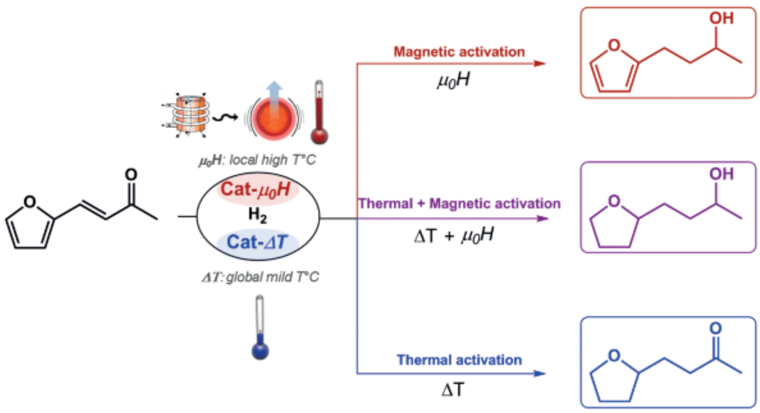

Figure 4. Catalytic system with switchable selectivity, example with the hydrogenation of furfuralacetone.

reactivity (and in particular selectivity) is not static (like in the previous examples) but flexible, and can be modified by changing the reaction conditions or applying external stimuli.

One of these systems consists of Ru NPs immobilized on an amine-functionalized polymer-grafted silica (Ru@PGS) and is developed in collaboration with the group of Prof. Philip Jessop (Queen's University, Canada). We show that the selectivity of the catalyst for the hydrogenation of a model substrate (furfuralacetone) "adapts" to the composition of the gas phase. In presence of H_2, furfuralacetone is fully hydrogenated to the corresponding alcohol. If hydrogen is mixed with CO_2, we observe a different selectivity where the furan ring and the double bond are still efficiently hydrogenated while the ketone is conserved (Figure 3a). We show that the change in selectivity is due to the formation of an ammonium formate species coming from the reaction between the amine functionality, CO_2 and H_2. This process is reversible, allowing us to switch back and forth between H_2 and CO_2 + H_2 in continuous flow reactor to produce either the saturated alcohol **1a** or the saturated ketone **1b** (Figure 3b).

We are currently working on another system involving the use of magnetic induction to locally heat and activate catalysts decorated with magnetic nanoparticles. Our idea is to take advantage of the localized heating of magnetic nanoparticles to selectively activate a catalyst at high temperature while the surrounding reaction media stays at low temperature. This opens the way to the combination of several catalysts possessing different reactivity and activation temperatures in a single reaction media, and their selective activation depending on the stimuli applied, the synthetic needs and the energy available. This concept is exemplified in Figure 4 using the hydrogenation of furfuralacetone as model reaction. This project also involves a close collaboration with the "Multiphase Catalysis" team led by Andreas Vorholt to tackle the challenge of developing a mini-plant suitable with the use of alternating magnetic fields in order to extend our catalytic study and proof of concept to continuous flow conditions.

For the future of the team, we aim at pursuing the design and development of innovative switchable/adaptive catalytic systems able to address the challenges associated to the chemical energy conversion.

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DEPARTMENT OF MOLECULAR CATALYSIS

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Objectives

The multiphase catalysis group focuses on understanding catalysts in different dimensions. The molecular, phase and system levels are important to shape stable, active and selective catalysts that are decisive for the energy conversion processes. The dynamics of the catalysts on the molecular level in complex systems are dependent on phase compositions and the overall process design.

To investigate these phenomena employing supported and molecular catalysts, long-term experiments must be designed to investigate the reuse of catalysts. Therefore, techniques that separate products from the catalyst are investigated to recycle the latter. Such recycling and separation implies the existence of phase boundaries like liquid/liquid, liquid/gas or liquid/solid, for which knowledge on their behavior is crucial to understand the performance of the catalyst and its eventual separation. Therefore, the multiphase catalysis group works on different fields starting from the catalyst development, then understanding catalyst recycling techniques and finally scaling up to developing continuous setups to investigate the dynamics of catalytic systems in long-standing experiments, as depicted in Figure 1.

Activities

In the investigation of catalysts in different dimensions, three main topics have been shaped:

- First is the development of catalytic systems that implies the adaption of known reactions to new problems and the development of new transformations in the context of energy conversion.
- The second topic is the implementation and understanding of recycling techniques for molecular catalysts, which includes operando optics and models to predict phase equilibria.
- The third one is the development of operando spectrometric techniques capable of detecting the dynamics of catalyst species over time in catalytic systems.

All three topics share the tools of operando techniques to observe phase behaviour, catalyst dynamics and kinetics. The possibility to apply these different approaches in continuously operated miniplants is able to investigate catalytic systems holistically.

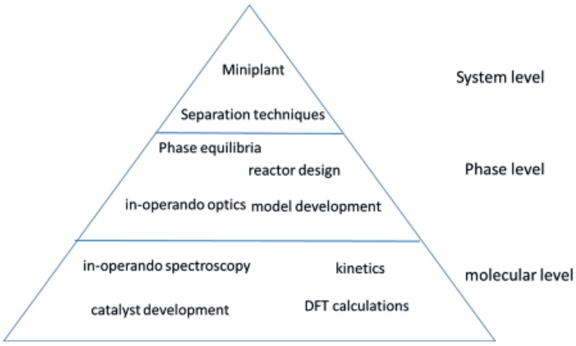


Figure 1. Different stages, tasks and tools in the development of multiphase catalytic systems.

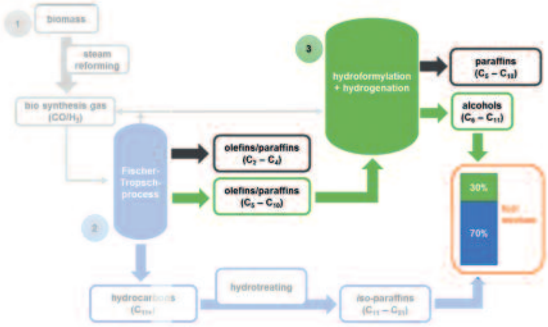


Figure 2. Reaction cascade from biomass to diesel fuels.

The group works on different fields of catalyst development, including CO_2 conversion, aminations, and reactions to isocyanates, anhydrides, amides, esters and alcohols. A prominent example of the work in the multiphase catalysis group is the EU-funded Redifuel project, in which 12 partners contribute to generate an EN590-compliant diesel fuel from biomass as starting raw material, as summarized in Figure 2.

Within the framework of the Redifuel project, the challenge for the CEC team is to find an efficient way to synthesize alcohols to be used as drop-in fuels from a crude Fischer-Tropsch mixture using tertiary amines as ligands in the catalytic system. A combination of hydroformylation and hydrogenation is capable of delivering the alcohol fraction that provides superior combustion characteristics of the fuel (Figure 3).

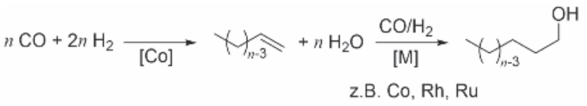
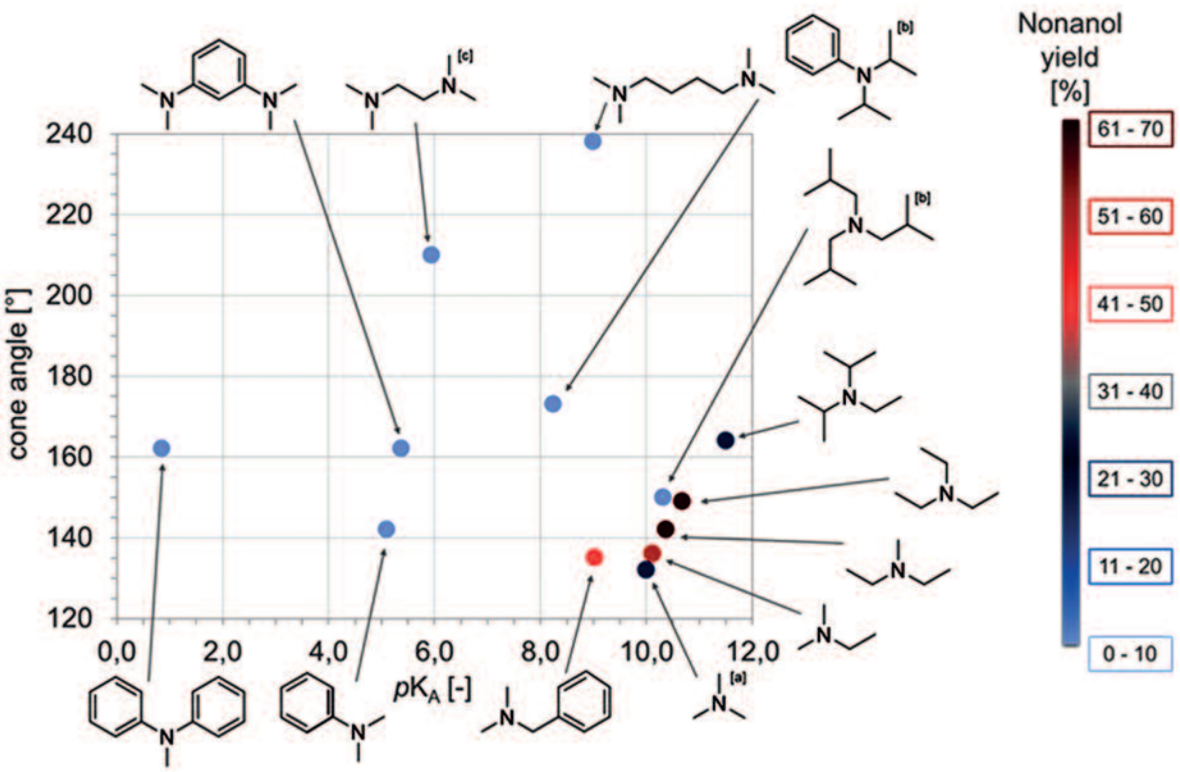


Figure 3. Reaction cascade from Bio Syngas to primary alcohols through the Fischer Tropsch synthesis of olefins and the subsequent hydroformylation and hydrogenation.

In general, a tandem reaction from an olefin to an alcohol or else a two-step approach that comprises a separated hydroformylation and hydrogenation step are possible. A novel catalyst system of rhodium and amine ligands has been developed to reach a high productivity for a one-step process. To this date, the effects of different amines as ligands on the yield to the product for these catalytic systems remain to be reported; thus, they have been investigated as a function of the basicity of the ligands and the calculated Tolman angles, as shown in Figure 4. In this way, optimal amine characteristics were identified for the reductive hydroformylation. Further investigations on the complexes that are responsible for this behaviour will follow.

The second alternative is to perform the hydroformylation and further hydrogenation of the C_5-C_{10} olefins separately. The hydroformylation step was investigated employing an immobilised rhodium catalyst in a water phase whilst having the olefin mixture as second phase. The high reactivity shown by this reacting system is unusual since the long-chain olefins are very poorly soluble in water and are therefore not accessible to the molecular catalytic system, i.e., there are mass transfer limitations from the catalyst containing phase to the substrates. To gain better understanding of this gas/liquid/liquid system and the kinetics of the reaction, additional experiments must be made to have a precise understanding of the relevance of the existence of interfacial areas in this multiphase catalytic environment.

Such interfaces are generated at the border of dispersed liquid droplets and gas bubbles within a bulk continuous liquid phase. The subsequent interfacial areas differ



Reaction conditions: 1-Octene (2.0 mmol), $[Rh(acac)(CO)_2]$ (20 µmol), 1.0 mol% Rh), Amine ligand (Rh/N 1:400), MeCN (1.54 g), CO/H_2 (30 bar, 1:2), 100 °C, 1.5 h, 700 rpm.

Figure 4. New Tolman-map of amine ligands in hydroformylation/hydrogenation reaction.

greatly depending on the equipment and the power input employed to put the various phases into contact. In traditional stirred tanks, the geometries of the vessel and the stirrer as well as the stirrer speed, which translates into power input, are the main decisive factors. To gain further insights into the behaviour of the dispersion and the equipment utilized, endoscopy is used as an in-situ optical technique to acquire images of the dispersion within the pressurized vessel where the reaction takes place. Subsequent automated image analysis is performed to obtain the droplet and bubble size distributions, which can mathematically be related to the interfacial area between the dispersed liquid/continuous liquid and the gas/continuous liquid phases, respectively.

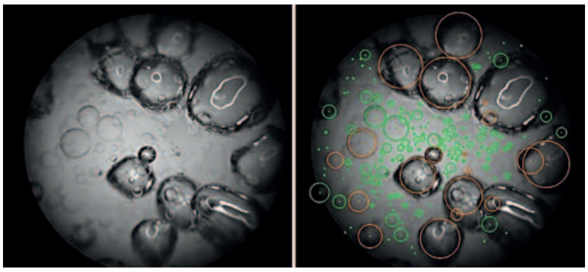


Figure 5. Operando image acquisition and analysis to identify bubble and droplet size distributions.

The combined data from the catalytic system and the interfacial behaviour of the gas/liquid/liquid environment will allow intensifying the reaction kinetics through an improved activity of the catalyst, the reduction of its leaching and a favourable design of the reactor to create large interfacial areas. These techniques can be employed in other recycling techniques that are at the moment under investigation in the group like, temperature controlled water systems, reactive ionic liquids and water based systems.

In the synthesis of synthetic fuels from Fischer-Tropsch-mixtures, the stability of the catalyst system plays a major role on the impact of the project. Only stable catalysts are able to be employed in scalable energy converting processes. There is a gap of knowledge of catalyst dynamics of molecular catalysts in continuously operated setups since in the classic catalytic literature only activity and selectivity is reported while information of stability of catalyst are very limited. Therefore, the group is currently working on a workflow that was recently published for the first time (Figure 6). (*ACS Catalysis*, 2019, 9, 5, 4308-4319)

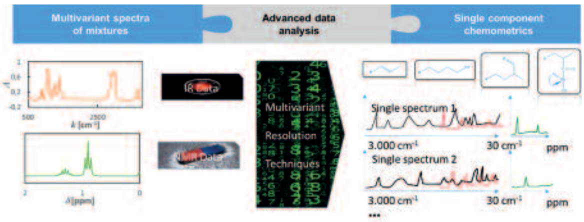


Figure 6. Workflow to access data on dynamics of catalyst while operation.

The data is acquired in a semi-batch or continuously operated system that implemented an infrared spectrometer and a benchtop NMR for ^{1}H and ^{31}P-measurements in a flexible setup that also allows GC-MS analysis, as shown in Figure 7. This data is then processed by a multivariant resolution algorithm to give the single component spectra that can then be assigned to those obtained from DFT simulations of the molecules involved molecules in the reaction.

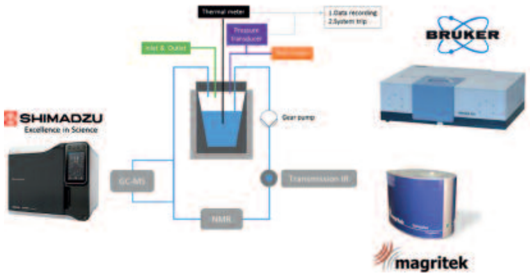


Figure 7. Operando spectroscopy in a semi-batch setup.

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DEPARTMENT OF MOLECULAR CATALYSIS

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Objectives

The search for benign chemical transformations using non-fossil carbon feedstocks is of paramount importance for a sustainable future. It can enable novel synthetic pathways through the manipulation of functional groups in the synthesis of fine chemicals and pharmaceuticals. Catalytic methods, following the principles of *Green Chemistry*, are at the core of this development. While numerous efficient catalysts for many transformations are known to date, they mainly rely on the utilization of noble and heavy metals of the periodic table. However, an earth-abundant, non-toxic, and biocompatible element, manganese, has recently experienced a growing interest in the field of catalysis. This transpired from the discovery that manganese complexes could compete with noble metal in a range of reactions. However, the applications of manganese as catalytically active metal are still limited, especially when compared to other first row elements such as iron or cobalt. Bridging this gap, through the valorization of renewable raw materials and alternative carbon feedstocks, such as carbon dioxide, constituted the focus of this research line. Our approach encompasses everything from fundamental organometallic chemistry to the use of renewable energy in the syntheses of affordable and environmentally friendly fuels and chemicals.

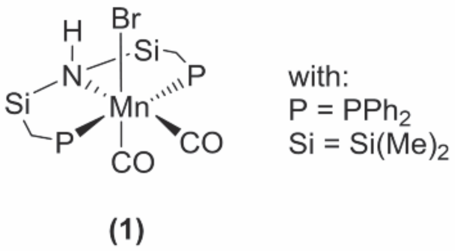


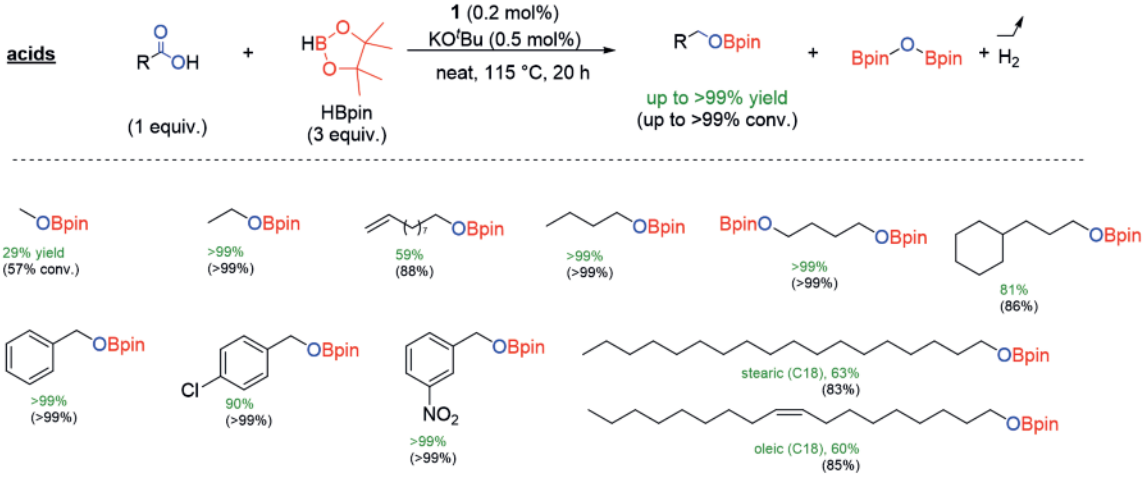
Chart 1. Structure of manganese pincer complex $[Mn(Ph_2PCH_2SiMe_2)_2NH(CO)_2Br]$ (**1**).

Results

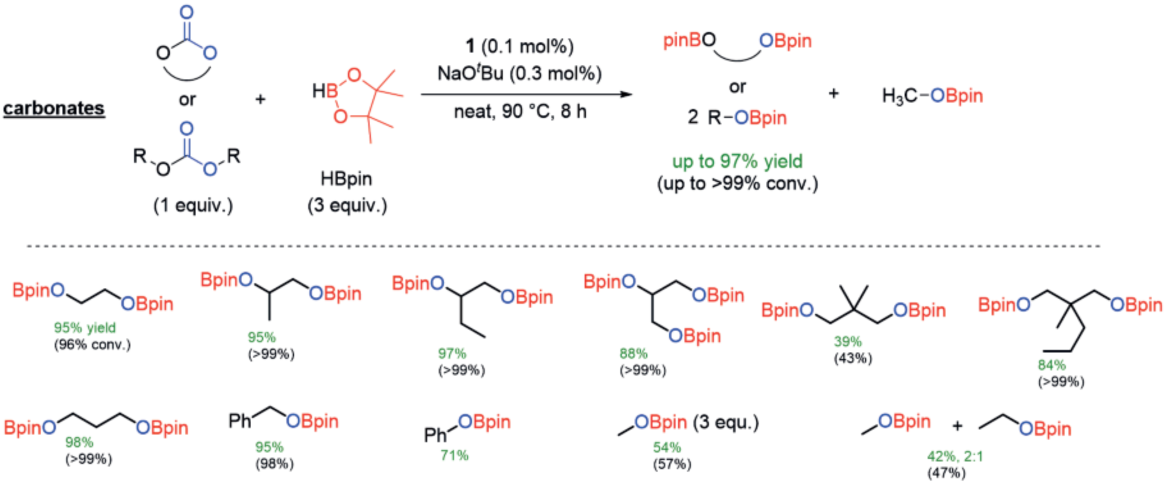
*Part 1***:** The reductive functionalization of the C=O unit in carboxylic acids, carbonic acid derivatives, and ultimately in carbon dioxide itself remains a challenging task of key importance for the synthesis of value-added chemicals. We discovered that a manganese pincer complex $[Mn(Ph_2PCH_2SiMe_2)_2NH(CO)_2Br]$ **(1)** (Chart 1), is capable of performing the catalytic reductive functionalization of a broad range of carboxylic acids (Scheme 1a), carbonates (Scheme 1b), and even CO_2 (Scheme 1c) using pinacolborane as reducing agent.[1] The complex operates under mild reaction conditions (80–120 °C), low catalyst loadings (0.1–0.2 mol%), and runs under solventless conditions emphasizing the remarkable potential of catalytically active Mn complexes.

Mechanistic studies revealed the formation of an unprecedented borane adduct **(IIa)** of the pincer complex **(1)** comprising a (-N-B-H-Mn-) four-membered ring, implying that substrate activation is facilitated by metal-ligand cooperation (Figure 1b). Based on this newly formed molecule, we were able to postulate the complete catalytic cycle for the hydroboration of carbon dioxide, as described below (Figure 1a).

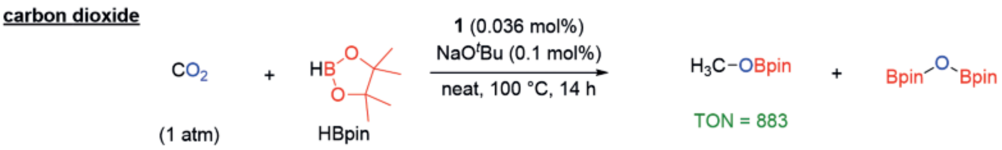
In the presence of the base, complex **1** is converted to the active species **I**. Subsequently, the reaction with pinacolborane leads to complex **IIa** with concomitant activation of the B–H bond. At this stage, **IIa** may react directly with carbon dioxide or with hydride species **II** (generated after B–H cleavage). However, given the slow rate of the B–H bond cleavage, we currently favor the direct attack pathway. Subsequently, the carbonyl group can interact with the Lewis acidic boron center, leading to activation for a nucleophilic attack as indicated in intermediate **III**. The reduced formoxyborane HC(O)OBpin is liberated to regenerate the active species **I**. Subsequently, pinacolborane reacts again with **I** to give the intermediate **IIa**. Analogous reduction of the C=O unit of the formoxyborane leads to the acetal $H_2C(OBpin)_2$ at this stage, that cleaves into formaldehyde and BpinOBpin. The same steps can be once more repeated with the carbonyl of the formaldehyde unit until it reaches the alcohol/methanol



Scheme 1a. Substrate scope for the hydroboration of carboxylic acids catalyzed by (1).



Scheme 1b. Substrate scope for the hydroboration of carbonates catalyzed by (1).



Scheme 1c. Hydroboration of carbon dioxide catalyzed by (1).

stage. In full analogy, carbonates can be converted into the corresponding alkyl boronate esters, while carboxylic acids can enter the catalytic manifold in the form of the boronate derivatives RC(O)OBpin that are spontaneously formed in the presence of HBpin as verified experimentally.

Part 2: Subsequently, we substituted the PNP-pincer ligand in 1 with a more versatile triazole donor unit. The synthesis of triazole moieties takes advantage of the high modularity of copper-catalyzed azide-alkyne cycloaddition (i.e., click-chemistry), an atom- and step-economic robust synthetic method, which is very convenient to access structurally different ligand frameworks. Hence, the stereo-electronic properties of the ligand architecture could be finely adjusted. Besides, their denticity can be controlled, and thus, bidentate or tridentate variations are accessible, leading to neutral (3, 4, 5) or cationic (2) complexes, respectively (Chart 2).

We have found that these complexes are catalytically competent in transfer hydrogenation of ketones with iso-propanol as a hydrogen source (Scheme 2).[2] We have demonstrated that good to excellent yields could be obtained for a large substrate scope spanning from aromatic ketones to aliphatic ketones in the presence of different functional groups. Iso-propanol serves as hydrogen donor together with different bases, including even

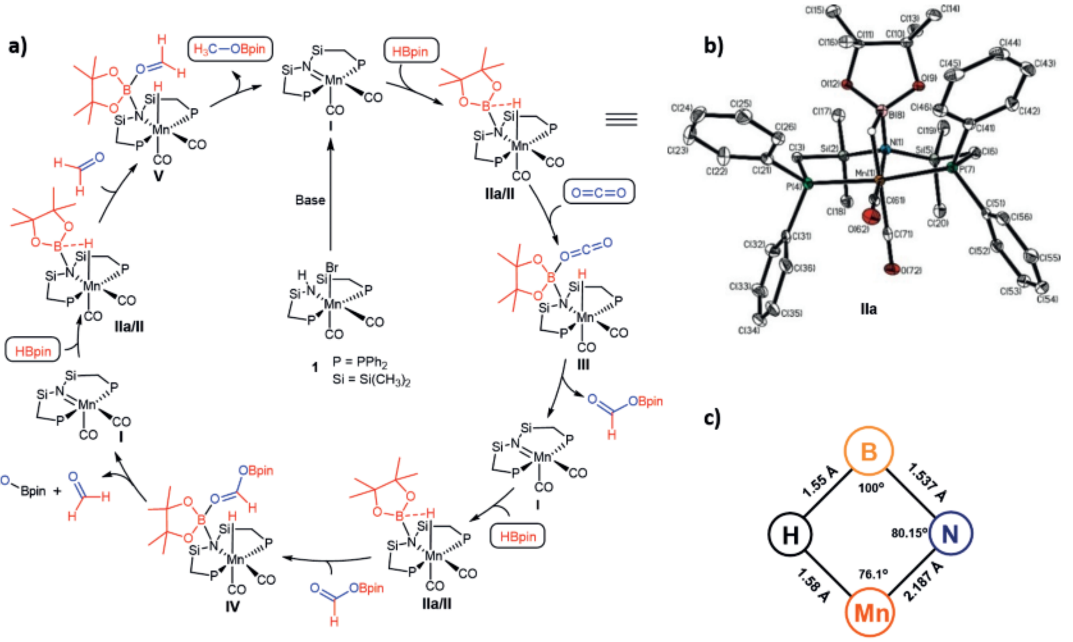


Figure 1: a) Suggested reaction mechanism for the hydroboration of carbon dioxide catalyzed by complex **(1)**; **b)** Molecular structure of intermediate **(IIa)**; **c)** Overall geometry for **(IIa)**.

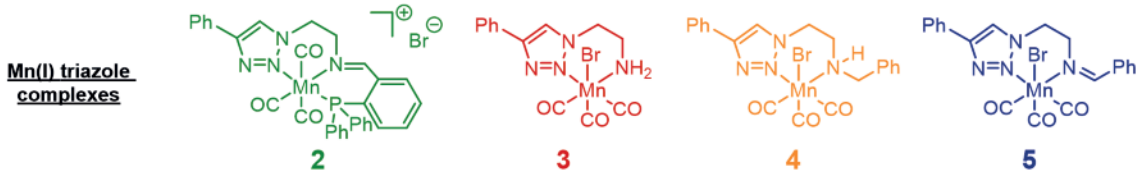
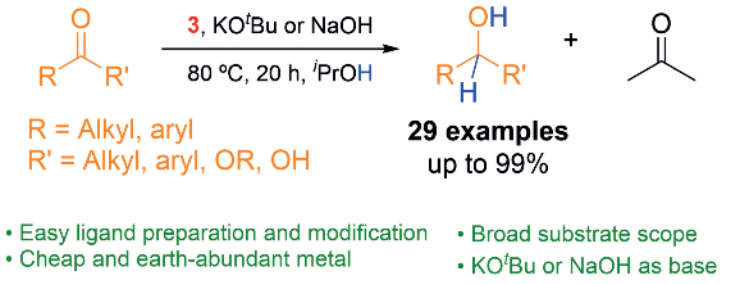


Chart 2. Examples of Mn(I) catalysts bearing triazole ligands.

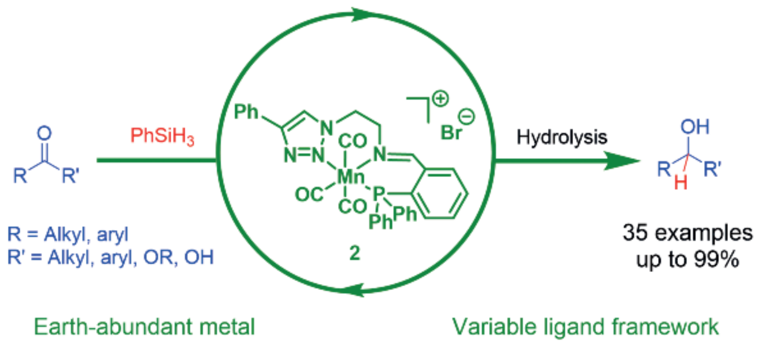
NaOH, as co-catalyst in some instances. Mechanistically, the catalytic results obtained with a systematic series of ligands suggest an outer-sphere hydrogen transfer involving the amino functionality as a proton source. Further mechanistic studies are currently ongoing to elucidate the complete catalytic cycle.

Part 3: Under the same lines, we have discovered that iminotriazole based manganese(I) complexes are efficient catalysts for the hydrosilylation of various carbonyl and carboxyl groups (Scheme 3).[3] This reaction allows the one-step synthesis of protected silyl alcohols, which can subsequently be hydrolyzed to the corresponding alcohols. Such an approach represents an alternative to hydrogenation reactions where easy and safe-to-handle silanes replace the use of hydrogen.

Aromatic and aliphatic ketones can be reduced with good to excellent yields at low catalyst loadings within one hour reaction time, using either neutral **(5)** or cationic complexes **(2)** comprising bidentate or tridentated ligands, respectively. Extending the reaction to carboxyl groups, esters were reduced with very high conversions, whereby complex **(5)** favored the formation of ether products while complex **(2)** lead preferentially to alcohols. Most significantly, complex **(2)** provides the first example for effective manganese(I) catalyzed hydrosilylation of carboxylic acids to alcohols. We believe that these results will encourage further investigations into the dynamic field of manganese(I) catalysis in the prospect of finding greener alternatives to existing catalytic methodologies.



Scheme 2. Transfer hydrogenation of ketones catalyzed by Mn(I) complexes bearing triazole ligands.



Scheme 3. Hydrosilylation of carbonyl and carboxyl groups catalyzed by Mn(I) complexes carrying triazole ligands.

Future directions

Taken together, these results significantly enlarge the potential of molecular catalysts based on earth-abundant and non-toxic manganese as an active metal for de- and re-functionalization of challenging substrates. We believe that the synthetic protocols and the molecular insight from our work will encourage further investigations into the dynamic field of manganese(I) catalysis. More generally, we hope that our approach will encourage the development of greener alternatives to existing catalytic methodologies, including the use of non-fossil carbon feedstocks derived from biomass or carbon dioxide and sustainable energy.[4]

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DEPARTMENT OF HETEROGENEOUS REACTIONS

DEPARTMENT OF HETEROGENEOUS REACTIONS

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Founding Director: MPI CEC (since 2011)

The Department is split between FHI Berlin, HZB (BESSY) and MPI CEC Mülheim. As outlined in the general report and in the last report for the Fachbeirat the fractional department in Mülheim has the purpose to introduce methods and concepts of interfacial catalysis into the forming MPI CEC. The lifetime of the operation at MPI CEC is finite and the operation will likely no longer exist at the forthcoming meeting of the Fachbeirat. For this reason, no longer-term obligations can be taken any more. One generation of Ph.D. students greatly helped to bring the function to life. The last representatives of the cohort will graduate in 2020 and no successors are taken on. Exceptions are students who are supervised by external academic staff guaranteeing continuity in supervision.

The Department is involved in several large and medium-term projects. Here the understanding is that the C2C project will continue with a contribution from MPI CEC operated by Holger Ruland. Robert Schlögl will participate and serve in the supervising "Koordinierungskreis" until 2023. An engagement in the COE „Fuel science centre" will (partly) transfer with Anna Mechler to Aachen with

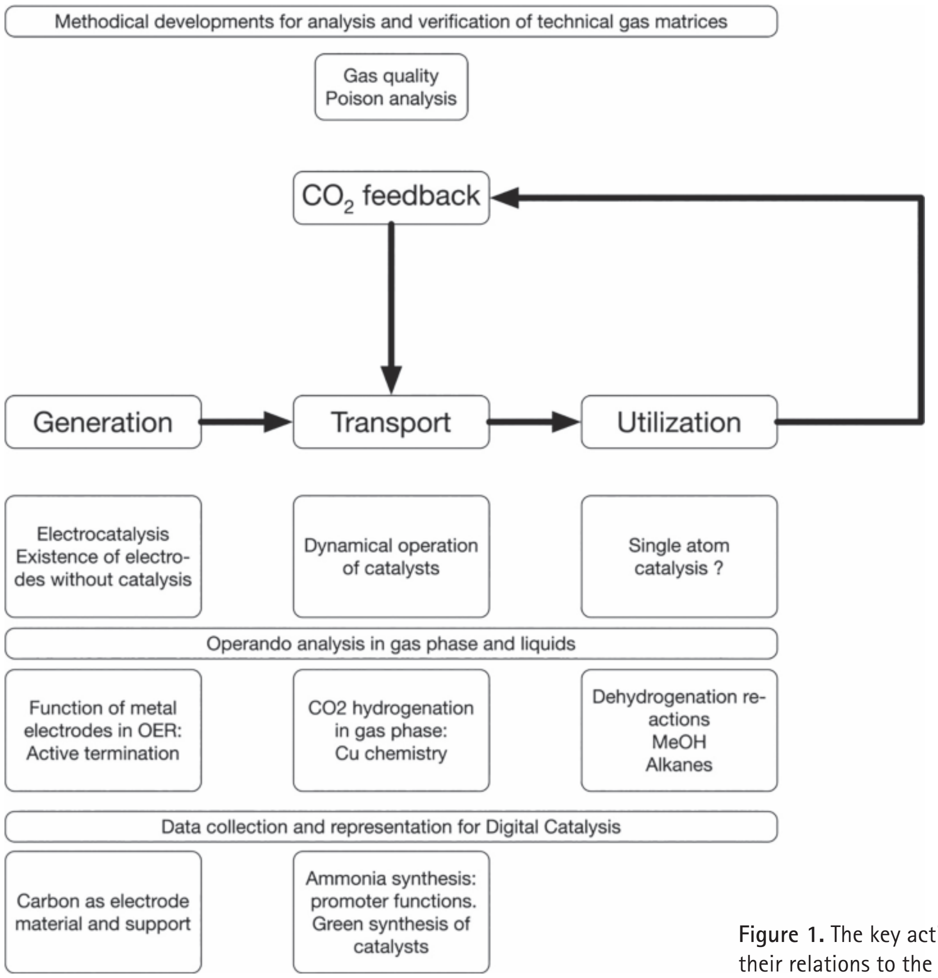


Figure 1. The key activities of the department and their relations to the CEC theme of the institute.

the understanding that Robert Schlögl will stay involved. In the CRC Transregio 247 the department will remain strongly involved with several group leaders contributing actively to the work. At least for the first funding period stability and continuity of the work is guaranteed. To this end the creation of a competent chemical electron microscopy group at MPI CEC with Walid Hetaba as the competence leader is currently ongoing with him moving in 2020 from Berlin to Mülheim and bringing personnel from FHI. Here the reverse exchange from MPI CEC back to Berlin is also practiced with the unique facilities of the ChemiTEM being used in the Berlin COE UniSysCat. The MPI CEC will further be involved in the emerging CATLAB project in cooperation with the HZB Berlin centred around the use of BESSY and the EMIL infrastructure. Here continuity will be given by keeping Serena DeBeer involved in supervising the project through the "Kollegium". It is expected that the dissolution of the Department will be organized with the advent of the next director. Details may change according to the practical developments.

Research concept

The Department is centred around the science involved with generating, transporting and using hydrogen as the universal chemical energy carrier in sustainable energy supply systems. In accordance with the mission of the Institute the work focusses on fundamental aspects and methodical developments needed in these contexts. The concept also includes collaborations with technical realizations of chemical energy conversion. Only in this way it can be ascertained that science solutions are applicable to later applications and that the true problems of present technology are brought in the focus of the science work. It is a surprising observation how fast the apparently solid foundations of our understanding became unstable once the application scenarios deviate from the current industrial practice. It is felt that a consistent picture about catalytic function that is free from simplifications that do not hold under performance conditions is still missing. Finding trajectories towards this picture is the common denominator in the projects of the department.

Figure 1 outlines the relation of key activities between each other and with the topic of chemical energy conversion. Individual projects are interconnected with methodical developments. All projects use the infrastructures of the MPI CEC compiled in last 5 years and keep close connections to the capabilities at the FHI. The instrument of regular and always joined group leader meetings (by video meeting) proved instrumental to maintain close contacts between the co-workers with impact on the practical work.

Many results and insights of the work are described in the individual reports of the group leaders. The present text outlines selected results for illustration of the approach.

Digital Catalysis

Politics has started in Germany the "national research data infrastructure" initiative (NFDI) in which substantial funding (min 100M€) are given to selected consortia for creating a data infrastructure and the supporting AI concepts for advanced and integrated exploitation of the science content of experimental and theoretical research data. The Department participated actively in creating a White Book on Digital Catalysis (by DECHEMA) from

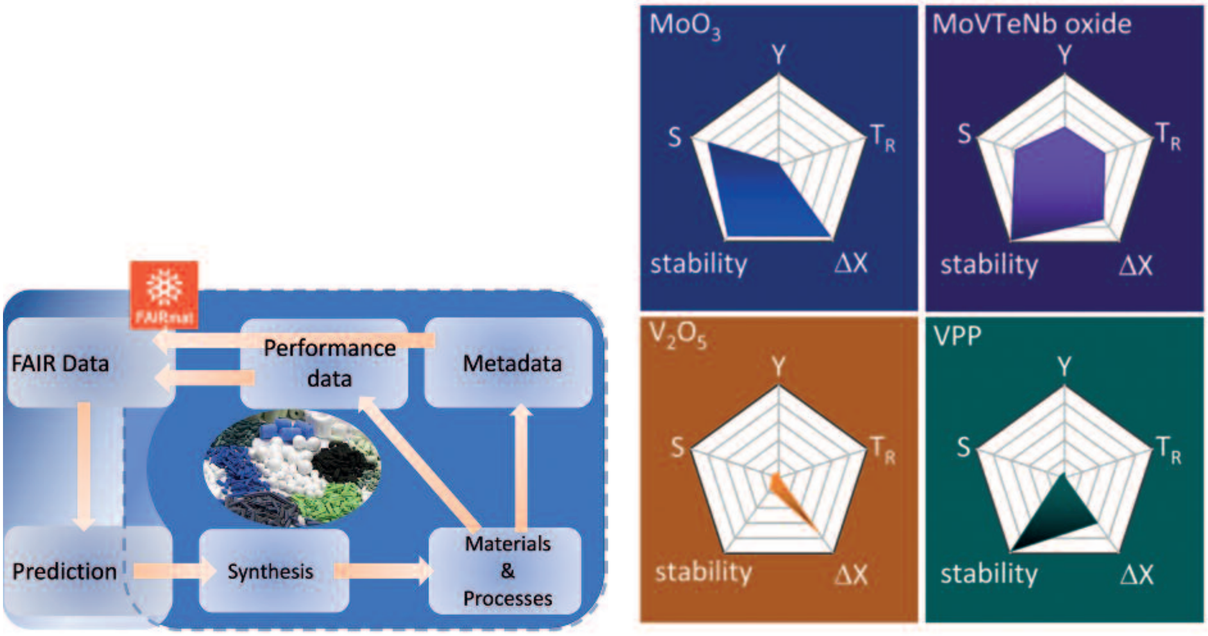
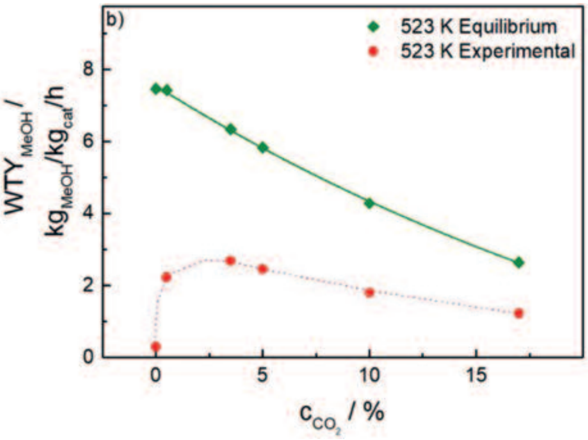


Figure 2. Concept and a representation of kinetic results from the digital data project of the Department. The results aim at defining a complex descriptor for kinetic performance and stability in a reaction with a selectivity branching (propane oxidation). The area enclosed in the radar plots serves as preliminary descriptor.



Catalysts	T [K]	P [MPa]	WTY [g_{MeOH} h^{-1} g_{cat}^{-1}]	X_{CO2} [%]	S_{MeOH} [%]	ratio CO_2/H_2	F/W [l kg^{-1} h^{-1}]	SV [h^{-1}]
$Cu/Zn/Ga/SiO_2$	543	2.0	0.349	5.6	99.5	3.0	18000	-
In_2O_3/ZrO_2	573	5.0	0.295	5.2	99.8	4.0	20000	16000
$Cu/ZnO/Al_2O_3$	573	5.0	0.122	2.1	10.9	4.0	20000	16000
$Cu/ZnO/Al_2O_3$	523	3.0	0.750	18.2	33.0	3.5	-	30000
$Cu/ZnO/Al_2O_3$	523	5.0	0.721	21.4	52.3	3.0	18000	-
$Pd/Zn/ZrO_2$	523	3.0	0.035	6.3	99.6	3.0	1800	-
$Ga/Pd/b\text{-}Ga_2O_3$	523	3.0	0.253	1.0	52.0	3.0	-	80000
$Cu/Zn/ZrO_2$	493	8.0	0.179	21	68	3.0		3300
$CuO/ZnO/Al_2O_3$	493	1.3	0.218	35.2	64.7	3.0	-	3600

Figure 3. Performance data for MeOH Synthesis catalysts with CO_2 as feed gas. The plot shows own measurements with a commercial Cu/ZnO catalyst after proprietary activation. The table lists values for comparison and indicates the different conditions used. For details see report of Holger Ruland.

which an application "NFDI for CAT" resulted to which the department is associated. We take the view that catalysis is a sub-section of material science and engaged thus to a larger extent in the material science initiative FAIR DI (co-led by M. Scheffler and C. Draxel Berlin). A section on metrology data generation and organization in there is co-led by Mark Greiner being responsible for XPS data infrastructures. In the respective sub-section for catalysis Annette Trunschke is active and supervises a joint pathfinding project with the TH department at the FHI and with Karsten Reuter (TU Munich).

These activities centre around the analysis that past and current experimental strategies in catalysis are unsuitable for digital catalysis tools[1] as they are incomplete both in kinetic analysis and in characterization metadata. This was observed may times before without causing any action. As kinetic data (in contrast to thermodynamic data) cannot be predicted or reconstructed, the quality assurance and error contents are difficult to assess. The only recipe against this deficiency of experimental catalysis science is the creation of best practice prescription (like DIN or ASTM norms) and the generation of datasets serving as benchmark or gold standard for verification and method development. The department has expertise in such questions both in heterogeneous catalysis[1] and in electrocatalysis[2] and has thus accepted the task to develop model solutions for both tasks. This is done in close and frequent discussion with the TH department and the FAIR DI initiative. We chose the topics of selective oxidation and the material class of perovskites as model systems. A handbook of best practice project design was created in collaboration with BASF as potential applicant and is being finalised at this moment. A gold standard of 13 catalysts stemming from industrial and own developments for lower alkane oxidation is currently generated. Figure 2 give a tiny impression from the concept how data reduction can be done such that data mining tools can work with the results.

We aim at rolling out this concept to all activities of the Department. As an emerging contribution the recent literature was screened for performance data of methanol synthesis. Here the allegation exists that the present Cu/ZnO/X system would be unsuitable as it deactivates too quickly. Without going into detail table 1 and Figure 3 show that this not necessarily so and can be misleading. The data in the table also reveal how different the testing conditions are and how little we know about the parameter landscape of the systems as rarely multiple data sets with the same catalyst are investigated.

Electrochemistry: Pt in OER

This project is prototypical for the approach the department takes in this topical area. Pt metal is only a fair catalyst in OER[3] but a very well-studied element in model and performance interfacial catalysis. By using this knowledge and referring to the nobility of Pt against oxidation the metal is well suited to answer the following question. In electrochemistry a fuzzy distinction between "electrochemistry" and "electrocatalysis" exists. This is not a semantic problem but rather touches on the conceptual understanding of the reaction and on the design of suitable materials. The reactions are executed in the common paradigm of electrochemistry by combining charge carriers with the reactant in a homogeneous environment. Then Marcus theory describes redox processes and the electrode is the source or sink for electrons. No specific interaction between electrode and reactant occurs and the material of the electrode has only to withstand the reactants and the applied potential. Occur electrochemical transformations as electrocatalytic reactions, then their kinetics is given by the Langmuir-Hinshelwood mechanism and specific interactions between reactant and electrode surface need to be considered. The material design must cater for bifunctionality addressing the specific needs of active sites under reaction conditions and the need to transport electrons in stoichiometric amounts from its surface to the current collector.

Electrochemistry in the context of molecular reactions assumes always a non-specific reaction (electrochemistry) whereas in the literature of interfacial reactions the situation is unclear. For sure, both cases coincide in the limit of zero conversion and thus zero current flow. Under finite conversion things get unclear. Taking into account the robustness of Pt against chemical attack it seems reasonable to follow the concept of molecular reactions and consider Pt an inert electrode in water and 0.1 molar acid or base.

Earlier experiments in our department indicated a slight reactivity of Pt under OER conditions[4] forming a surface oxide indicated by a small shift of a small component of the electrode in photoemission. This shift is well compatible with surface oxides but it remained elusive why at room temperature such a reaction should occur knowing that one can melt Pt in air without stable oxide formation (we omit here volatile PtO_2 as option due to the low temperature of the experiment).

Meanwhile the modified operando set-up with a graphene lid[5] over the working electrode was developed by our group allowing to study the OER in liquid water and not only in a water film. This can be verified through analysis of the O K-edge spectrum of water revealing the hydrogen-bridged water feature for a liquid film and its absence for an adsorbed state.

Figure 4 shows that the answer to this question depends on the conditions[6]. In the limit of low reaction and a water adsorbate little reaction occurs on Pt despite activity. If, however a liquid water film is present several observations change the picture completely. The water is strongly densified immediately in front of the electrode (several nm) as can be seen from the intensity change of the oxygen O-Kedge. The platinum is oxidized to a tetravalent state likely in the form of a oxi-hydroxide allowing for specific and strong interaction of the electrolyte with the electrode. The fact that the inner parts of the ca. 5 nm Pt particles remain metallic seems to support the good conductivity of the electrode.

Most interestingly is the complete and instantaneous reversibility of the densification of water and the oxidation of Pt with the sweep of the applied potential. Under open circuit conditions after reaction no sign is left of these drastic changes in interface chemistry.

The observation clearly shows that an intimate synergy exists between the surface chemistry of Pt in electrolyte under potential and the chemical state of water under these conditions near the interface. The observation questions the localization of the interface at the physical boundary of the materials under functioning conditions. Mechanistic concepts ignoring this form of chemical dynamics[7] and working with the structure of the interface without catalytic reactions will likely fall short in elucidating all atomistic details of the reaction under performance conditions. The fragility of the working interface was probed earlier[8] with RAMAN spectroscopy that also revealed the irreversible electro-crystallisation of oxi-hydrate phases upon extended use of the electrode as a pathway of deactivation.

Ammonia: also splitting is important

The concept to use ammonia as carrier for hydrogen bulk storage and transportation was put forward[9] several times. Recently, it got more attention as it can provide a clean way for energy transport without the need to transport back the carrier as it is necessary with all carbon-based solutions.

A not irrelevant side issue is the ammonia decomposition process needed to regain the hydrogen. As direct combustion of ammonia raises concerns about N_2O emissions with its extreme GHG potential it is likely that much ammonia will be split back to hydrogen before use. The Department was active in the field with different catalysis[10] concepts. In the context of the actual ammonia project the function of the promotor package occurs as the oxide scaffold of the novel catalysts is made up from typical promoter systems.

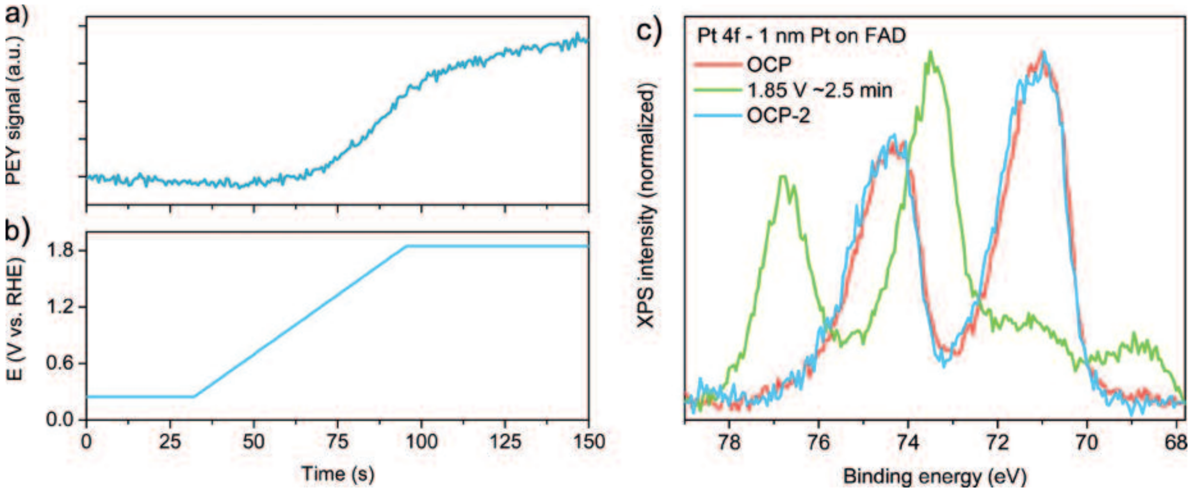


Figure 4. Operando O-Kedge NEXAFS **(a)** and Pt XPS **(c)** of nanostructured Pt particles (ca. 2-5 nm wide) during OER in front of a synchrotron beam. The data were taken from ref.[6] that also report the experimental details. The spectral changes shown are induced by sweeping the applied potential as shown in **(b)**.

For details see report by Holger Ruland. A systematic variation of the so-called structural promoters containing earth alkaline and row 3 element oxides resulted in the interesting observation that the ratio between the synthesis rate and the decomposition rate can be changed. This also applies for partial substitution of Fe by cobalt. Figure 5 collects some data on the ratio of conversion between synthesis and decomposition.

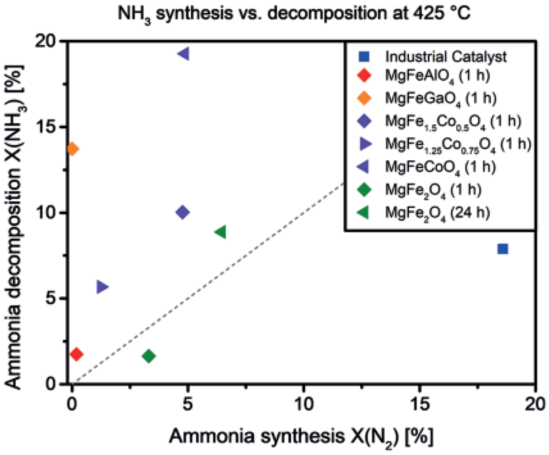


Figure 5. Conversion of a stoichiometric feed mix to ammonia and of ammonia back to the elements. The various catalysts were varied both in the "iron part" and in the promoter part to arrive at a wide library of systems. The conditions of the two reactions were strongly different in pressure and flow rates.

The data reveal clearly[11] that the expectation of a constant ratio of the two activities (different from unity due to the different rds for the forward and backward reaction) is not met. It is relevant here that one can completely supress the synthesis activity but retain a high activity for cleaving ammonia despite of both systems containing iron as active transition metal. Relevant for the present context is the finding that cheap iron catalysts can be promoted into effective ammonia splitting catalysts. Much deeper remains the challenge to describe the role of the "promoter" that should help a reaction but not control it. The role of a structural promoter seems more complex than only keeping the transition metal nanostructures apart from sintering. Ongoing is a systematic correlation of structure and performance using operando TEM and related methods.

Outreach to politics

The energy transformation is a multi-generation project involving to interrogate the foundations of our society. Such a process would be better conducted if the knowledge and options provided by science in general and by chemistry specifically would be taken into account. At least in Germany this knowledge is almost absent in the public debate giving room for multiple ideological concepts protecting particular interests of stakeholders. The current debate about e-mobility and the electricity market design debate are characteristic examples.

The MPI CEC is a suitable institution to counteract this trend. Its political and financial independence and its in-depth involvement into the relevant questions create a pool of knowledge that needs to be brought to the table of societal and political debate.

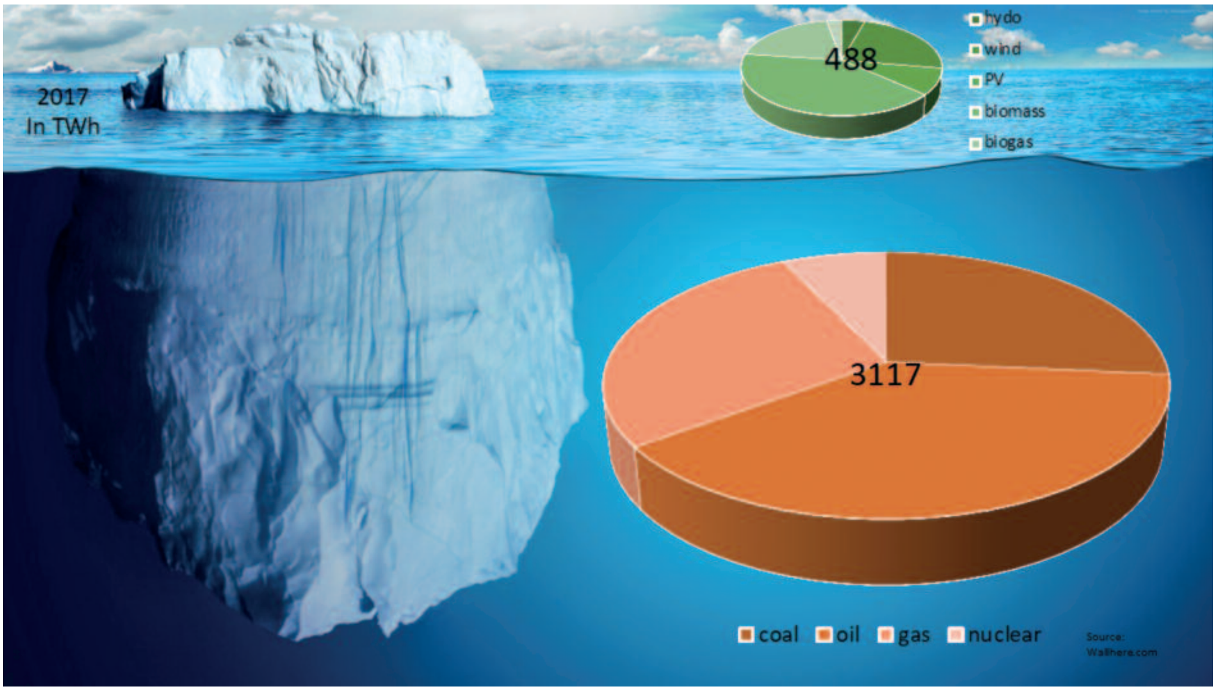


Figure 6. Visualization of the dimensions of the German national energy system. The underwater part is largely blanked out in the debate and usually covered with rather general assumptions about saving large amounts of primary energy without stating any transformation path.

Two lines of action were found to be effective in this context. The engagement in the national academy and its energy transition project ESYS (founded by Robert Schlögl) and the intensive and constant interaction with ministry of research and technology (e.g in the context of the Kopernikus projects) either directly or through organizations like DECHEMA and the Bundesverband der Deutschen Industrie BDI created a gateway into the societal discussion. Impact was achieved in the awareness for synthetic fuels (in cooperation with Walter Leitner) and for the need to design measures in research and technology in a systemic rather than in a sole process-related context (biofuels, tank-to-wheel quota).

The specific research domain for energy was discussed and structured in several rounds of funding initiatives under the involvement of Robert Schlögl. The family of Kopernikus projects (RS serves as chairman of the supervisory board) the MANGAN national research network (RS created the structure and funding conditions) and the C2C project (RS serves on the board of directors and co-created it with Fraunhofer and Thyssen-Krupp) are direct effects of the activities. Multiple strategic positions of the national politics are co-developed and informed by activities of RS as well as by WL[12].

The condition that the Max-Planck-Society always stays independent and is not involved as institution is a critical success factor as no immediate resource advantage can be assigned to these activities. Personal contacts with deciders in government and parliament directly and/or through the MPG provide an alternative gateway for indirectly enhancing the understanding and the number of decision options in energy politics. An example is the current debate about the dimension of local electrical supply with renewable energy as compared to the need to import renewables through a carbon circular economy and green (or blue) hydrogen. Figure 6 gives an impression about the dimensions and illustrates that traditional energy politics ignores the "underwater" part by neglecting the systemic nature of energy supply.

This activity could not happen without the solid foundation of the discussion in the practical research work[10b, 13] done at the institute. The fact that the MPI CEC broadly engages in the field of chemical energy conversion that is politically still in its infancy or even strongly opposed gives these outreach activities a particular relevance that is barely covered by other stakeholders including the national chemical industry. It is needless to state that many aspects require also engagement in the European domain (SAPEA process of the national academies, DG Energy in the Commission) and in specific countries (UK, Italy, France) where RS was and is active as advisor.

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DEPARTMENT OF HETEROGENEOUS REACTIONS

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Group Leader: MPI CEC (since 2017)

Summary

The Surface Analytics Group in the department of Heterogeneous Reactions focuses on analysis of chemically active materials (i.e. catalysts) in reactive environments, as well as the design and development of novel catalysts based on new design paradigms, such as single-atom alloying. The approach is to understand the underlying physics of the material properties, how these properties come to be and how they play a role in catalytic reactions. As the group's research is centered around experimental observation of these phenomena, several advanced in-situ spectroscopic, microscopic and spectromicroscopic methods are used. These methods generate large quantities of data that require ever evolving data analysis techniques to extract useful knowledge from the data. For this reason, the group is heavily involved in developing new analysis algorithms and applying modern machine learning algorithms to the experimental data obtained.

Research themes

2D metastable oxides formed under reaction conditions on dilute bimetallic alloys

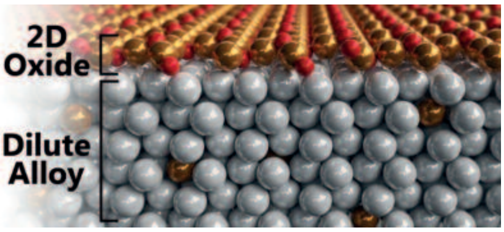

Figure 1. Rendition of the 2D copper oxide formed on AgCu alloys in oxidative environments.

Alloy catalysts are a promising class of materials that could enable fine tuning of catalytic properties and the development of novel catalysts. However, the behavior of these materials when exposed to reactions conditions is still in its infancy.

One the phenomena that occur when exposing alloy catalysts to an oxidative atmosphere is the formation of meta-stable surface species. We have found that AgCu alloys in epoxidation conditions for 2D Cu-oxides that are the 2D analogues to Cu_2O. These structures are found to be correlated with ethylene epoxide selectivity, and could play an important role in similar catalytic reactions.

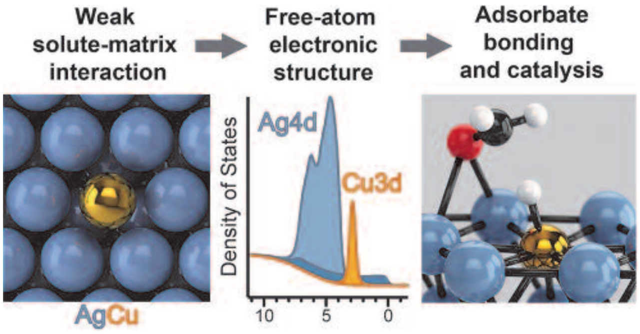

Figure 2. a) Illustration of AgCu single-atom-alloys, **b)** density-of-states of free-atom-like alloy, **c)** single-atom alloy mechanism in a methanol reforming.

Free-atom-like d-states in single-atom alloys

We recently found that some metal combinations give rise to an unique electronic structure when mixed together in dilute amounts. In particular, when small quantities of Cu are added to Ag, free-atom-like d-states are formed in the metal's valence band. These states resemble electronically, the states for free atoms. We have found that a number of alloys exhibit this property, including AgPd and AgMn. We have synthesized AgPd alloy catalysts, and have experimentally confirmed the existence of free-atom-like Pd states in AgPd single-atom-alloys. We have found that Pd exhibits different chemical behavior when present as a free-atom-like state compared to bulk Pd.

Synthesis of dilute alloy nanoparticles

In order to examine the wide array of possible alloy compositions, and to relate spectroscopic investigations with catalytic properties, one requires a general means of synthesizing high surface area alloys. Two approaches have been employed to synthesize nanometer-sized alloy particles: 1) laser ablation of bulk alloys, 2) polyol synthesis. The laser ablation method has the benefit that one can start from bulk alloy foils, produced using well-known traditional metallurgical methods. The down side is that the rate of particle production is rather slow, resulting in small yields. We have successfully synthesized AgCu particles using this method. Alternatively, one can use the polyol method, where one heats metal precursors in a polyol such as ethylene glycol, to reduce the metal precursors into metal nanoparticles. The method is simple to employ, but is restricted in the metal combinations that can be formed. We have successfully used the method to make CuPt nanoparticles.

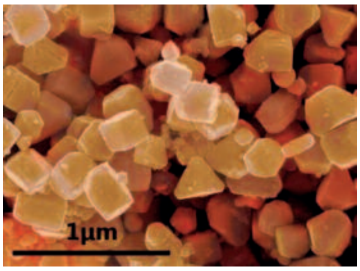

Figure 3. SEM image of CuPt nanoparticles

Machine learning in photoemission spectroscopy

Modern experimental methods generate large volumes of data. The datasets can be complex and high dimensional. In order to analyze the data as fast as it is generated, and to extract the most knowledge from the data as possible, we utilize many modern data science, chemometrics and machine learning algorithms. As an example, a spectromicroscopy map (i.e. a single data set, that is generated in 30 minutes of measurement time) generates an array of 120 000 XPS spectra. We have developed clustering algorithms for rapidly analyzing these large data sets. The algorithms are based on k-means clustering, principle component analysis, non-negative matrix factorization, hierarchical clustering, DB-SCAN and spectral clustering. The scripts developed with these methods allow us to perform nearly live data analysis during data collection.

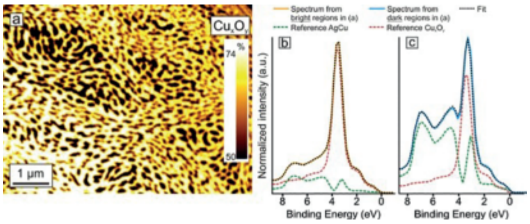

Figure 4. a) XPEEM Spectromicroscopy image stack for oxidized AgCu, **b)** and **c)** are the spectra extracted from the image stack using clustering methods.

Information modeling in XPS research

Research groups collect large quantities of diverse data over the years. Many researchers contribute to these collections of data. In order for the complete body of data to be useful for large scale analytics, as well as being useful for future generations of scientists, the data must be well organized and stored with all necessary metadata. To this end, it is necessary to develop an information model for the data. We have developed an information model for in-situ XPS data that enables one to query a large collection of XPS data according to material type, spectrum type and conditions. This data model will be implemented in the coming FAIR data initiatives.

Metrology

The in-depth interpretation of experimental data requires high certainty in the validity of the results. Yet experimental methods are continuously evolving. Thus methods continuously need to be evaluated. We have invested substantial effort into validating the modern in-situ XPS methods. For instance, we have found that the presence of a gas phase introduces artifacts to the photoemission signal, such that a modified background fitting routine needs to be employed in order to correctly quantify spectra.

Additionally, analysis of XPS spectra where complex line shapes are involved, requires the use of reference standards. However, we have found that when heating a sample to elevated temperatures, or close to phase transitions, the reference spectra measured at room temperature in ultra-high vacuum are no longer valid. We have developed a large collection of reference spectra for oxides with complex line shapes, such as cobalt, iron, manganese, titanium and nickel oxides at elevated pressures, elevated temperatures and close to phase transitions. These data sets are additionally being used as training sets for neural network models to enable rapid analysis of in-situ XPS spectra.

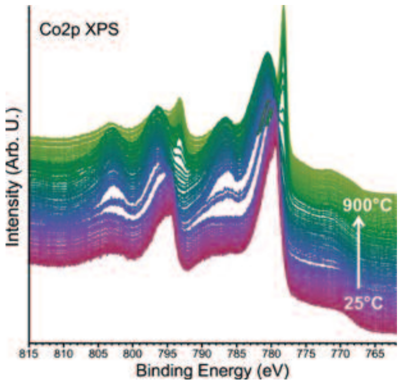

Figure 5. Stack of Co2p XPS spectra measured during a phase transition from Co_3O_4→CoO→Co.

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DEPARTMENT OF HETEROGENEOUS REACTIONS

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Carbon Synthesis and Applications

The aim of our research is the knowledge-based development of advanced carbon-based electrode materials for the water splitting process to replace current expensive and non-abundant materials in a sustainable way. In order to overcome the scarcity of conductivity of catalytic active metal oxide species, composite materials with a conductive carbon framework are investigated. The carbon support materials are synthesized by bottom-up or top-down methods. The generation of specific functional groups that have the ability to anchor the catalytically active metal species, to allow a homogeneous distribution and stabilization is investigated in detail. Furthermore, metal free carbon-based electrode materials have moved into our focus. Detailed investigations and method developments have been performed to allow the characterization of the carbon structures and the functional groups. Structure-property-correlations could be achieved and specific functional groups and structural motifs could be related to electrocatalytic activities by the synthesis of model catalysts.

Carbon based materials: Synthesis and characterization

One synthesis approach of carbon-based electrode materials is the use of molecular precursor and controllable condensation reactions in liquid phase. The incorporation of nitrogen into the carbon structures is widely discussed in literature and the impact on the electrocatalytic performance and stability is not understood in detail. Therefore, glucose was used as carbon and urotropine as nitrogen source in an autoclave process to obtain functionalized carbon materials.[1] Detailed characterization, for example by experimental infrared spectroscopy (IR) which were supported by computed vibrational spectra, was performed. 2D nuclear magnetic resonance (NMR) investigations enabled to identify the chemical environment and to determine connectivities that allowed us to propose model structures of the hydrothermal carbons (HTC) (Figure 1). With increasing molar ratio of urotropine to glucose, a gradual exchange of O-functional groups by N-functional groups can be induced. In the absence of nitrogen, mostly furanic entities linked to aliphatic groups are proposed.

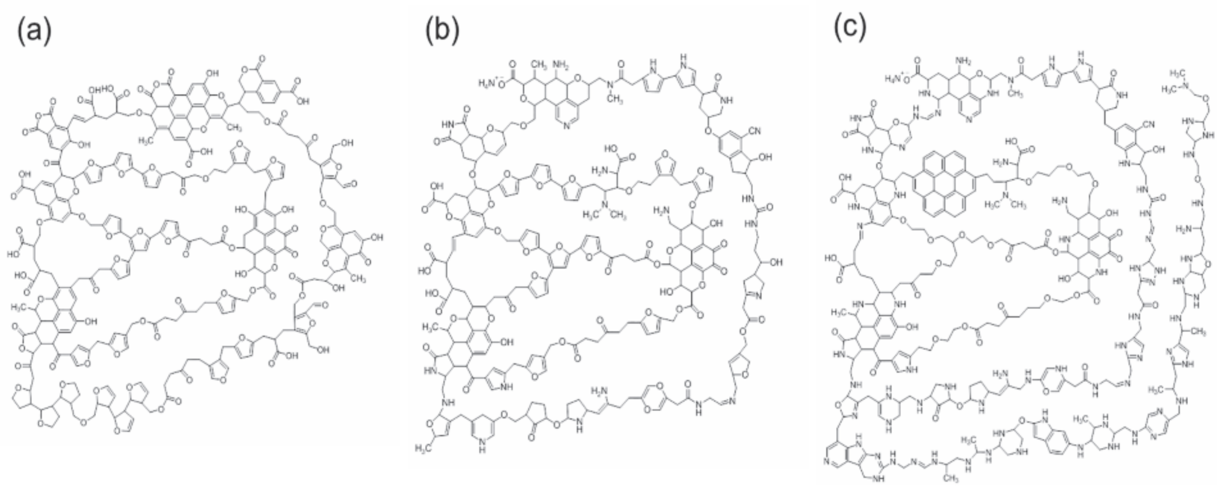

Figure 1. Proposed model structures of a) nitrogen free, b) low N containing (7 wt %) and c) high N containing (19 wt %) hydrothermal carbons.

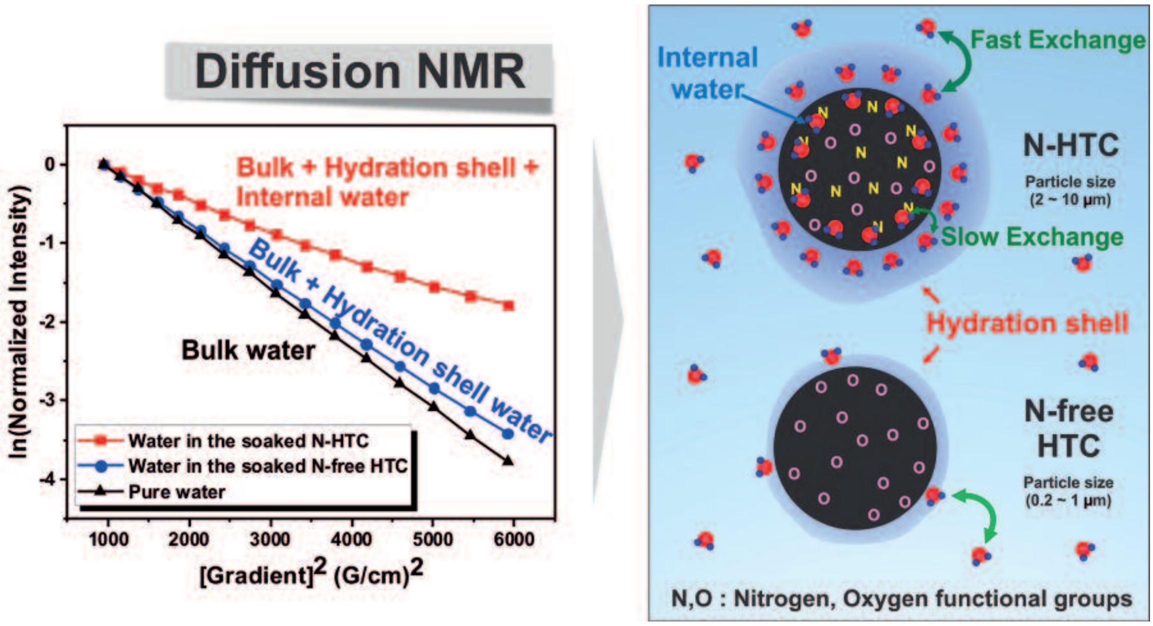

Figure 2. Left: Plot of log intensity vs. squared gradient strength for self-diffusion of water in the presence of N-free and N-containing HTC. **Right:** Scheme of water interaction with (N)-HTC.

Through the addition of N-precursor, a multitude of parallel reactions occurs to form several types of N-functional groups and N-based structural motifs due to the increasing presence of NH_3 in the reaction mixture. Only with the addition of a high amount of N, more temperature-stable N-functional groups, such as pyrrole or pyridine, are formed. Investigations of annealed HTC materials are more difficult to measure using NMR technique due to their increased conductivity and are still ongoing.

NMR investigations were also performed to investigate the water interaction at the interface of the N-containing and N-free HTC materials, which is crucial to understand if these materials are applied as electrocatalysts.[2] It turned out that the type and amount of N-functional groups can be tuned by the ratio of the carbon and nitrogen precursor, while the amount of conjugated species is influenced by the synthesis temperature. The water motion was more restricted in N-HTC than in N-free HTC, thereby suggesting that N-HTC interacts with water molecules via the N-functional groups and oxygen functional groups play rather a minor role (Figure 2). The increased water interaction in case of N-HTC is resulting in a more complete or thicker hydration shell and internal water. Furthermore, although HTC shows a larger surface area than the N-HTC samples, the faster water dynamics in HTC proves that the N-functional groups have a greater effect on the dynamics of the water than the pore size. Understanding the water interaction with the N-HTC surface is expected to help tailoring the surface structure, especially when applying N-HTC as an electrode for water splitting. Further studies are ongoing to reveal the relationship between the hydration shell on N-HTC and the performance as an electrocatalyst for oxygen evolution reactions.

Carbon based materials: Stability and activity

Fundamental requirements for sustainable and efficient electrode materials are the performance and stability under applied potentials.

We have explored the degradation of glassy carbon, as representative for related carbon materials, under electrochemical oxidative conditions, which occur under oxygen-involving reactions like oxygen reduction reaction (ORR) and oxygen evolution reaction (ORR).[3] The electrochemical performance was investigated in alkaline, neutral and acidic media, revealing the same chemical processes which are caused by different degradation mechanism. In alkaline media a radical mechanism is assumed to be responsible for the initiation of oxide formation. Predominantly the edges of small graphitic structures are oxidized as far as they become sufficiently hydrophilic and dissolve in the electrolyte. This delamination process leads to a stable electrochemical performance but to a continuous consumption of the electrode. At low pH an acid catalyzed electrophilic reaction is proposed resulting in the oxidation of the bulk structures of the glassy carbon electrode. However, in spite of the instability of glassy carbon electrodes at highly oxidizing conditions, carbon materials are still electrochemically competitive for a catalyst support compared to conducting metal oxides and are promising for metal-free electrocatalysts due to their high conductivity and low cost. Investigations with graphite pellet electrodes revealed that highly graphitic structures increase the stability of carbon-based electrodes, indicating the future direction of synthesis.

The large abundance and coexistence of various functional groups and edge structures of carbon materials make it more difficult to identify relevant configurations for the OER or ORR.

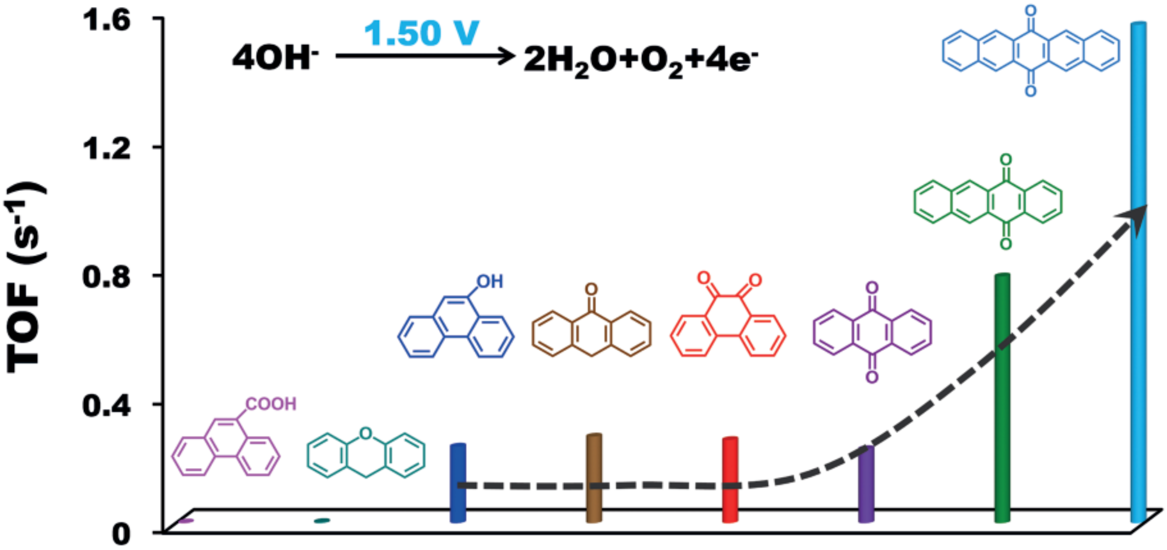

Figure 3. Investigated model structures of typical oxygen functional groups and configurations as well as conjugated π systems and their related turnover frequencies (TOF).

We developed a procedure to investigate the exact role of specific functional groups and edge structures by using model structures decorated on highly graphitic defect free carbon support materials like onion-like carbons (OLC) multiwalled carbon nanotubes (MWCNT) or high temperature carbon nanofibers (HHT).[4, 5]

Quinone functional groups were identified to contribute positively to the OER activity (Figure 3). Each C=O group contributes independently to the OER. The location at armchair or zigzag configurations was demonstrated to be independently on their performance. Phenolic groups were also identified to contribute positively to the OER by a proton-coupled electron transfer relationship between quinone and phenolic groups. An increase of the π conjugated structure further improves the OER activity.

Composite materials: Intense metal oxide – carbon support interactions

The strategy to synthesize composites of a conductive carbon support and catalytic active metal oxide species is often applied for catalytic materials. A strong interaction between the two components is essential to prevent dissolution or agglomeration and furthermore to grant good charge-transfer properties which is required for electrocatalytic materials. Atomic dispersion is desired since the properties of their bulk analogous can be exceeded.[6] We applied three different methods to achieve the conditions, which are covalent bonding, mediation by an ionic liquid and large contact areas by 2D nano-lamellae.

Vanadium oxide was covalently bonded on MWCNT by atomic layer deposition (ALD).[7] Atomic dispersion could be confirmed and a selective covalent anchoring on carboxylic, anhydride and phenol groups could be detected (Figure 4a). The thermal stability could be increased by depositing on only phenol functionalized carbon support, which extends the lifetime and range of application as a catalyst.

We exploited a scalable way to place single cobalt ions on a carbon-nanotube surface bridged by polymerized ionic liquid (Figure 4b).[8] The electronic environment of the Co^{2+} species could be tuned by changing the molar

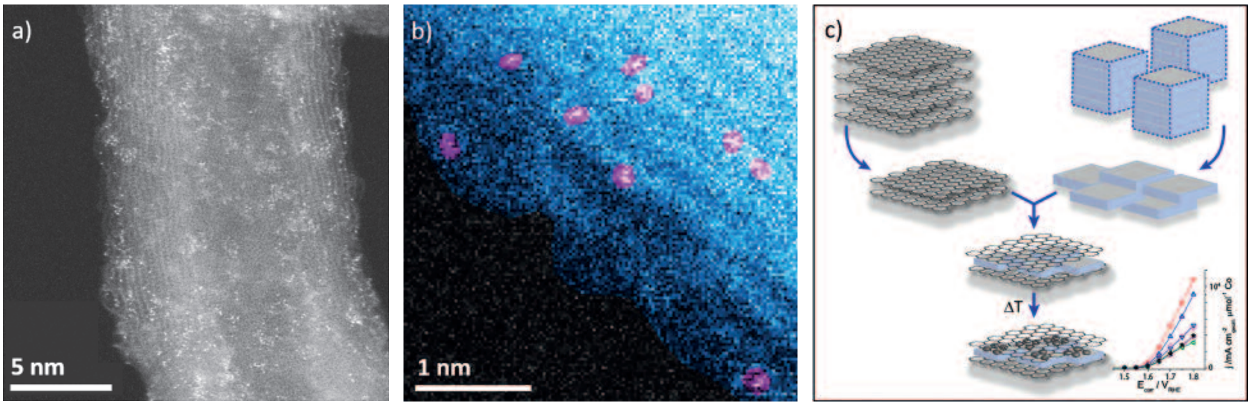

Figure 4. Microscopic images of a) Covalently bonded vanadium oxide species on MWCNT by ALD b) Atomically distributed cobalt oxide species on MWCNT mediated by a polymerized ionic liquid. c) Schematic idea of the 2D nano-lamellae composite.

ratio of ionic liquid (IL) and $CoCO_3$ precursor. A transformation from a six-coordinated octahedral structure of the Co^{2+} species to a four-coordinated tetrahedral structure is induced by higher IL content. High electrocatalytic activities are achieved per Co unit, which can be further improved with increasing amount of polymerized ionic liquid. An excellent stability of the electrocatalysts was confirmed by in-operando measurements at high potentials while no Co leaching could be detected in the electrolyte by inductively coupled plasma optical emission spectroscopy (ICP-OES). Nevertheless, the IL content cannot be increased indefinitely .Excess of ionic liquid cause poor dispersion and therefore poor coating on the carbon support, which leads to a decrease of the stability.

A new synthesis route was developed that integrates 2D MOF (metal-organic-framework) nanocrystals and graphitic carbon nano-lamellae into layered composites (Figure 4c).[9] The graphitic carrier contributes excellent charge–transport properties, and the 2D macromolecular MOF precursor provides a suitable shuttle for introducing highly dispersed metal species. Furthermore, their direct chemical environment could be controlled via selection of organic linker. Thermal decomposition of 2D cobalt tetrafluoro benzene-dicarboxylate MOF nanocrystals within such composites enabled the stabilization of cobalt oxyhydroxyfluoride nanoparticles on the graphitic carrier, which display an extraordinary activity for the OER in alkaline media, with low onset overpotential (310 mV_{RHE}) and current densities >104 mA cm^{-2} $\mu molCo^{-1}$ at an operating overpotential of 450 mV, alongside excellent operational stability. The wide compositional array of MOFs makes this synthesis approach versatile toward advanced (electro)catalysts and other functional materials for applications from sensing to energy storage and conversion.

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DEPARTMENT OF HETEROGENEOUS REACTIONS

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Main Research fields

We focus our research on the investigation of the electronic structure of catalysts and electrode surfaces used in heterogeneous catalytic reactions and electrochemical processes like propylene epoxidation over Ag, the oxygen evolution reaction (OER) and the CO_2 reduction reaction (CO2RR). 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 [1-4].

Noble metal oxides in the OER

In case of Ir anodes in OER a strong hybridization between iridium and oxygen leads to holes shared between the two; the further the material is charged, the more charge transfer from iridium to the oxygen ligand is expected [2]. Depending on its coordination, oxygen can ultimately end up as a radical oxyl species, μ_1-O. Such a species was proposed to be highly active in O-O bond formation [5]. We were able to find that species under wet conditions via its O K-edge absorption signal. A small amount appeared at the onset of the OER. Calculations and experiments are in good agreement about the deprotonation potentials and the O K-edge absorption energies of the considered surface oxygen species.

To probe active electrocatalyst surfaces in a liquid environment, we have developed an XPS/XAS cell in which the catalyst is confined between a proton exchange membrane and graphene. While the proton exchange membrane supplies a steady flow of electrolyte to the electrode, the X-ray and electron-transparent graphene layer greatly reduces the evaporation of water into the NAP-XPS chamber. Using O K-edge spectra, we confirmed that this can lead to the formation of a thin layer of liquid electrolyte between the graphene and the membrane. Thus, electrocatalysts can be studied under operating conditions using surface sensitive soft X-ray XPS and XAS [3,4].

With this methodology, we have studied the potential-driven restructuring of Ru, Pt and Au oxides in 0.1 M H_2SO_4 during the oxygen evolution reaction. Using Ru 3d/M-edge, Pt 4f and Au 4f spectra, we identified the distribution of cationic oxidation states as a function of potential (e.g. Figure 1b). For Au oxide, which is strongly covalent, only Au^{3+} is found, whereas the more oxophyllic

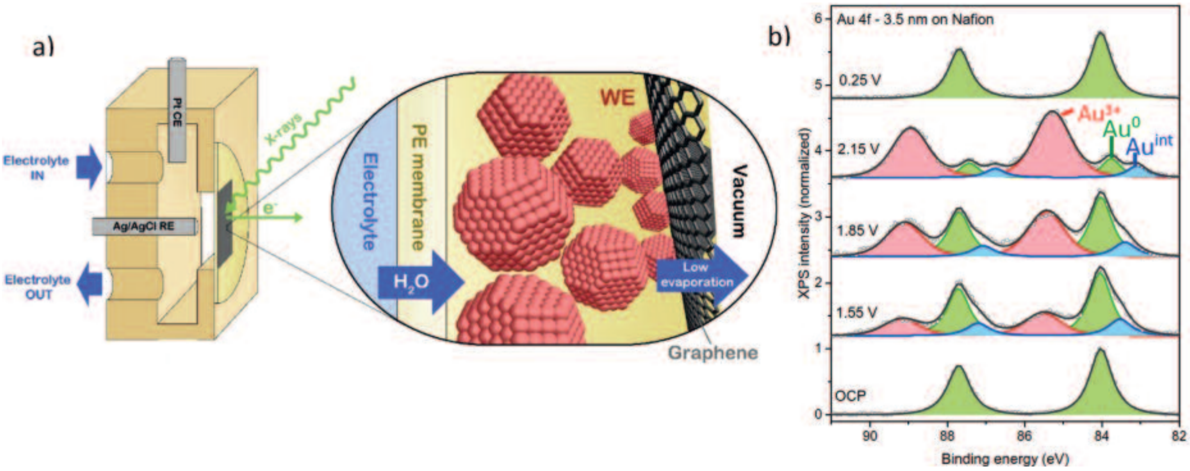

Figure 1. a) Cell design. **b)** In situ XPS spectra recorded with 0.1 M H_2SO_4 electrolyte.

Pt displays a gradual transition from Pt^0 to $Pt^{+}/Pt^{2+}/Pt^{4+}$ and further to Pt^{4+} [4]. For the yet more oxophyllic RuO_x, we find a gradual oxidation to primarily Ru^{4+} under OER conditions, with some minor contributions of higher oxidation states.

O K-edge spectra, complemented by theory, indicate that the final stages of oxidation of the catalysts occur through deprotonation, even in the bulk of the materials. The deprotonation proceeds through multiple stages: hydroxyl groups with higher coordination deprotonate at lower potential. Interestingly, we find that deprotonation is not complete during the oxygen evolution reaction on Ru oxide, in contrast to *ab initio* thermodynamic predictions [6].

Several studies have identified that the degree of crystallinity of OER electrodes influence their activity and stability [7]. Our in situ studies suggest that the reactive (deprotonated) oxygen species that dominate the surface of amorphous and crystalline Ru oxides under OER conditions are similar in nature. Rather, we explain the correlation between crystallinity and activity/stability by the larger amount of reactive species on amorphous electrodes.

CuO_x in CO2RR

Copper is unique due to its ability to electro-reduce CO_2 to hydrocarbons and alcohols in aqueous electrolytes, as was probed by Hori et al [8]. Nevertheless, the selective electroreduction of CO_2 into fuels is challenging due to the multiple complex proton-coupled electron transfer steps that must occur [9]. This complex network makes the cathodic CO_2 reduction reaction (CO_2RR) run with relative low current density and high overpotential and in addition electrode deactivation may occure over time. By tracking the electronic structure of the Cu catalysts, using in situ X-ray spectroscopies, we have tuned and precisely set the initial Cu redox state, such as Cu^0, Cu^+ and Cu^{2+}, by controlled applied potential protocols [10]. It was shown, that the magnitude of the CO_2 dissociation barrier depends on the degree of surface oxidation and on the nature of surface defects. Therefore, we calculated the barrier associated with dissociative CO_2 adsorption on several copper catalysts, indicating that the dissociation barrier is lowered in the presence of missing oxygen on the surface and enhanced in presence of extra oxygen on the surface.

Propylene Epoxidation over Ag

We used near ambient pressure X-ray phototelectron spectroscopy (NAP-XPS) to study the Ag surface under propylene epoxidation conditions. Opposed to ethylene epoxidation, $SO_{4,ads}$ is not present under steady state propylene oxidation conditions. $SO_{4,ads}$ can, however, be formed by introducing an SO_2 pulse to the reaction feed, resulting in an increase in selectivity to PO. Though, $SO_{4,ads}$ is rapidly titrated under reaction conditions and PO selectivity decreases with time following the decrease in $SO_{4,ads}$ coverage. During this process we observe the formation of $SO_{3,ads}$. As for ethylene epoxidation, it seems that $SO_{4,ads}$ is also responsible for propylene epoxidation and $SO_{3,ads}$ is seen as a titration product. However, NAP-XPS demonstrates atomic O has a low coverage under propylene epoxidation conditions compared to those for ethylene epoxidation. As a consequence, $SO_{4,ads}$ is continuously titrated under propylene epoxidation conditions, resulting in a low steady state coverage. In addition, low coverage of adsorbed atomic O precludes the formation of oxygen induced surface reconstructions, necessary to partially lift the Ag/SO_4 reconstruction and make the active species $SO_{4,ads}$.[11,12]

Instrumentation

Figure 2 compares the experimentally determined photon flux of three beamlines operated by the FHI: ISISS (under operation since 2007) BEIChem beamline (under commissioning since 2018) at comparable spectral resolution

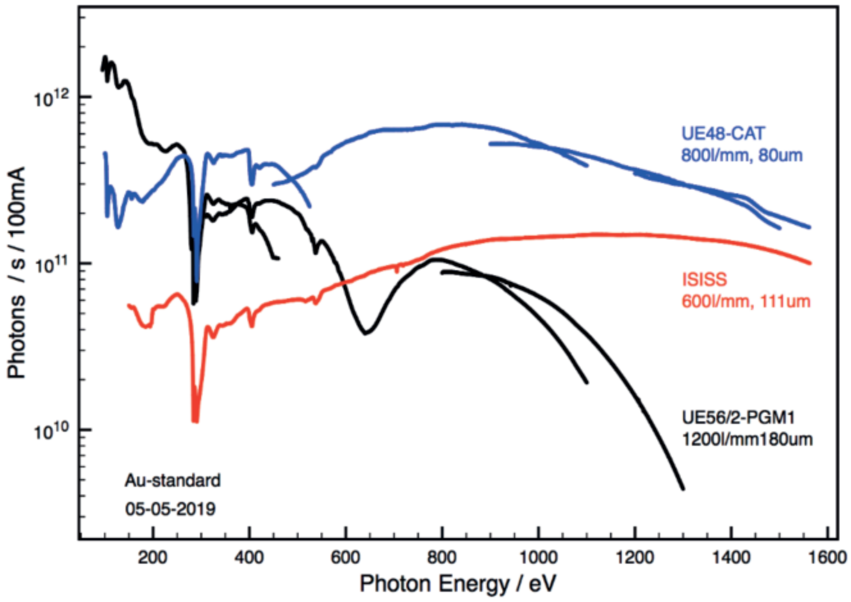

Figure 2. Comparison of the photon flux at sample position of the soft X-ray beamlines ISISS, BEIChem (UE56/2-PGM1), and CAT@EMIL at BESSY dedicated to AP-XPS spectroscopy.

under standard AP-XPS working conditions and sample position, along with CAT@EMIL. It becomes apparent that the beamline characteristics of BEIChem and ISISS nicely complement each other. The photon flux of the soft X-ray branch of EMIL (Energy Materials In-Situ Laboratory Berlin) served by the UE48 undulator at the focus position in the CAT laboratory (red line) is shown in Figure 2 as well. It is obvious that the soft EMIL beamline provides a broad photon energy range with a high photon number in the whole energy range.

A strategy of commissioning phases combined with user experiments (e.g. within the CRC project cobalt based catalysts in isopropanol oxidation) is applied to put the CAT@EMIL facility into operation. This station combines an AP-XPS spectrometer equipped with a wide acceptance lens and high kinetic energy capabilities (up to Ekin=7000eV) with a sophisticated laboratory infrastructure optimized for in-situ XPS experiments with a chemical background. The photon energy range will be extended to the tender X-ray regime up to 8000eV by exploiting the radiation of the cryogenic in-vacuum undulator U17 in a second installation phase of this project [13,14] in the end of 2019/beginning of 2020, hence providing a perfect match with the spectrometer specification with its broad kinetic energy range.

In summary, while the permanent user operation of the workhorse ISISS is ensured, the new AP-XPS facilities BEIChem and CAT@EMIL have been put into operation step by step within the last year. All set-ups are equipped with the modular endstation/reaction cell concept developed at the FHI to optimize flexibility and possibility to adapt the instrumentation to the user needs.

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DEPARTMENT OF HETEROGENEOUS REACTIONS

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Introduction

The direct use of electrical energy to produce chemical products, thereby storing the energy in chemical bonds, is probably the most efficient way of energy conversion. Still catalysts are needed in this process to make the conversion efficient and directive. The role of the group "Electrocatalysis" is not only to analyze prospective catalyst materials for their performance, but also to develop the electrochemical techniques and analysis methods further to enable the fundamental understanding of working principles and kinetic data.

Method Development

Starting with the MAXNET Energy initiative, electrochemical flow cells (EFCs) as complementary analysis techniques to the classical rotating disc electrode (RDE) setup were developed. In contrast to an RDE, where the electrode is rotating, in the flow cell a controlled mass-transport is achieved by a continuous flow of electrolyte over the catalyst surface. This not only closer reflects the reality of industrial applications (as e.g. in an electrolyzer, where the electrolyte is circulated around static electrodes), but also allows a simultaneous online analysis of the processed electrolyte. Our EFC is therefore combined with an oxygen sensor as well as a mass spectrometer (ICP-OES), detecting the amount of produced oxygen and possible degradation products of the catalysts dissolved in the electrolyte (Figure 1a). This system was used to evaluate different catalysts for the oxygen evolution reaction (OER) for their activity, selectivity, and stability (Figure 1b).[1] More recently, this was further developed for the utilization of extended, thin-film electrodes. This significantly widens up the possible sample and preparation space.

Beside dissolved species, also gaseous products are of relevance. Especially when using carbon electrodes, a regular side reaction of the OER is carbon corrosion, leading to CO and CO_2 formation. Figure 2 shows the so-called "submarine cell", with a closed, defined volume, the possiblity for a flow of electrolyte, and ports for sample extraction. By accumulation of gaseous products over several hours, the amount of produced O_2 as well as

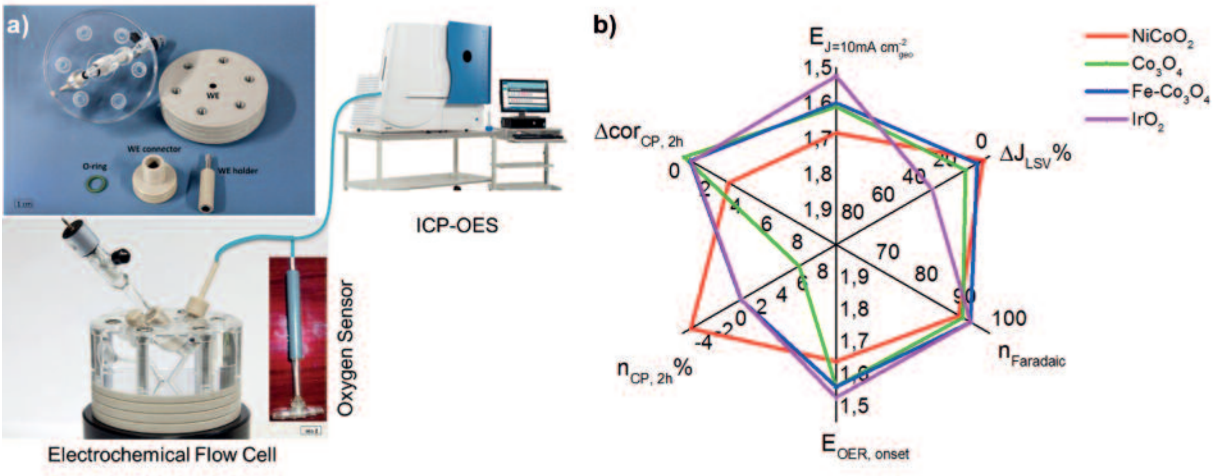

Figure 1. a) Electrochemical flow cell (EFC) connected with online analytics for detection of the oxygen content and dissolved products by mass analysis with ICP-OES. **b)** Various activity and stability parameters of OER catalysts by combined EFC/O2-sensor/ICP-OES measurements visualized as "spider graphs".

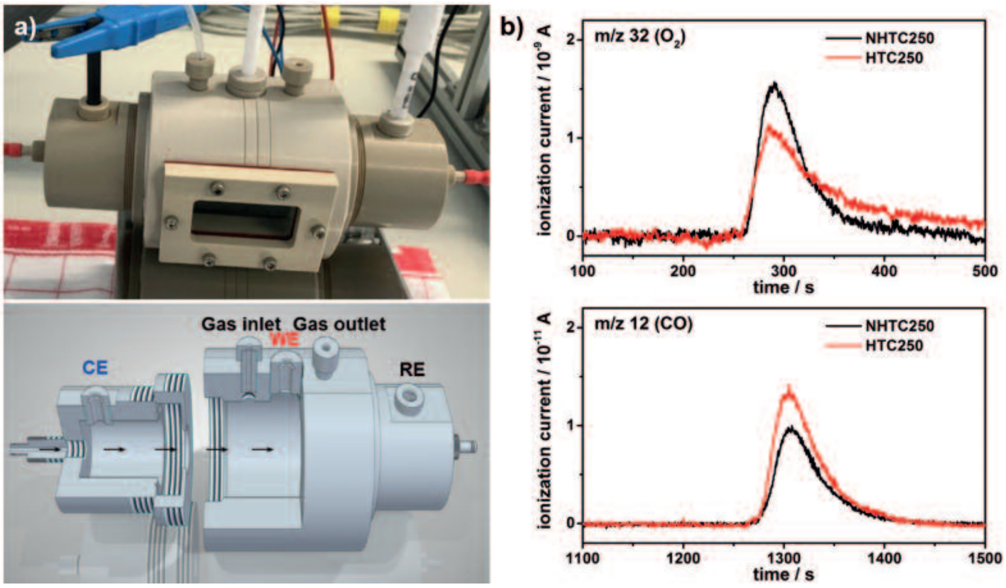

Figure 2. a) Electrochemical "submarine cell" for the collection of product gases after long-time operation. **b)** Comparison of produced gases for two different carbon materials (with or without N-doping).

CO and CO_2 (if not dissolved in the electrolyte) can be measured by mass spectrometry or gas chromatography. An example for gas products detected from an N-free and an N-doped carbon pellet, produced by the "Carbon Synthesis and Application" group, is shown in Figure 2b. It can be seen that the addition of N into the carbon matrix results in a higher selectivity towards OER and suppression of carbon corrosion.[2]

Influence of External Parameters

In the examples above, the influence of catalyst composition on the measured activity and stability have been shown. We, however, also realized that external parameters play a crucial role on the measured performance of a catalyst.

Applying the abilities of the EFC/ICP-OES system, we could demonstrate that Fe-impurities in the electrolyte are adsorbed on or into a Ni-Co-based catalyst during OER. Interestingly, the incorporation of Fe not only significantly enhances the activity of the catalyst, but also suppresses to a large extend the leaching of active components into the electrolyte.[3] To characterize pure catalytic properties in the future, we need large quantities of Fe-free electrolyte. Therefore, we developed an electrochemical method to purify effectively a large volume of electrolyte within several hours.[3]

Another parameter that influences the measured performance is the use of polymer binders for the preparation of thin-films of powder catalysts. To characterize those materials, they are typically dispersed into a so-called "ink", and then drop-casted on RDE electrodes. However, the choice of binder will influence the measured activity as well as stability, as demonstrated in Figure 3. Depending on the binder, those can have an electrochemical response of their own, block active sites or alter the hydrophilicity of the surface. We found that PTFE, in the present case, leads to the most reliable results, as it just acts as an inactive, stable glue, keeping the film mechanically stable, as well as supports a proper bubble detachment.[4]

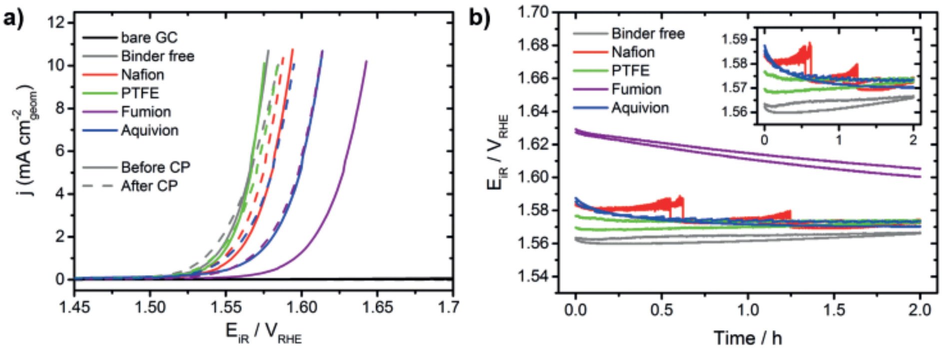

Figure 3. a) Linear sweep voltammetry of a reference catalyst (Ni,Co-Oxide, Sigma Aldrich), prepared with different polymer binders. Solid lines are the initial values, while dotted lines represent the same measurement after a 2h stability test. **b)** Chronopotentiometry during 2 h at a constant current density of 10 mA cm^{-2}. The electrolyte is 1 M KOH.

Pt-FeNC Hybrid Catalysts

We also pursue the development and understanding of catalysts for the oxygen reduction reaction (ORR) in low-temperature fuel cells. Here we focus on iron-nitrogen-carbon materials (FeNC), which are promising catalysts to replace Pt-based materials in the future. However, their stability is a significant issue. Recently, we found that the addition of small amounts of Pt (0.5 – 2 wt.%) stabilizes the catalyst under fuel cell operation.[5] Utilizing transmission electron microscopy (TEM) in combination with energy dispersive X-ray spectroscopy (EDX), we could reveal that Pt is most likely not present in its metallic form, but covered by a thin Fe-shell, rendering the deposited Pt-particles ORR inactive (Figure 4 a).

Interestingly, these hybrid catalysts produce less H_2O_2, which can upon accumulation in the fuel cell be a significant source of degradation. Additionally, the formation of radical oxygen species was reduced by the addition of Pt. By a close collaboration with the group of Dr. Schnegg, OH-radicals could directly be monitored by the addition of a spin-trap (DMPO) to the dispersion of catalyst and H_2O_2. The DMPO/•OH spin adduct was detected and quantified by electron paramagnetic resonance (EPR) spectroscopy (Figure 4b). Simulation of the spectra reveals that the hybrid catalyst produces about 70% less OH-radicals than the pure FeNC catalyst.[6]

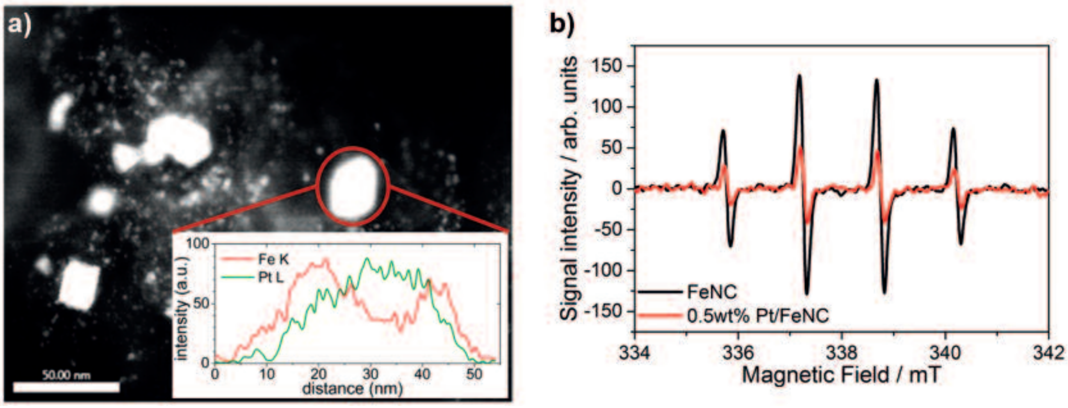

Figure 4. a) TEM image of 1wt% Pt/FeNC and an EDX line-scan through the indicated particle; **b)** X-band EPR spectra of DMPO/•OH spin adduct as collected after H_2O_2 treatment of the FeNC and Hybrid catalyst (recorded at 304 K with a microwave frequency and power of 9.495 GHz and 0.25 mW, respectively).

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DEPARTMENT OF HETEROGENEOUS REACTIONS

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Group Leader: MPI CEC (since 2018)

Catalytic Technology Group

The focus of the catalytic technology group is on the investigation of 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 catalyst lowers the activation barriers of chemical reactions by influencing the reaction mechanism. A deeper understanding of the working catalyst can help to improve available catalysts or provide suggestions for the development of alternative catalysts. A more effective catalyst will increase the overall efficiency of a process and, therefore, reduces the utilized resources for both, materials and energy.

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 storage capability, like e.g. ammonia or methanol, is suggested as more efficient for energy storage [1]. Furthermore, 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.

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

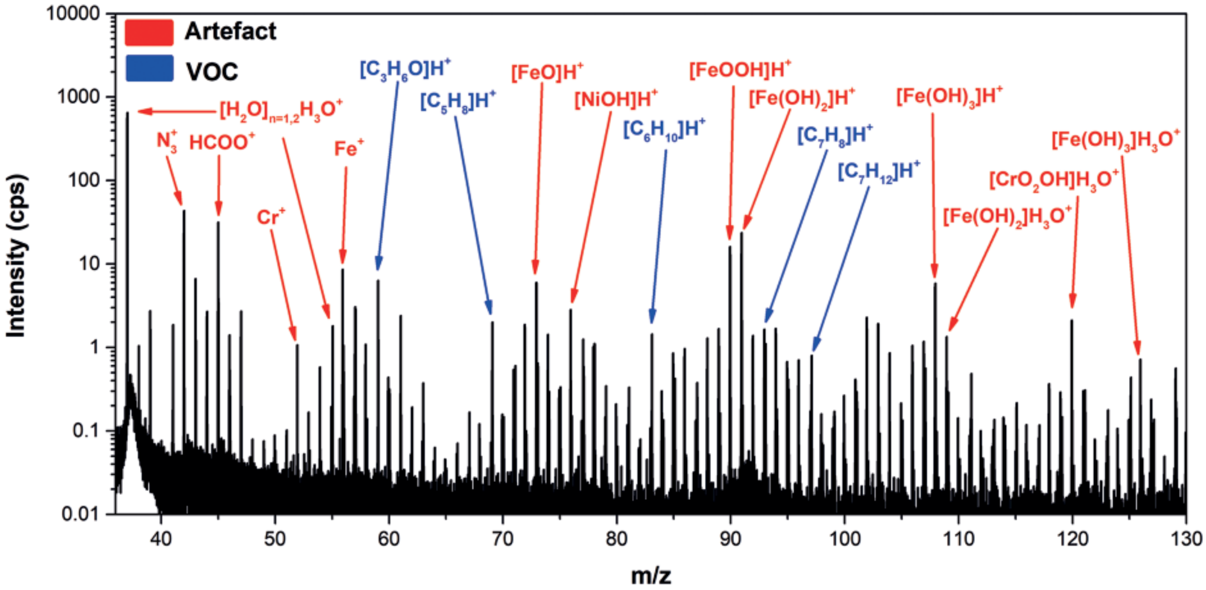

Figure 1. Average mass spectrum from a background measurement using nitrogen 5.0 under dry conditions for the m/z range 36 – 130 with the PTR-QiTOF-MS for the identification of instrument artefacts. [2]

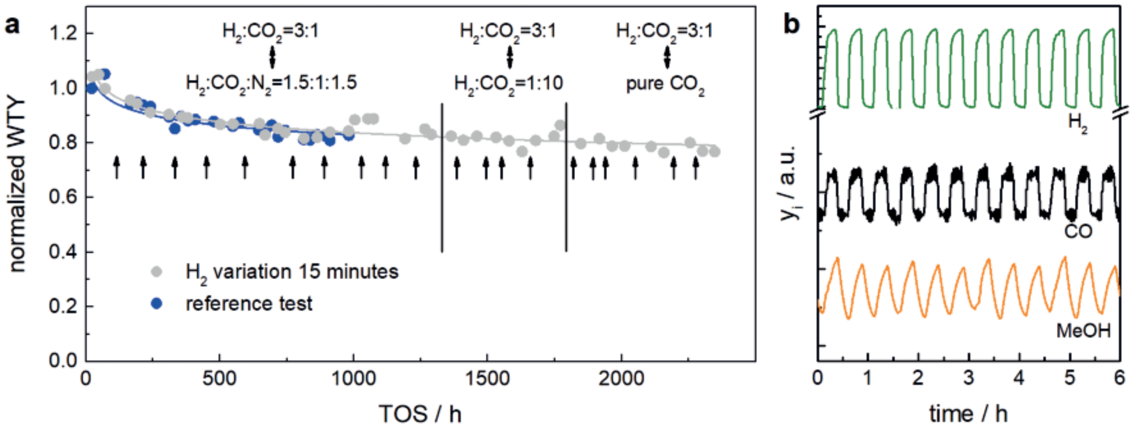

Figure 2. a) Stability of the catalyst under steady-state conditions (blue) and during dynamical operation (grey) with several scenarios. Reaction conditions: 500 NmL/g_{cat}/min, 523 K, 30 bar. **b)** Time-resolved effect of H_2 switches every 15 min for MeOH production measured by IR [3].

be considered and may require adjustments for the gas cleaning 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 the 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 mobile high-end gas analysis housed in a container was constructed and is operated directly on-site at the steel mill. 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 (Figure 1) [2].

Methanol synthesis

Methanol is one of the most important industrial bulk chemicals and 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 environmental 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. Therefore, a deeper understanding of the industrially applied catalyst under conditions for CO_2 hydrogenation is required for its realization. Especially, the incorporation of renewable resources within this process chain will cause dynamic changes of synthesis conditions which may damage the catalyst and therefore, reduce its lifetime. To address this task, the influence of intermitting process conditions on the stability of an industrial Cu/ZnO/Al_2O_3 catalyst in CO_2 hydrogenation to methanol is investigated in detail. From the obtained results we can conclude, that dynamic switches of process parameters in the investigated regime during CO_2 hydrogenation to methanol does not accelerate the deactivation of an industrial Cu/ZnO/Al_2O_3 catalyst and supports the idea of applying methanol synthesis from CO_2 in a renewable network for energy storage and/or production of chemicals [3]. 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.

Ammonia synthesis

Besides methanol ammonia represents an alternative to store hydrogen produced from renewable energy. Ammonia synthesis is a structure sensitive reaction, but the active phase of the Fe-based catalyst under industrially relevant conditions is still unclear [4]. This is related to the large pressure and material gap between activity data at industrially applied conditions and surface science approaches. To overcome this a systematic series of catalysts with different surface structures is investigated and their activity is correlated to their structure. In particular, $MgFe_2O_4$-based model catalysts synthesized from a layered double hydroxide precursor prepared by the group of M. Behrens in the University of Duisburg-Essen as well as FeOOH-based nanosheet catalysts prepared in the inorganic chemistry department at the FHI in Berlin are in the focus of this work. Especially, the $MgFe_2O_4$-

based catalysts are promising candidates for further studies as they 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 structure can be modified and the impact of this modification on the activity is investigated. These alternative catalyst preparation routes 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. In addition, further studies are performed on industrially based samples prepared via the high temperature melting process for comparison.

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OTHER SCIENTIFIC ACTIVITIES

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Assoc. Professor: Experimental Physics, Universität Stuttgart (1989-1991)
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Director: at the institute and Scientific Member of the Max Planck Society (2000-2017)
Director Emeritus: since 8/2017

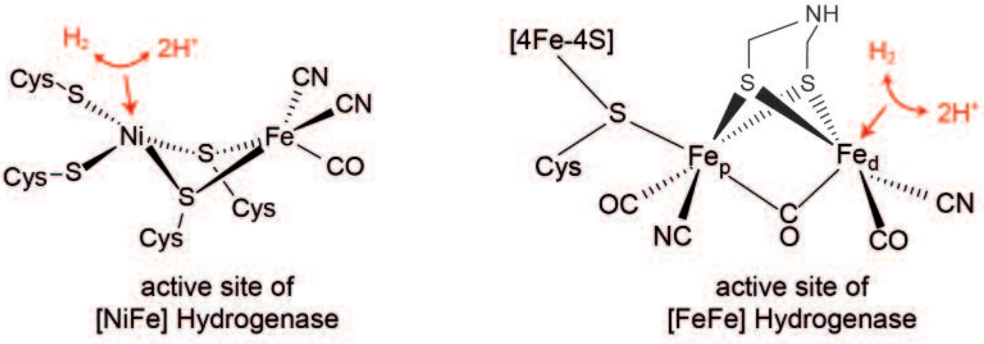
The Department of Biophysical Chemistry, established in 2000 by Prof. Wolfgang Lubitz following his appointment as a director at the Institute, has been formally closed since August 2017 following his retirement. The central spectroscopic facility devoted to the development and application of modern EPR techniques was assigned to Dr. Alexander Schnegg, a new independent group leader at the MPI CEC who is now, together with Dr. Edward Reijerse, continuing the EPR activities tailored to the new direction of the institute. The laboratories for preparation of biological materials have been taken over by Dr. Laure Decamps and Dr. James Birrell, two group leaders in the Department of Inorganic Spectroscopy (Prof. S. DeBeer). In the same department Dr. Olaf Rüdiger is continuing and expanding his activities as a group leader in electrochemistry. The other group leaders of the former Department of Biophysical Chemistry (Dr. Anton Savitsky, Dr. Nicholas Cox and Dr. Hideaki Ogata) have left the MPI and found scientific positions at universities in Dortmund (Germany), Canberra (Australia) and Sapporo (Japan), respectively.

In the Department of Biophysical Chemistry we have studied native enzymes and related model systems to understand the ingenious concepts of Nature to use sunlight to oxidize water, release oxygen and produce (or use) hydrogen. Water oxidation takes place in photosystem II (PSII) of plants, algae and cyanobacteria – and H_2 conversion or production is performed by the hydrogenases. All these enzymes use earth-abundant metals in their catalytic centers (Mn/Ca, Fe, Ni). Knowledge of the underlying concepts is important for designing and synthesizing systems for efficient light capture, energy conversion and storage in chemical compounds. We used a variety of different physical techniques to study these systems (see last 2 scientific reports). The information obtained has been supplemented by modern quantum chemical approaches to understand the catalytic function at the atomic level (cooperation with Prof. Frank Neese). In the last 3 years we have concentrated on finalizing experiments on the water oxidizing complex (WOC) in PSII and on the [FeFe] hydrogenases. The results are briefly described below.

Hydrogenases

Hydrogenases are Nature's catalysts for the oxidation of molecular hydrogen or the reverse reaction, the production of H_2 from protons. A basic understanding of these enzymes is of key importance for a future biologically based hydrogen production technology and also for the design and synthesis of bioinspired catalysts for hydrogen conversion or production. In our department both the [NiFe] and the [FeFe] hydrogenases have been studied (Lubitz et al., *Chem. Rev.* 2014) along with appropriate model systems.

[NiFe] Hydrogenase: During the previous report period (2014-2016) the structures of all intermediates in the activation path and catalytic cycle of the [NiFe] hydrogenases could be characterized and a catalytic cycle was



active site of [NiFe] Hydrogenase

active site of [FeFe] Hydrogenase

Scheme 1.

set up. Furthermore, the problem of O_2-sensitivity was studied, which is a major drawback for practical applications of such hydrogenases in (bio)fuel cells or water electrolysis. Together with the groups of Wolfgang Schuhmann and Nicolas Plumeré (RU Bochum) we could show that a special designed smart matrix (a viologen-based polymer/hydrogel) is able to protect an embedded O_2-sensitive [NiFe] hydrogenase against oxygen attack and high potential deactivation (Plumeré et al. *Nat. Chem.* 2014). Based on these results, several devices have recently been constructed, e.g. a microbiosensor for local H_2 detection and different polymer/hydrogenase-based bioanodes that were successfully used in biofuel cells.

[FeFe] Hydrogenase: In [NiFe] hydrogenases the catalytic H_2 splitting and H_2 formation is performed by the nickel ion aided by a terminal cysteine sulfur (or a nearby amino acid) acting as a base (cf. scheme 1). In the [FeFe] hydrogenases the active site (H-cluster) is composed of a classical [4Fe-4S]$_H$ cluster linked to a unique [2Fe]$_H$ complex coordinated by CO and CN ligands and bridged by an azapropane-dithiolate (adt) ligand (see scheme 1). In these hydrogenases a Fe ion (Fe_d) is employed as Lewis acid and the nitrogen of the adt functions as a base (end of the H^+ transfer channel). The existence of the nitrogen, first shown by pulse EPR and ENDOR in our group (Silakov et al., *PCCP,* 2009), was finally proven correct by the insertion of different biomimetic [2Fe]-complexes into the apo-protein of bacterial and algal [FeFe] hydrogenases. This seminal work has been done together with Marc Fontecave (Paris), Vincent Artero (Grenoble) and Thomas Happe (Bochum) and was published in 2013 (Berggren et al., *Nature*; Esselborn et al. *Nature Chem. Biol.,* 2013). The discovery of artificial maturation of [FeFe] hydrogenases had far-reaching consequences for hydrogenase research [1], since the observed spontaneous assembly of the synthetic diiron cluster with the apo-protein produced in *E. coli* could be used i) for obtaining (much) larger amounts of hydrogenases than from natural sources, ii) for making various mutants, iii) for specific isotope labeling, iv) for changing the metals and v) altering the substituents or ligands of the H-cluster.

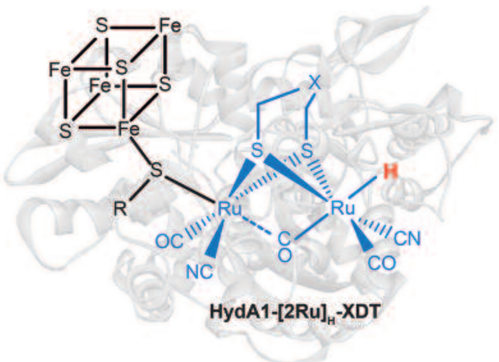


Figure 1. Structure of the [RuRu]-hydrogenase in the protein (from *C. reinhardtii*) with a stabilized terminal hydride (red); bridging atom X=NH or CH_2 [2]

To this end there was hope to obtain improved structural and functional properties of these hybrid hydrogenases. Subsequently, a few results obtained at the MPI in Mülheim during the last 3 years will be highlighted.

- An important result of the incorporation of different [2Fe]-clusters is that the activity of the hydrogenases could *not* be improved by changing the substituents of the adt ligand or the CO/CN ligands. These results show that Nature has highly optimized the structure of the H-cluster for efficient H_2 conversion or production. Together with Thomas Happe (Bochum) we have also studied the impact of the protein matrix to learn more about the channels for electrons, protons and hydrogen.

- Incorporation of a [2Ru] complex into the apoprotein has been accomplished forming a [RuRu] hydrogenase [2]. The complex is known to react with traces of water to form a hydride bridge Ru(II)(H$^-$)Ru(II). Interestingly, when inserted into the apoprotein and bound to the [4Fe-4S]$_H$ cluster, the bridging hydride rearranges to a terminal form (Figure 1). The hydride is, however, very tightly bound and the [RuRu] hydrogenase is not active in producing H_2 [2].This shows how important the binding situation and bond strength are to yield the correct hydricity and thus a highly active enzyme.

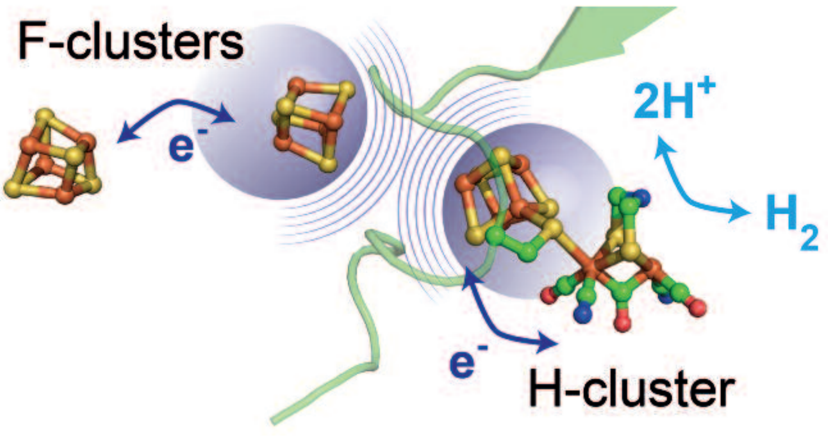


Figure 2. Redox state of the additional F clusters found in several [FeFe] hydrogenases affecting the electron distribution within the H-cluster and in turn the catalytic activity and bias of the hydrogenase; for details see [6].

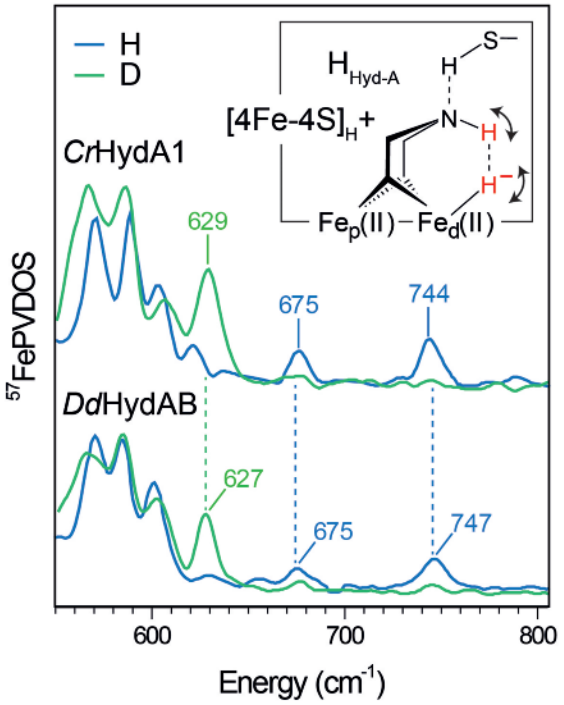


Figure 3. NRVS spectra (blue) of the H_{hyd} state of algal (top) and bacterial (bottom) ^{57}Fe-labeled [FeFe] hydrogenase showing two bending vibrations each of the hydride bound to Fe_d. The resonances shift to lower energy upon H/D exchange (green traces). DFT calculations corroborate the assignment. The higher energy vibration near 750 cm^{-1} correlates with the H_2 formation coordinate in catalysis (insert) [12].

- In the course of our work the structure of practically all intermediates of the catalytic cycle could be determined, the redox transitions and their pH dependences were measured. This led to deep insight into the PCET (and ECPT) processes of the cycle [3] (for a reaction cycle see Figure 3, report of J. Birrell). The identity of the O_2-insensitive as-isolated state H_{inact} (H_{ox}^{air}) of some hydrogenases could also be clarified; it carries an SH^- ligand at the active site protecting it against O_2 attack [4].

- To prove the kinetic competency of all the states in the cycle we have performed time resolved infrared spectroscopy with Brian Dyer (Emory Univ. Atlanta, USA). The reaction is started by a short laser pulse exciting a photosensitizer (CdSe/CdS) followed by mediated transfer of the electrons to the hydrogenase on a µs time scale. Using the IR bands of the hydrogenase states the population flux through all intermediates of the algal hydrogenase HydA1 from *C. reinhardtii* could be measured. This kinetic approach corroborated all states of the catalytic cycle and also identified a new intermediate that might be related to the final H_2 release step [5].

- The large differences in the activity of the bacterial and algal hydrogenases were traced back to interactions with the additional iron-sulfur clusters (F-clusters) in a detailed publication on redox anti-cooperativity between the ET components; see Figure 2 [6].

- [FeFe] hydrogenases are very O_2 sensitive. We could show that a well-designed redox polymer can almost completely eradicate O_2 sensitivity (Oughli et al., *ACIE*, 2015). The concept also works for model systems; in special cases they exhibit self-defense against O_2 [7]. In recent work the concept has been extended using viologen groups attached to electrodes [8]

- For the first time, using artificial maturation we could obtain and fully characterize a sensory (or regulatory) [FeFe] hydrogenase of *Thermotoga maritima* [9]. The overexpression of the apoprotein allowed the generation of mutants to better understand its function as a sensor. From the same organism a bifurcating hydrogenase could also be obtained [10]. The mechanism of this complex hydrogenase is not yet understood. This work should allow further insight on the electron bifurcation principle, a recently discovered alternative energy conservation pathway (Buckel & Thauer, *Chem. Rev.* 2018).

- The targeted labeling of the [2Fe]-cluster with ^{57}Fe allowed not only specific Mössbauer studies of the H cluster (see previous report) but also made it possible to perform Nuclear Resonance Vibrational Spectroscopy (NRVS) (inelastic Mössbauer scattering), together with the group of Stephen Cramer (UC Davis, USA), to measure the vibrations of the ligands of the labeled ^{57}Fe in different states of the H-cluster. Of particular importance was the detection of the hydride-carrying state $H_{hyd.}$ This has been successful and showed – together with QC calculations – the existence of a terminal hydride at the distal Fe of the cluster [11, 12], see Figure 3.

- An alternative method to detect the hydrogens in hydrogenases and also the hydride is magnetic resonance. Unfortunately, in the H_{hyd} state vanishing spin density is found at the $[2Fe]_H$-cluster and EPR techniques have

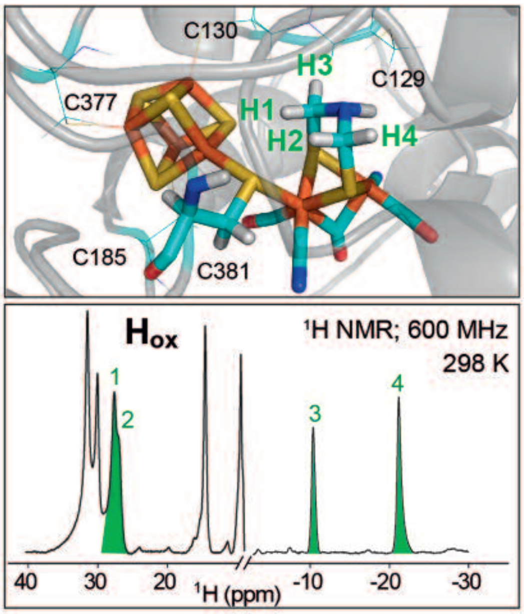


Figure 4. Paramagnetic ^1H NMR spectrum of H_{ox} in [FeFe] hydrogenase of HydA1. The contact shifted resonances of the adt protons are shown in green (for assignments see top), the other resonances are from cysteines at the $[4Fe\text{-}4S]_H$ subcluster [13].

therefore not been successful. However, we have developed together with Claudio Luchinat (Florence, Italy) a method to detect the nuclear resonances of the protons using paramagnetic NMR and applied it for the first time to a hydrogenase [13]; later this work was extended to the H_{hyd} state [14] for which we could also detect the hydride. A great advantage of these measurements is that they are performed under physiological conditions in aqueous solution at room temperature, Figure 4.

- In NMR an interesting polarization effect was detected for the protons of the adt ligand (Fig. 4). This phenomenon was further investigated by ^{13}C ENDOR/ TRIPLE resonance on the H_{ox} state and interpreted with the help of DFT calculations [15]. It has been speculated that this effect is important for the optimal stabilization of the Fe-hydride state in the catalytic cycle.

- For advanced EPR studies on hydrogenases it is necessary to know the g tensor magnitude and orientation. This can only be obtained with confidence through EPR experiments on single crystals. Using a novel highly sensitive resonator (self-resonant micro helix) constructed in our laboratory (see report of Alexander Schnegg) this has been accomplished for crystals of a bacterial [FeFe] hydrogenase (*Chlostridium pasteurianum* I) [16]. In this work it was shown that several other pulse EPR experiments (ESEEM, HYSCORE etc.) are also possible on the tiny single crystals (< 30 nl).

Wateroxidase

The process of light-induced water oxidation in photosystem II (PSII) of oxygenic photosynthesis is performed by a unique protein-bound Mn_4CaO_x cluster in a complex catalytic cycle (S-state cycle), in which protons and electrons are released and molecular oxygen is produced as waste product. The protons form a gradient across the membrane and contribute to ATP production, and electrons and protons are finally used to form "biological hydrogen" in the form of NADPH. Both ATP and NADPH are employed in the dark reactions (Calvin cycle) to reduce CO_2 to carbohydrates. In the S-state cycle the cluster passes through five intermediate states, S_0 to S_4, before one O_2 is released. The S subscript denotes the number of transiently stored oxidizing equivalents in the Mn-cluster.

For a rather long period of time there was limited progress in the understanding of the water oxidation cycle. With the publication of an atomic level X-ray structure of PSII from Japan (Umena et al., *Nature* 2011; PDB 3ARC) and the development and application of fs-time resolved X-ray diffraction using free electron lasers (XFEL) by groups in USA and Japan – together with X-ray spectroscopy and the deployment and use of novel magnetic resonance techniques here in Mülheim, this field has witnessed an explosion of research activities in recent years.

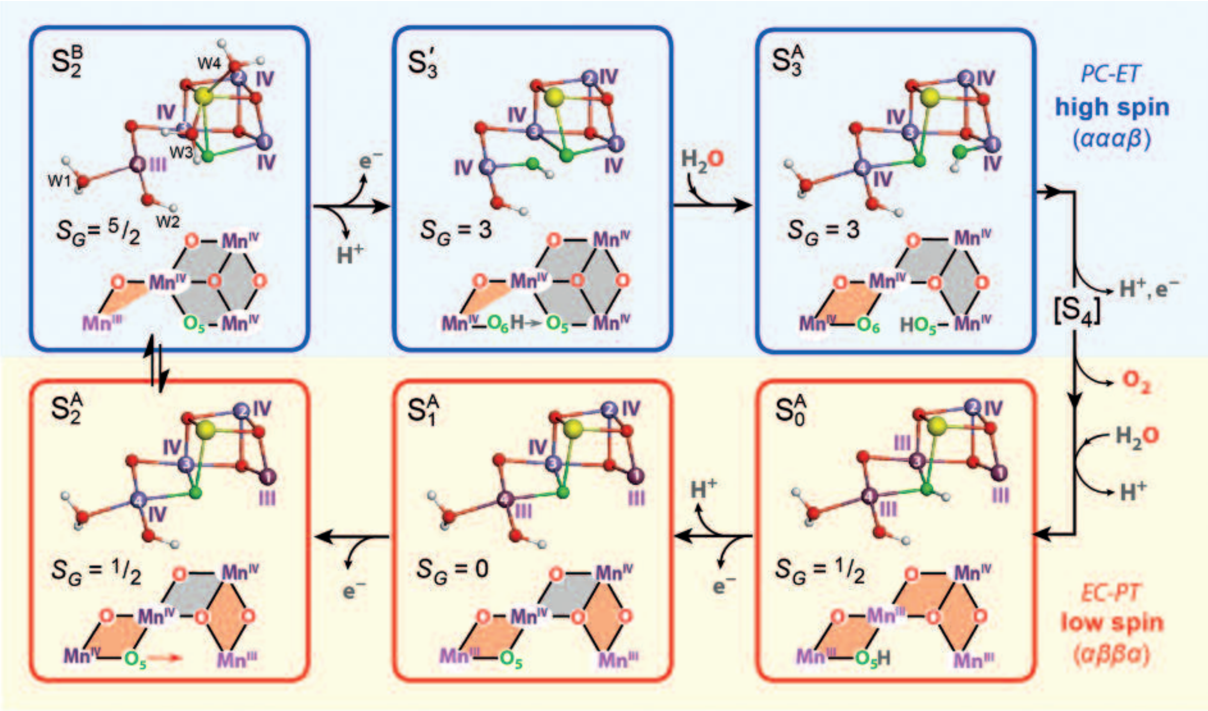


Figure 5. Water splitting cycle of PS II showing the structural, oxidation and spin state evolution of the Mn_4CaO_x cluster during the S states. In the early S-states (bottom) the cofactor adopts an open cubane structure with a low spin ground state following ECPT (electron coupled proton transfer). The higher S states (top) show a closed cubane structure with high spin ground state. Here S-state advancement follows a PCET mechanism [20]. For S_2^B all 4 waters attached to the cluster are shown. Note that the reacting oxygens are in green, all others in red.

In our department we have continued to use magnetic resonance methods supported by QC calculations (in collaboration with Dimitrios Pantazis and Frank Neese) to study the trapped S-states of the water oxidase. During the report period we published an extensive investigation on S_0, the first state of the water splitting clockwork, in which it was finally shown that *no* Mn(II) is present in S_0 and the whole cycle, and that the Mn oxidation states are $Mn1^{III}Mn2^{IV}Mn3^{III}Mn4^{III}$, from which all other states are derived (cf. Figure 5). Furthermore, uptake of the first substrate water molecule as an OH^- ligand (after deprotonation) could be demonstrated and the oxygen assigned to O5 (see Figure 5) [17]. This completed the picture of the site oxidation and spin states of all Mn ions of the flash-generated, freeze-trapped paramagnetic S-states.

The binding of the first substrate water and its incorporation into the Mn-cluster had already been measured by us using magnetically labeled water ($H_2{}^{17}O$) and detection by high field ^{17}O EDNMR on a slow time scale (Rapatskiy et al., *JACS,* 2012). Ongoing work is performed to determine the kinetics of the substrate water uptake using a rapid freeze quench apparatus and by following the intensity of the ^{17}O EDNMR signals. These data are crucial for comparison with the membrane-inlet mass spectrometry experiments performed earlier to detect and assign the water binding in the flash-advanced water splitting cycle. The second water binding event was proposed to take place in the $S_2 \rightarrow S_3$ transition; S_3 is the last metastable intermediate of the complex prior to O-O bond formation (Cox et al., *Science,* 2014). Further information was gained by detecting an intermediate state S_3' in which Mn oxidation had already taken place but not the water binding [18]. In the S_3 state, the two substrate oxygens O_5 and O_6 are ideally located, bound between two Mn sites (Figure 5), allowing efficient O-O bond formation in the final S_4 state. This has been corroborated by recent XFEL data obtained on the S_3 state independently by 2 laboratories. This supports an oxo-oxyl coupling model originally proposed by Siegbahn (Stockholm), but does not exclude other, probably less likely, O_2 formation mechanisms (see Figure 6).

We have recently written 2 publications, in which the mechanistic details are outlined [19, 20]. Figure 5 summarizes the collected knowledge about the water oxidation cycle in oxygenic photosynthesis based on our joint spectroscopic and theoretical results in Mülheim (for states S_0 to S_3) and Figure 6 presents possible models for the final step of O-O bond formation either by internal oxyl-oxo coupling (A, B) or by nucleophilic attack of an oxygen or water on a highly electrophilic oxygen at Mn4 (C) [19].

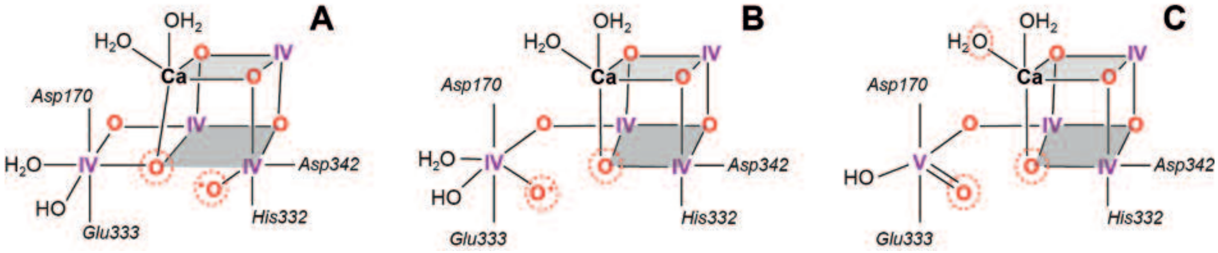


Figure 6. Three representative model structures for the final step of O-O bond formation in S_4, **A**: Mn(IV)-oxyl at Mn1, octahedral coordination, open cubane; **B**: Mn(IV)-oxyl at Mn4, octahedral, closed cubane; **C**: Mn(V)=O at Mn4, trigonal pyramidal, closed cubane. Putative reacting oxygens are indicated by red circles.

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JOINT WORK SPACE – MPI CEC / KOFO

The MPI CEC and the MPI für Kohlenforschung (MPI Kofo) have many overlapping research interests with respect to the design and analysis of catalytic reactions and the characterization of reactive chemical species. In order to elucidate the geometric and electronic structures of such species a host of modern analytical techniques are necessary. The Joint Work Space (JWS) constitutes a combined effort of the MPI CEC and the MPI Kofo to realize the high-potential for synergy on the Mülheim chemistry campus (MCC). This is realized in both institutes by giving the other institute access to their own analytic facilities that are largely complementary. Given that both institutes have different legal structures, this turned out to be a non-trivial undertaking that, however, has been tackled through the construction of the JWS. Through the JWS, both institutes exchange scientific infrastructure and analytic techniques in roughly equivalent amounts. The activities of the JWS in the past evaluation period encompass the high-pressure laboratory at the MPI Kofo (primarily used by the Department Leitner) and a number of spectroscopic facilities (Mößbauer, MCD, SQUID, resonance Raman) hosted at the MPI CEC and that are part of the Department Neese. Below reports of the scientific staff that are part of the JWS are collected.

Molecular Catalysis (Prof. Dr. Walter Leitner) and Technical Laboratories
(Dr. Nils Theyssen, MPI KoFo)

Before his appointment as Director of the Department "Molecular Catalysis" at the MPI CEC, Prof. Leitner had a longstanding collaboration as External Scientific Member at the MPI KoFo since 2002. This included an associated scientific group in the technical laboratories (led by Dr. Theyssen). This intensive and well-established collaboration is now continued within the JWS framework. In the reporting period, five collaborative scientific projects can be assigned to JWS, involving staff of MPIs CEC and KoFo (partly via third party funding), and use of infrastructure in the Technical Laboratories and analytical service departments of both institutes.

The use of supercritical carbon dioxide ($scCO_2$) as a reaction medium for chemical transformations featured in two projects. This research topic defines a long-term link between KoFo and Prof. Leitner as part of an internationally recognized research program. In the reporting period, we collaborated with Prof. Manfred Reetz to revisit a study of González-Núñez and co-workers on the role of $scCO_2$ in S_N1-type reactions. Our results disproved the claimed stabilization of carbon cations by this medium. The study involved series of elaborate control experiments using dedicated home-built reactors and high-pressure UV/Vis spectroscopic measurements in which the degree of carbocation formation was measured as a function of individually applied solvents [1].

$ScCO_2$ was also evaluated for the preparation of Pt/Pd bimetallic nanoparticles supported on SBA–15 using the chemical fluid reactive deposition approach. The method exploits the combination of gas-like diffusion and liquid-like solubility properties of the supercritical medium to transport the organometallic metal precursor into structured materials (Figure 1). The unique property resulted in a highly uniform distribution of particles in the 5 nm range inside the pores that could be corroborated with their catalytic performance in the hydrogenation of levulinic acid to γ-valerolactone [2]. This transformation is an important step for the conversion of carbohydrate-based feedstocks to platform chemicals. The project was part of the KoFo contribution to the Cluster of Excellence "Tailor–Made Fuels from Biomass", now continued as "The Fuel Science Center (FSC)".

Another FSC related project focused also on carbohydrate conversion. The natural clay mineral kaolin was identified as effective bifunctional catalyst for isomerization and etherification of glucose in methanol. Using this exceptionally cheap and abundant layered alumo-silicate (0.15 €/kg), methyl-fructoside could be produced with up to 52% yield [3]. Detailed studies on the reaction network and extensive characterization of the materials provided insight into the parameters affecting the activity of catalysts from varying natural sources.

Initiated by a serendipitous finding during the preparation of silica-supported nanoparticles, a novel method for synthesizing iron(III) silicates was developed. The known procedures to generate synthetic iron silicates typically require hydrothermal conditions with temperatures in the range of 1000 °C and pressures in the kilo bar zone. Surprisingly, we were able to produce the phyllosilicates $Fe_2[Si_4O_{10}](OH)_2$ (Ferripyrophilite) from Fe powder, a silica source such as SBA-15 and water at 100 °C in a simple glass flask under air. The material has an ultrathin two-dimensional (2D) nanosheet morphology, shows very high thermal stability (up to 800 °C), and provides interesting potential for catalytic applications, including activity in ammonia synthesis [4].

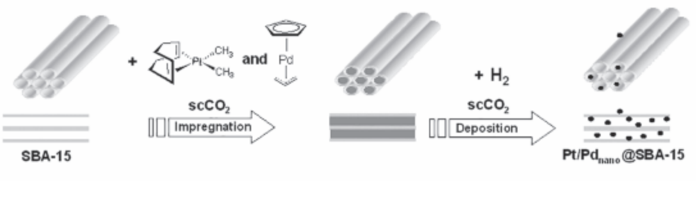

Figure 1. Preparation of supported nanoparticle catalysts using chemical fluid deposition from organometallic precursors in supercritical CO_2.

An ongoing project concerns the development of supported metal nanoparticles for CO_2 hydrogenation. In particular, we aim to evaluate whether and how the mechanistic concepts of organometallic catalysis can be translated to solid materials. At this preliminary stage, silver on γ-Al_2O_3 was found to exhibit catalytic activity for the hydrogenation of CO_2 to formic acid under base-free conditions. Further studies are underway to elucidate the exact nature of the Ag particles and the synergistic action with the support material.

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EPR, magnetic Mössbauer, vis/NIR-MCD spectroscopies and SQUID magnetometry Lab
(Dr. Eckhard Bill)

In the period under review (2017 – Nov. 2019), the Joint Work Space labs for multi-frequency cw-EPR, magnetic Mössbauer, vis/NIR-MCD spectroscopies and SQUID magnetometry increasingly lived up to expectations concerning their role as a package of complementary and high-level chemical research techniques that help to consolidate common research interests of the different theoretical and experimental departments in both institutes. This is reflected in a number of publications with essential and equivalent contributions from both, theory and spectroscopy within the Neese department [1-10], or emerging from intense collaboration with the DeBeer department [11-14], or from both the Neese and the DeBeer Departments [15-18]. Fruitful collaborations and common publications materialized also with the Schüth department [19,20], the Fürstner department [21,22], and even with the rather newly installed Leitner department [23]. Scientifically, we focused our work as before on new aspects of the activation of oxygen by molecular compounds for selective functionalization of C-H bonds and other oxidative reactions, on the properties of nitrogen in high-valent iron complexes, and also on fundamental aspects of CO_2 activation by low-valent iron compounds in this period. In these programs, the magnetic inorganic spectroscopy methods again yielded the major part of the experimental insight necessary for unique understanding of the electronic structures of the molecular catalysts. Equivalent to this work, important results and high-ranking publications could also be obtained in fundamental magnetochemistry and magnetism of molecules [1,6,8,15]. The lessons learned there help to better use magnetic/spectroscopy data as tool for the electronic structure and function of transition ion complexes. The scientific output became possible in particular because of intense and fruitful collaboration with M. Atanasov and F. Neese, and Shengfa Ye, providing quantum-theoretical interpretation of data and the spectroscopic observables.

Technically, we succeeded in the recent years to reduce the dependence of the labs on the expensive and increasingly un-reliable availability of liquid helium by replacing the classical, and in the meantime outdated, cryo-magnets for Mössbauer spectroscopy and MCD spectroscopy by closed-cycle magnet cryostat systems with Gifford-McMahon and pulse-tube cold heads, respectively. The new systems provide easy-to-use and readily available field and temperature adjustments (7 Tesla field, 1.7 – 300K for Mössbauer, and 11 T field, 2 – 300 K for MCD spectroscopy). In addition, in this year 2019 thanks to Frank Neese's Max Planck grant we could replace also the 25 years old, but still well operational SQUID magnetometer by a modern instrument with closed-cycle 'evercool' liquid helium dewar. The new magnetometer offers a variety of new, modern experimental options beyond static DC SQUID measurements, such as frequency-dependent AC measurements, single-crystal options as well as 500K measurements and light-access, aiming for studies at conditions that are closer to eventual catalytic processes. With these renovations and upgrades, the labs should be ready for interesting future challenges.

EPR, Raman and Hydrogen production Group
(PD. Dr. Maurice van Gastel)

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 expanded our instrumentation development efforts by creating an entire new Raman Lab equipped with multiwavelength Raman lasers.

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) and Prof. Fürstner (Dr. L.R. Collins). In this project we have investigated di-rhodium paddlewheel complexes and bismuth-rhodium analogs that are indispensable tools in modern organometallic catalysis for the controlled decomposition of diazo-compounds. In particular, tuning the reactivity of the transient carbene species remains an active and dynamic field of research. Our findings obtained on a synergistic approach between synthesis, spectroscopy and theory (Figure 1) have indicated that the distal metal center plays an as yet underappreciated role in modulating this reactivity. Replacement of one rhodium atom in the bimetallic core for bismuth results in the formation of a significantly more electrophilic carbene complex. Bismuth-rhodium catalysts thereby facilitate previously unknown modes of reactivity for α-diazoester compounds, including the cyclopropanation of alkenes as electron deficient as trichloroethylene. While dirhodium paddlewheel complexes remain the catalyst of choice for many carbene-mediated transformations, their bismuth-rhodium analogues exhibit complimentary reactivity and show great potential for small molecule and solvent activation chemistry. DFT calculations highlight the importance of metal-metal bonding interactions in controlling carbene electrophilicity. The paucity of these interactions between the 4d orbitals of rhodium and the 6p orbitals of bismuth results in weaker π-back-bonding interactions for bismuth-rhodium carbene complexes compared to dirhodium carbene complexes. This leads to weakening of the rhodium-carbene bond and to a more carbene-centered LUMO, accounting for the observed enhancement in bismuth-rhodium carbene electrophilicity.

These findings are supported by a detailed spectroscopic study of the 'donor-donor' carbene complexes $Rh_2(esp)_2C(p\text{-}MeOPh)_2$ and $BiRh(esp)_2C(p\text{-}MeOPh)_2$, employing a combination of UV-Vis and resonance Raman spectroscopy. The results reveal that carbene chemoselectivity in $MRh(L)_4$ catalysis can be modulated to be previously unrecognized extent by the distal metalloligand [24].

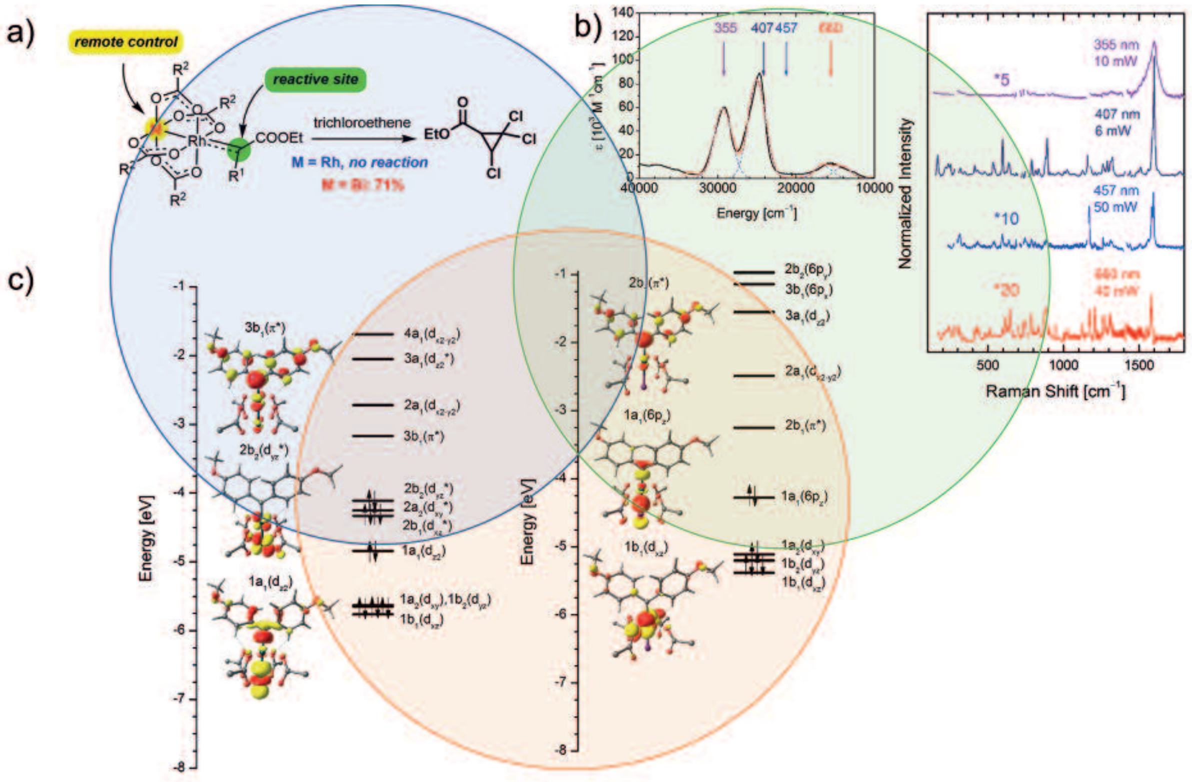

Figure 1. Artist's impression of our synergistic approach entailing **(a)** synthesis, schematically depicting the cyclopropanation reaction catalyzed by the paddlewheel complex **(b)** spectroscopy, here, UV/VIS spectrum and state-selective normalized resonance Raman spectra of $BiRh(esp)_2C(p\text{-}MeOPh)_2$ and **(c)** theory, here indicating the orbital structure of $RhRh(esp)_2C(p\text{-}MeOPh)_2$ and $BiRh(esp)_2C(p\text{-}MeOPh)_2$. For details of nomenclature and detailed interpretation, cf. reference [24].

O_2 and CO_2 Activation Group
(Dr. Shengfa Ye)

Research in the Ye's group focuses in understanding the catalytic mechanisms of enzymatic reactions at the atomic level using quantum chemical calculations. A characteristic case study performed within the period under evaluation refers to the experimental verification of the O_2 activation mechanism. Our earlier computational investigations on O_2 activation at non-heme iron centers proposed a step-wise single-electron reduction mechanism. Specifically, O_2 activation may pass through an unreported intermediate denoted as half-bond intermediate, the three-electron reduced form of O_2 featuring only half s-bond in the O_2 motif. Our recent detailed electronic-structure and spectroscopic analyses revealed that the active species that is responsible for stereoselective functionalization of C-H and C=C bonds catalyzed by low-spin ferric complexes and H_2O_2 is, in fact, the half-bond intermediate [7]. Another case study refers to the electronic structure and reactivity of low spin tetragonal Fe^V-nitrido complexes. Our combined spectroscopic and computational study evidenced an unusual orbitally nearly doubly degenerate $S = 1/2$ ground state for low spin tetragonal Fe^V-nitrido complexes. Based on these observations, we proposed a characteristic electron paramagnetic resonance (EPR) signal for such species [4]. Very recently, we investigated oxygenation of a fleeting Fe^V-nitrido intermediate to furnish the corresponding Fe-nitrosyl complex using in situ EPR and Mössbauer spectroscopy [25].

Molecular Magnetism Group
(Prof. Dr. Michail Atanasov)

The Atanasov's Molecular magnetism group deals with the magnetic properties of molecules (complexes) with open d- and f-shells. The main goal in this field is the exploration of the relation between electronic and geometric structures and their magnetic and spectroscopic properties.

Single molecule magnets are subject of intense research efforts due to their ability to switch between two distinct states under the influence of an external magnetic field. Thus, they could potentially pave the way to the ultimate miniaturization of storage devices. The ultimate goal in this field is to rationally design molecules that are switchable at room temperature and retain the stored information in long term. However, in practice, interactions of the molecules with their surrounding lead to a „shortcut" and consequently to a loss of magnetic information. Understanding of how this happens is of crucial importance in order to explore possible workarounds. We have succeeded for the first time to directly observe the molecule/environment interaction in trans-$Co(acac)_2(H_2O)_2$ using advanced magnetic Raman and magnetic IR methods and to interpret the experiments using elaborate models based on quantum mechanics (Figure 2a). The results have been published in Nature Communications [6].

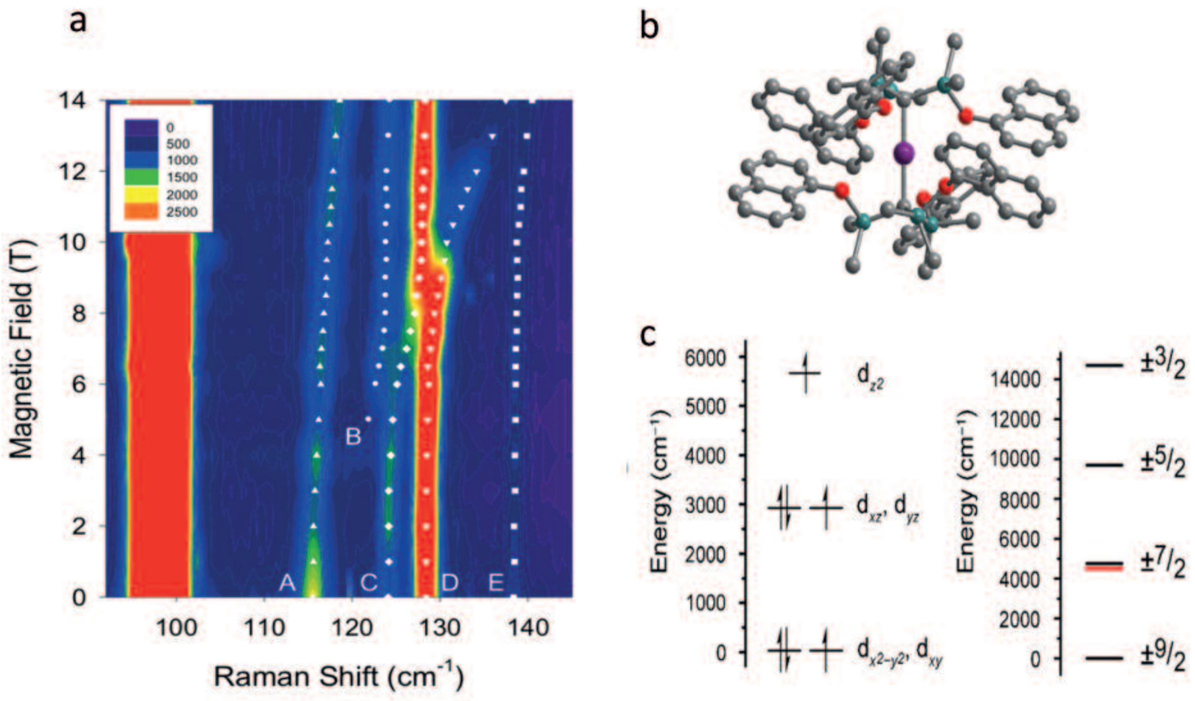

Figure 2. a) 2D-Visualization of molecular vibrations of a single molecule magnet trans-$Co(acaca)_2(H_2O)_2$, measured as a function of strong magnetic fields up to 14 Tesla. **b)** Molecular structure of $Co(C(SiMe_2ONaph)_3)_2$. Purple, gray, turquoise, red, and yellow spheres represent Co, C, Si, and O respectively. Hydrogen atoms have been omitted for clarity. **c)** An orbital energy diagram depicting the non-aufbau electron occupations of the 3d-orbitals together with the calculated splitting of the ground ^{4} state. The red line is the experimentally determined energy of the $M_J = \pm{}^7/_2$ state.

The magnetic properties of a single metal center are determined by a combination of its total spin, *S*, and orbital angular momentum, *L*. Importantly, orbital angular momentum gives rise to magnetic anisotropy, a property that is essential for applications such as magnetic data storage and high coercivity magnets. Unquenched *L* arises from an odd number of electrons in degenerate orbitals and is typically observed only for free ions as well as complexes of the f-elements. For the majority of transition metal ions, however, orbital angular momentum is quenched by the ligand field, which removes requisite orbital degeneracies. Maximal orbital angular momentum for a transition metal (L = 3) in turn requires an odd number of electrons in two sets of degenerate orbitals. For the later transition metals, which are more likely to exhibit large magnetic anisotropies, this value of *L* requires a non-Aufbau electron configuration-i.e., the electrons do not fill the d-orbitals in order of lowest to highest in energy. In a combined experimental and theoretical study, we have been able to show that the isolation of a pure, non-Aufbau ground state is possible in the $Co(C(SiMe_2ONaph)_3)_2$ complex (Figure 2 b, c). Hence an f-element-like electronic structure can be achieved for a transition metal within an extreme coordination environment. More importantly, our results demonstrate that this non-Aufbau ground state enables realization of maximal orbital angular momentum and magnetic anisotropy near the physical limit for a 3d metal. In this respect, use of the linear L–Co–L moiety may be useful in the design of materials with high magnetic coercivity. The results from this study were subject to a publication in Science [26].

Advanced Experimental and Theoretical Spectroscopy Group (Dr. Dimitrios Manganas)

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 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.

One of the main activities of the group is to develop computational protocols that are able to compute X-ray spectra of molecules and solids (Figure 3). In particular the pair natural orbital restricted open shell singles and its DFT variant (PNO-ROCIS, PNO-ROCIS/DFT) allows for computing XAS spectra of real-life systems [27, 28]. Recently even more accurate computational protocols based on the complete active space configuration interaction in conjunction with N-electron valence second order perturbation theory (CASCI/NEVPT2) as well as multireference configuration interaction (MRCI) and multireference equation of motion coupled cluster (MREOM-CC) methods have been employed to compute challenging metal L-edge XAS spectra of medium sized molecules with high predictive accuracy [29, 30].

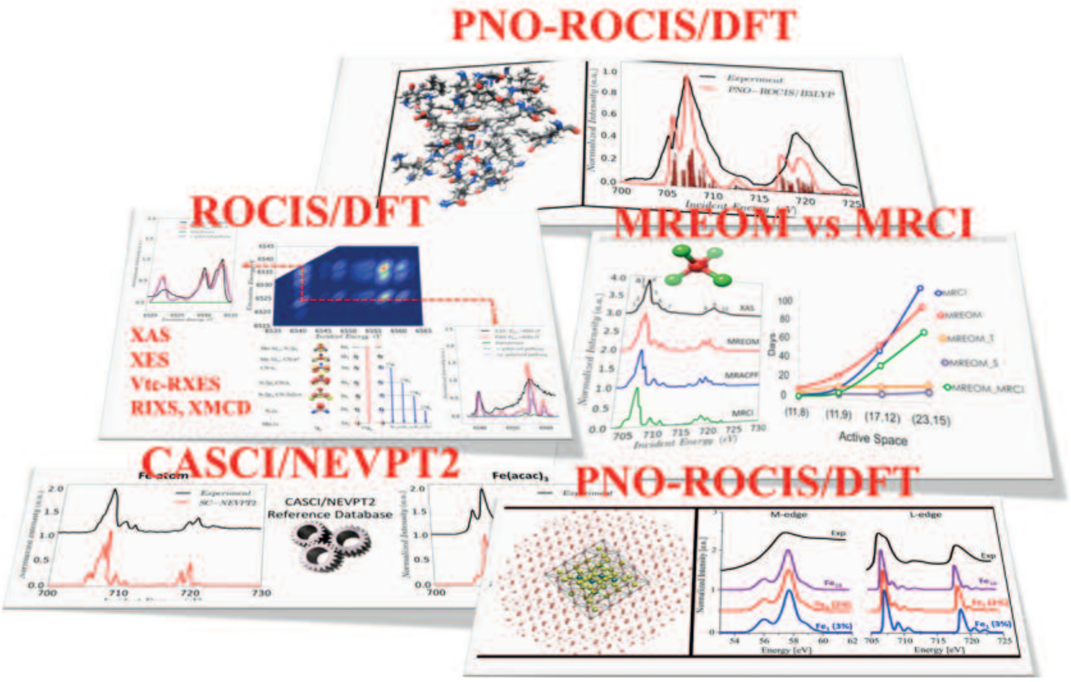

Figure 3. An illustration showing various wavefunction based protocols that have been developed to compute a wide variety of X-ray spectra of molecules and solids.

An important activity in the group is to develop valid spectroscopic protocols that are able to treat relevant problems that are met in the field of materials sciences. In a recent example it has been demonstrated that for both organic and inorganic semiconductors the back-transformed Pair Natural Orbital Similarity Transformed Equation of Motion Coupled-Cluster (bt-PNO-STEOM-CCSD) method provides the best agreement with the available experimental values resulting in errors that are on average lower than 0.2 eV [32]. In addition, the group shows activity in defining protocols that can deliver accurate energetics in problems similar to those met in solid state catalysis. In a characteristic example it has been recently shown that using the domain-based pair natural orbital local correlation concept (DLPNO-CCSD(T)), allows for *ab initio* calculations providing reference adsorption energetics of small molecules at solid TiO_2 rutile surfaces with an accuracy approaching 1 kcal/mol and at affordable computational cost while allowing for a thorough investigation of the nature of the chemical bonding in the concept of Local Energy Decomposition technique [32].

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EPR RESEARCH GROUP

DR. ALEXANDER SCHNEGG

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Research Group Leader: MPI CEC (since 2018)

Fields of Research

The *EPR Research Group* at MPI CEC was established by Dr. Alexander Schnegg in 2018. Presently there are five scientists, a PhD student, and a technician who work under the direction of Dr. Schnegg. Research in the group focuses on the development and application of electron paramagnetic resonance (EPR) methods to gain insight into structure-function relationships of earth-abundant transition metal ion (TMI) active-sites in heterogeneous and homogeneous catalysts. These systems are relevant for the next generation of sustainable chemical synthesis and efficient chemical energy conversion and storage.

TMI catalysis frequently exhibits paramagnetic key intermediates in the catalytic cycles. An ideal technique for their study is EPR, which allows rapid identification, tracking and structural characterisation of function-determining paramagnetic TMI sites, as well as occurring radical products.

The *EPR Research Group* operates a unique array of advanced pulse and continuous wave (cw) EPR spectrometers (3 GHz up to THz) with electron nuclear double resonance (ENDOR) capabilities. To relate catalytic activity with structure and oxidation state, we employ *in situ* EPR under applied potential bias[1] or light,[2] as well as trapping techniques (*e.g.* rapid freeze quench) for studies of transient paramagnetic states. Pulsed EPR methods allow for high-resolution EPR experiments[3] and hyperfine spectroscopies.[4] To further boost the detection sensitivity of these techniques for studies of TMI cofactors in tiny protein crystals, micro-resonators are used.[3] Particularly relevant for TMI research is the ability to ascertain spin coupling parameters of paramagnetic states with varying oxidation and spin states, including half integer and integer high spin (HS, $S > ½$) states. A very powerful approach in this context are magneto-structural correlations,[5-8] where experimentally obtained zero field splitting (ZFS) is employed to conclude on coordination environments and electronic structures. However, large ZFSs are difficult or even impossible to obtain with conventional EPR spectrometers. Only high-frequency EPR (HF-EPR, with excitation energies 0.1 - 10 THz/ 3 cm^{-1} – 300 cm^{-1})[9] can directly measure ZFS larger than the microwave energy applied in conventional EPR spectrometers (~0.01 THz/ 0.3 cm^{-1}). The *EPR Research Group* in Mülheim is one of very few groups that can perform such experiments up to the THz range. Recent HF-EPR studies in the group focused on catalytically relevant TMIs (*e.g.* Co^{I},[7] Co^{II},[10-11] Fe^{II},[12] Fe^{III},[5] Fe^{IV},[8] and $Mn^{II,III,IV}$; see Figure 1).

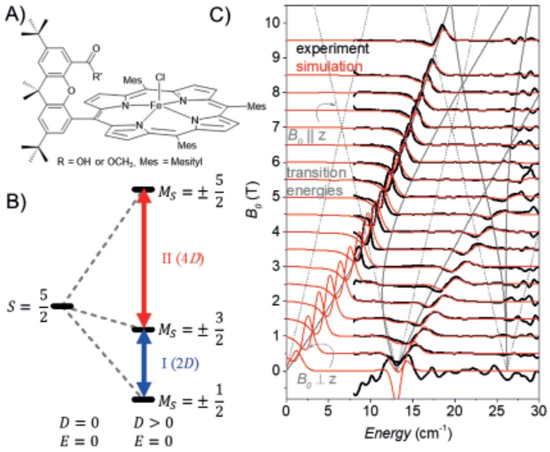

Figure 1. ZFS determined by HF-EPR allows for magneto-structural correlations in $S > ½$ TMI states. **A)** Ferric Hangman porphyrins are relevant as models for haem hydroperoxidase enzymes featuring an acid/base group in close vicinity to the metal centre. **B)** Spin energy level diagram absent a magnetic field. **C)** Hangman Frequency-Domain Fourier-Transform THz-EPR spectra at 2 K. Comparing Hangman ZFS, extracted from THZ-EPR experiments, to related ferric iron porphyrins, established correlations of the ZFS with the geometric ligation structure.[5]

Collaborations have been established with researchers and organisational units at MPI CEC, MPI KOFO, and with external partners on the following topics:

- Research with members of the *Joint Work Space* (*JWS*) of the *Molecular Theory and Spectroscopy Department* of Prof. Neese at MPI KOFO focuses on magneto-structural correlations in TMIs. *JWS* and the *EPR Research Group* share laboratory infrastructure, enabling cooperative instrument usage and research at the Mülheim Chemistry Campus. Through this collaboration, advanced EPR methods are complemented with magnetic characterisation techniques like SQUID magnetometry, MCD and applied-field Mössbauer spectroscopies, as well as quantum chemical calculations developed in the Neese Department. Thereby, detailed insight into a TMI's electronic structure,[10] reactivity and magnetic properties are provided, which are hardly obtainable with alternative techniques. Ongoing research projects between members of the *JWS*, the *Neese Department* (Dr. Bill and Dr. Ye) and the *EPR Research Group* target magneto-structural correlations and the electronic structures of low coordinate Fe^{II} and Co^{II} complexes,[12] Fe^{II} porphyrins, Mn^{IV} hydroperoxo complexes, Cu^{II} peroxo dimers and Co^{II} single ion magnets.[10]

- Together with the *Heterogeneous Reactions Department* of Prof. Schlögl at MPI CEC, complementary *in situ* EPR and X-ray studies of Co, Ni and Mn oxides as water oxidation catalysts are conducted.[13] Additional joint research is dedicated to iron-nitrogen-carbon (FeNC) oxygen reduction reaction (ORR) catalysts for proton-exchange membrane fuel cells. Research work on FeNC degradation mechanisms during ORR catalysis with Dr. Mechler revealed the mechanism by which minute amounts of Pt enhance FeNC catalyst stability.

- With the *Organic Synthesis Department* of Prof. Ritter at MPI KOFO, joint research on iridium based photoredox catalysis has been established. The Ritter group reported an approach to generate aryl radicals in the presence of high-valent Cu species to enable the first highly selective late-stage aromatic C-H fluorination reaction. To identify the intermediates, mechanistic studies were performed using EPR in combination with quantum chemical calculations. EPR studies led to the detection of a Cu^{II} species and a thianthrene radical cation (TT radical), thus elucidating the catalytic cycle (see Figure 2).[2]

- Dr. Rüdiger (*Inorganic Spectroscopy Department* of Prof. DeBeer at MPI CEC), Prof. Lubitz (former *Department of Biophysical Chemistry* at MPI CEC), and the *EPR Research Group* collaborate on the development of *in situ* spectro-electrochemistry.

  First *in situ* EPR results obtained on a self-healing electrodeposited Co-Pi water splitting catalyst revealed a correlation between Co^{IV} formation and catalytic activity.[1]

- With Dr. Cutsail (newly appointed W2 leader of the Max Planck Research Group *EPR Spectroscopy of Metallorganic Compounds* at MPI CEC), novel EPR methods are developed and applied. This collaboration is expected to significantly grow within the next years.

- With Prof. Bordignon and Prof. Tschulik (both Ruhr Universität Bochum) a project within the DFG funded cluster of excellence RESOLV on the determination of solvent dependent g- and hyperfine tensors, and the application of spectro-electrochemical EPR methods, has recently been started.

- Prof. Muhler (Ruhr Universität Bochum and Max Planck Research Fellow at MPI CEC), and the *EPR Research Group* collaborate on the photocatalytic oxidation over Pt-loaded Rh-doped strontium titanate, which allows efficient and selective conversion of alcohols to aldehydes and ketones under anaerobic conditions and visible light.[14]

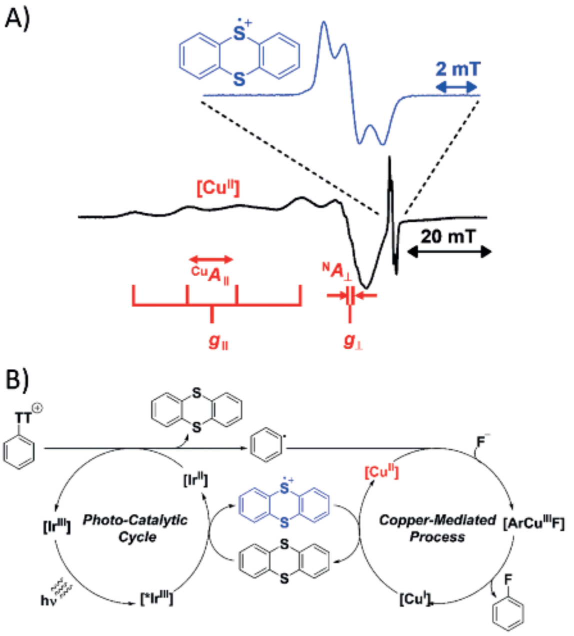

Figure 2. EPR identifies reaction intermediates in iridium based photoredox catalysis to generate aryl halides. **A)** X-band CW EPR spectra recorded for a mixture containing Ir^{III} catalyst, Cu^{I}, arylthianthrenium salt (ArTT) and CsF after irradiation (black) and TT radical (blue) at 100 K. EPR detection of Cu^{II} species and a TT radical helped elucidate the mechanism for the fluorination of thianthrenium salts depicted in **B)**.[2]

EPR Method Development

Driven by remaining challenges for the EPR detection of paramagnetic TMI states and radicals, method development in the *EPR Research Group* focuses on the following scopes:

- Development of *in situ* EPR facilities (with applied potential bias and/or light).
- Detection of $S > 1/2$ TMI states exhibiting large ZFS, using HF-EPR.
- Achieving ultimate sensitivity and the possibility to incorporate EPR sensors in other experimental set-ups or chemistry environments, by micro-EPR and EPR-on-a-Chip (EPRoC) probes.

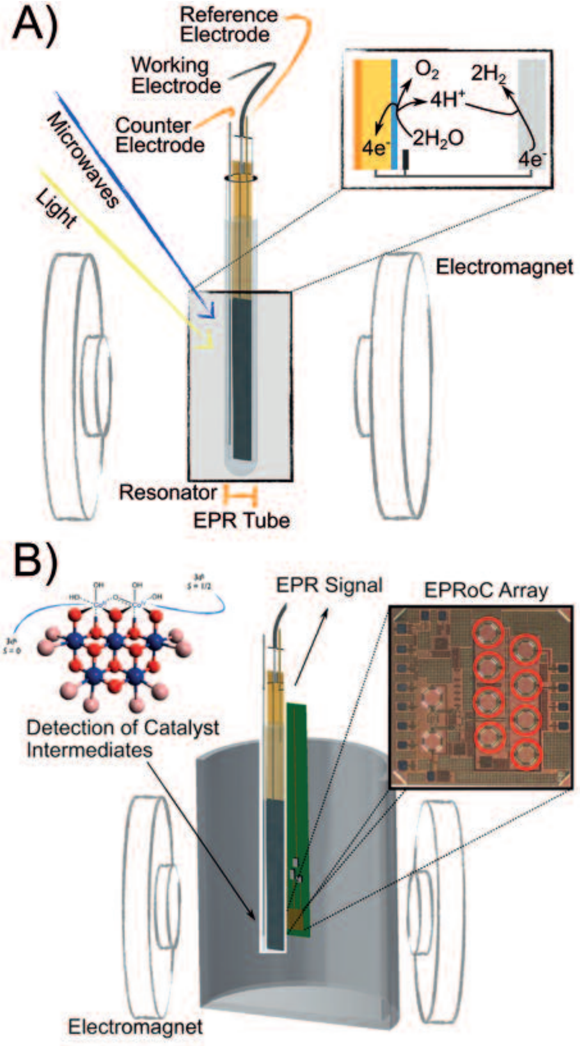

Figure 3. *In situ* EPR and EPR-on-a-Chip (EPRoC) techniques allow for EPR measurements under conditions relevant to catalytic reactions. **A)** Scheme of an *in situ* set-up employed for EPR experiments under applied potential bias[1] or light.
B) Scheme of a planned set-up, with an EPRoC sensor array attached to a working electrode in an electrochemical cell. The inset shows an enlarged view of the EPRoC array, with the micro-resonators in red.

In situ EPR

Function determining paramagnetic states are frequently encountered only under operational conditions. This motivates our group to develop methodology for *in situ* EPR methods,[1] where EPR spectra can be recorded under illumination and/or applied potential bias (see Figure 3 A).

High-Frequency EPR

Difficulties in extracting spin-coupling parameters for $S > 1/2$ systems, with large ZFS arise from the fact that their spin transition energies can easily exceed the excitation energies of commercial EPR spectrometers. To overcome this restriction, we develop HF-EPR techniques.[9] Depending on the targeted energy range and detection sensitivity, EPR experiments can be performed at fixed frequency and variable external magnetic field between 3 GHz and 244 GHz (this range is currently being extended to 950 GHz by funds from a MPG "Großgeräteantrag") or at fixed field and variable excitation frequency from 100 GHz to 10 THz.[9, 15] Access to synchrotron based THz-EPR is enabled by the joint laboratory *EPR4Energy* of MPI CEC and Helmholtz Zentrum Berlin für Materialien und Energie (HZB), which allows the *EPR Research Group* to use 30 % of the user time of the FD-FT THz-EPR spectrometer at HZB's synchrotron.

Micro-resonators and EPR-on-a-Chip sensors

In order to significantly advance EPR spectroscopy for samples with nanolitre volumes, a novel sub-mm-sized X-band micro-helix resonator has been developed in collaboration with Prof. Lubitz (see Figure 4).

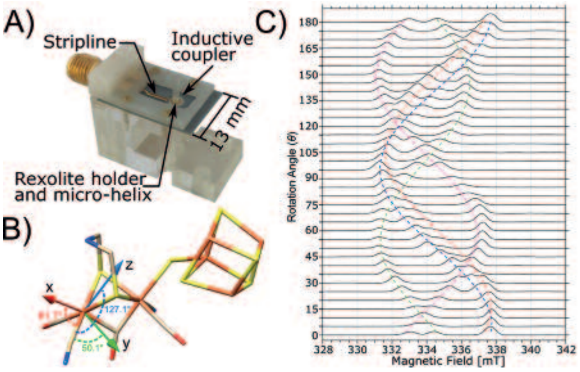

Figure 4. EPR micro-resonators provide unsurpassed absolute detection sensitivity for TMI protein cofactors. **A)** Coupling and support assembly of a five-turn micro-helix EPR resonator. **B)** Molecular structure of the [FeFe]-hydrogenase active site, the H-cluster, from PDB ID 4XDC (S, yellow; Fe, orange; N, blue; C, tan; O, red). The analysed *g*-tensor (g_x, red; g_y, green; and g_z, blue) is mapped on the crystal structure. **C)** X-band pulse EPR spectra collected on a [FeFe]-hydrogenase single crystal in H_{ox} state with the micro-helix resonator. Here, one plane for a full rotation of 180° in 5° steps at a temperature of 15 K is shown. The crystal dimensions were ~ 0.3 mm by 0.1 mm by 0.1 mm.[3]

The sensitivity enhancement obtained with this resonator, makes protein single crystals of dimensions typical for X-ray crystallography accessible to advanced EPR techniques.[3] To enable future EPR experiments inside other experimental set-ups or chemical environments, and to increase the applicability of EPR spectroscopy, we are developing EPR detection schemes employing novel integrated EPRoC sensors. These spectrometers incorporate the EPR probe and microwave bridge in a sub-cm-sized sensor (see Figure 3 B).[1] EPRoC sensors are a fundamental paradigm shift in EPR spectroscopy allowing for the *in situ* study of paramagnetic samples on the chemistry benchtop instead of at a costly large-magnet facility.

This research is conducted within the BMBF funded project "In situ EPR-on-a-Chip for catalysis and battery research".

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MAX PLANCK RESEARCH GROUP

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Electrochemistry for Energy Conversion

The group is focused on investigating relations between material and electrolyte properties and electrocatalytic performance, namely activity, selectivity and stability. The focus of the research is on reactions that are of relevance for energy conversion and storage. The group seeks to implement well-defined surfaces and electrochemical modification techniques followed by exact and careful assessment of electrocatalytic properties.

One of the proposed pathways of addressing the challenges of the intermittency of renewable energy sources is the generation of fuels during peak production. In this concept electricity from renewables is used to produce fuels such as: hydrogen by water electrolysis or carbon-compounds from CO_2-reduction. Such hydrogen could later be used in fuel cells or directly combusted to generate energy, thus allowing energy storage for times when consumption exceeds production.

Oxygen and Hydrogen Electrochemistry

The reactions taking place in an electrolyzer are the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), while in a fuel cell the oxygen reduction reaction (ORR) and the hydrogen oxidation reaction (HOR) are taking place. In both these types of devices the reactions involving oxygen (OER and ORR) have slower kinetics and are the limiting factor to making these devices more efficient. Additionally, the best performing catalysis for these reactions are noble platinum group metal catalysts, so there is considerable interest in improving the activity, thus reducing loading, as well as reducing the noble metal content in these catalysts.

The group will primarily investigate metal and metal-alloy catalysts for these reactions. The factors that determine the electrocatalytic properties of these materials can be, in principle, viewed as belonging to 3 groups: the ensemble, ligand and strain effects, Figure 1. Nonetheless, these effects can rarely be considered independently as there is significant interplay between them (1).

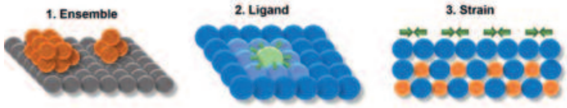

Figure 1. Scheme of different effects that affect the electrocatalytic properties of a surface.

Ensemble effects exist due to the different functional roles ensembles of atoms may take and can be exploited by creating various structures on the electrode surface (2). However, with the increase of the complexity of the surface various other effects can come into effect (mass transport, edge effects, etc.). This requires the gradual increase in complexity levels in surface structures coupled with careful measurement of electrocatalytic properties in order to establish relations between these variables. Surface structures can be introduced to model electrode surfaces by electrochemical means[2], but also various structuring techniques (e.g., laser-based bed melting) will be applied in cooperation with other groups.

Ligand effects, which arise due to due to the presence of a dissimilar neighboring atom in the immediate vicinity of an active site, are particularly important to consider in alloys and surface/near-surface alloys. However, since dealloying is common under electrochemical conditions[1], ligand effects are very often coupled with strain effects, which occur due to the difference in the lattice parameters between different metal phases, which introduces strain in the crystal lattice. This necessitates the application of different surface science techniques such as XPS, XRS, SEM, TEM, and others in order to assess the state of materials before and after the reaction takes place in order to determine the state and uniformity, or lack thereof, of the present phases.

When investigating the influence of these effects numerous other factors need to be carefully controlled for: particle size (for powders and nanoparticles), catalyst-support interactions, poisoning by side-products, catalyst surface degradation, etc. This mandates the use of well-defined systems with electrodes with known crystal orientation, high-purity electrolytes, ultrapure conditions, and careful electrochemical measurements of the system in question (3).

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. The alloy synthesis is considered both by electrochemical/thermal and other ex-situ techniques. The group seeks to further the prospects of rational catalyst design by linking the activity, selectivity and stability of these catalysts to easily assessable physical properties. The group focuses on precise in-depth characterization of electrocatalytic systems and relating these properties to controllable parameters in order to capitalize on such knowledge.

Catalysts for the synthesis of wide-use chemicals

An alternative approach for the application of electric power from renewable sources is the electrochemical synthesis of wide-use chemicals. For instance, the previously mentioned ORR can go through two different pathways, the so-called 4-electron one, which is desirable in fuel cells, and the 2-electron pathway which results in the generation of hydrogen peroxide. H_2O_2 is a widely used chemical an oxidant and a disinfectant. Therefore, a good control of the selectivity of ORR is of high interest for different applications (4). Ammonia is another important chemical, the second most produced in the world, and there is certain interest in developing processes that could use renewable electricity and function in a more decentralized manner. Electrochemical ammonia synthesis in that sense would be an interesting option. While the process has been investigated for decades, it suffers from the lack of standards, protocols and general understanding of the challenges of the reaction, which have led to a general state of confusion regarding the viability of the process. Only recently have these issues been seriously addressed (5) and the main challenge in this field is the proper, standardized, and reliable testing of catalytic systems.

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MAX PLANCK RESEARCH GROUP

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Electron Paramagnetic Resonance (EPR) Spectroscopy of Organometallic Complexes

George Cutsail started his Max Planck Research Group (MPRG) in September 2019 at the MPI-CEC and will work in cooperation with the University of Duisburg-Essen (UDE) and its Faculty of Chemistry located in Essen. The cooperation of the MPRG between the MPI CEC and UDE allows for new and exciting research collaborations, additional training of students and continued expansion of shared knowledge and resources between both institutions.

O_2 Bond Cleavage and Formation.

Both the cleavage and formation of the O-O bonds of O_2 by transition metal centers are critical chemical processes for chemical energy solutions. The Cutsail MPRG is interested in understanding the fundamental mechanics of O-O bond cleavage and formation facilitated by copper centers in either metalloproteins or small biomimetic complexes. The Cutsail group first aims to expand the utility of advanced EPR techniques such as Electron Nuclear Double Resonance (ENDOR) and Electron Spin Echo Envelope Modulation (ESEEM) spectroscopies to study and elucidate the structure and electronic properties of O_2 molecular coordination with transition-metals. These advance techniques possess the ability to produce high-level structural and bonding information of dilute catalytic intermediates. Monocopper proteins such as lytic polysaccharide monooxygenases (LPMO) bind and activate O_2 (Figure 1) to cleave the O-O to potentially form a strong copper-oxygen oxidative intermediate. This intermediate is strong enough to activate and break the strong C-H glycoside bond (>95 kcal/mol) of polysaccharide substrates. The active intermediate of these monocopper systems has yet to be spectroscopically observed.

Figure 1. Chemical schematic of the copper active-site of LPMOs also referred to as a histidine 'T-brace.'

The Cutsail MPRG first aims to understand the activation and formation of the O-O bond by monocopper centers from two directions. First, looking at native LPMO proteins to trap copper-oxygen intermediates and characterize them by advanced electron paramagnetic resonance methods. Techniques such as electron nuclear double resonance (ENDOR), electron spin echo envelope modulation (ESEEM) and hyperfine sublevel correlation (HYSCORE) spectroscopies allow for detailed insight into the copper center's electronic structure to be gained. From these techniques, coordinating ligands can be identified and their geometric structure along with their covalency. Isotopic labelling (^2H, ^{13}C, ^{15}N, ^{17}O, etc.) can further aid in the selectivity of these studies.

Heavy Main-Group Radical Characterization.

Working in close collaboration with chemistry research group of Prof. Stephan Schulz (UDE), the Cutsail MPRG performs and produces complete (advanced) EPR characterization of heavy Group-15 radicals. Previously, the Cutsail Group has characterized stable neutral arsenic,[1] antimony and bismuth radicals[2] stabilized with gallium ligands forming unique metal-metalloid bonds. The electropositive character of the Ga ligands allows for significant electron delocalization of the unpaired electron spin on the ligand. The heavy Group-15 radicals exhibit significant *g*-anisotropy due to large spin-orbit coupling, and complex resolved hyperfine splittings from the numerous NMR-active isotopes.

The multifrequency EPR characterization of these radicals has afforded high precision electronic and nuclear structural information. Recent electronic structure studies of novel neutral heteroleptic coordinated Sb radicals has revealed systematic control of the Sb radical electronics by tuning of the electronegativity of the coordinating ligand, Figure 2. We have shown that EPR spectroscopy is able to directly measure the stabilization of the unpaired electron in excellent agreement with other spectroscopic and analytical measurements.

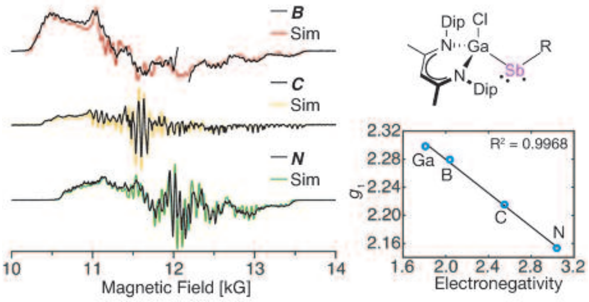

Figure 2. Q-band EPR of heteroleptic Sb radicals exhibiting dramatic shifts of the g_1 feature correlated to the ligand's electronegativity.

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Nanobased Heterogeneous Catalysts

Introduction

As an approach to utilize (sun)light for energy conversion reactions, heterogeneous photocatalysis has attracted lots of attention during the last decades because it bears potential to contribute to novel strategies in the sustainable energy sector and the fossil fuel phase-out. Unfortunately, despite years of considerable research effort, there has been no major breakthrough and today's highest reported yields of any photocatalytic energy conversion reaction are far away from any industrial relevance. A prominent example is the photocatalytic conversion of CO_2 which has first been reported in 1979.[1] Yet, the exact mechanism is still unknown and the formation rates of CH_4, one of the regularly observed main products, range from a few nmol g_{cat}^{-1} h^{-1} to an order of µmol g_{cat}^{-1} h^{-1}, depending on the catalyst. A possible explanation is that the reactions are highly complex and the heterogeneous catalysts have to fulfill several tasks, i.e. the absorption of photons and generation of charge carriers with sufficient redox potential, the separation and migration of the charge carriers to the catalyst surface and finally the exposure of suitable catalytically active sites.

The research in the Nanocat group is dedicated to contributing to a basic understanding of fundamental processes in heterogeneous photocatalysis. Of great interest are mechanistic studies on the photocatalytic conversion of gas phase CO_2 with H_2O to CH_4 over P25-TiO_2, one of the most prominent photocatalyst materials, consisting of titania particles in the nanosize range. As the conversion rates are very small, we use a high-purity photoreactor setup and employ a thorough in situ cleaning of the photocatalyst prior to a reaction to ensure reliable results without any potential contribution of impurities.

Within the second major research interest, we evaluate the feasibility of a thermochemical phase analysis of binary manganese oxides, including amorphous or nanocrystalline components, as part of the attempt to create a reliable reference database for the four fundamental binary bulk manganese oxides (MnO, Mn_3O_4, Mn_2O_3, MnO_2), complementing the MANGAN cluster project. Although increasingly complex manganese-based materials, e.g. birnessites and todorokites, have recently become very popular in general oxidation catalysis, including electrocatalysis and photocatalysis, only very few studies can be found on the fundamental thermodynamically stable binary manganese oxides. This makes a classification of any results from even the seemingly less complex binary oxides a difficult task. We utilized temperature programmed oxidation (TPO) and reduction (TPR) complemented by X-ray diffraction and Raman spectroscopy for a comprehensive phase analysis without beam damage which is often induced in these types of compounds. Furthermore, these techniques allow simple and quick phase analysis without the need for sophisticated methods, such as synchrotron-based techniques. To complete the set of reference data, we examined the performance of the samples in two common catalytic reactions, i.e. the total oxidation of CO to CO_2 and the partial oxidation of 2-propanol to acetone.

Development of a Tubular Continuous Flow Reactor

As the high-purity photoreactor generally used in our photocatalytic gas phase CO_2 reduction studies has a few limitations due to the overflow geometry (Figure 1. A), i.e. the lack of scalability and a rather moderate interaction between catalyst and reactants, we developed a tubular continuous flow reactor (Figure 1. B) to examine the effects of an improved gas-solid interaction in photocatalytic CO_2 reduction over P25-TiO_2 and test the scalability of this reaction in a feasibility study. This reactor consists of a fluorinated ethylene propylene (FEP) tube which can be varied in length, filled with the photocatalyst material and wrapped equidistantly around a self-built centered UV-LED light source. As anticipated, we were able to demonstrate a beneficial effect of an intensive gas-solid interaction in heterogeneous gas phase photocatalysis.[2] Although the FEP tube proved to be of limited suitability for upscaling due to critical O_2 diffu-

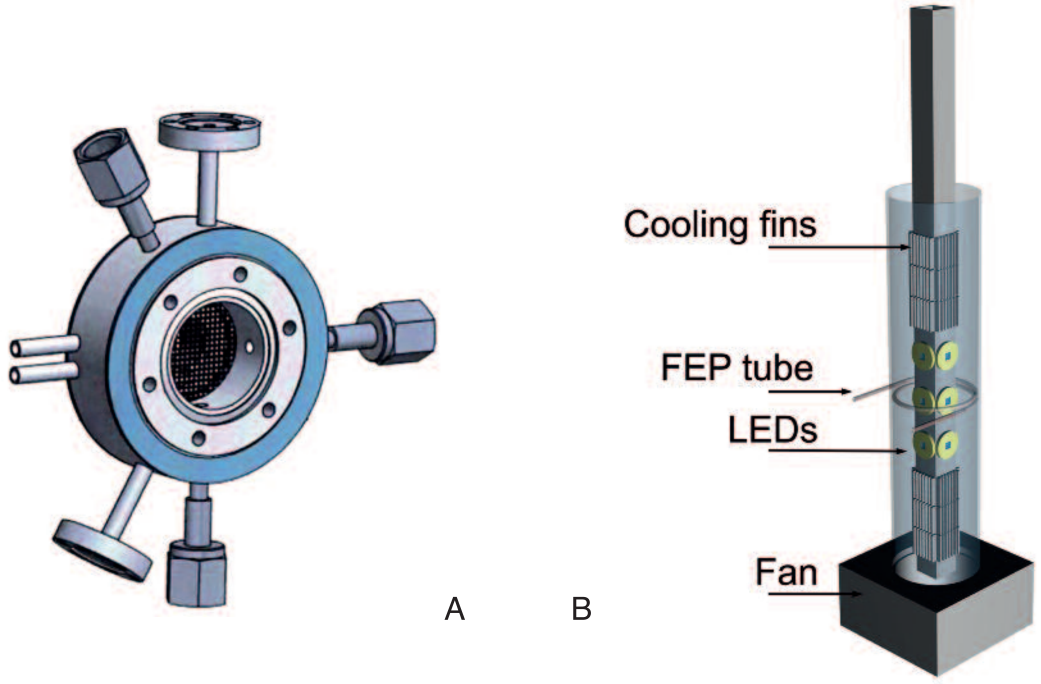

Figure 1. A) Illustration of the overflow reactor geometry; **B)** Illustration of the newly developed tubular continuous flow reactor.

sion properties (0.33 ppm cm^{-1}), this simple and in principle scalable reactor design might be an interesting choice for other photocatalytic gas phase reactions which are not as sensitive towards O_2 in the ppm range.

Understanding photocatalytic CO_2 reduction: The fate of oxygen and quantitative reactivity determinants

One of the major issues in the mechanistic understanding of the photocatalytic CO_2 reduction over TiO_2 is the unsolved fate of oxygen. Although the formation of the most regularly reported products CH_4, CO and CH_3OH from CO_2 presupposes the release of oxygen, even more so when utilizing H_2O oxidation as a source for H$^+$, it is in most cases either not regarded during product analysis or it cannot be detected at all. To understand the absence of oxygen as product, we modified P25-TiO_2 with IrO_x to improve the H_2O oxidation properties and were consequently able to observe the photoinduced formation of almost stoichiometric amounts of O_2 and H_2 from gas phase H_2O without using sacrificial agents. We found that a certain amount of O_2, similar to the amount missing in CO_2 reduction over pure P25-TiO_2, was consumed under reaction conditions. Corresponding CO_2 reduction experiments over IrO_x/P25 revealed that CH_4 formation from CO_2 is not possible when H_2 and O_2 are formed simultaneously.[3] Although all proposed elementary steps of water oxidation contain the formation of H$^+$, which is in turn favorably reduced to H_2 by photogenerated electrons, we were not able to see a formation of H_2 on pure P25-TiO_2. Based on these observations, it is questionable if H_2O can actually constitute the proton source in the overall CO_2 reduction with H_2O, while it is highly probably that the photocatalyst TiO_2 initially

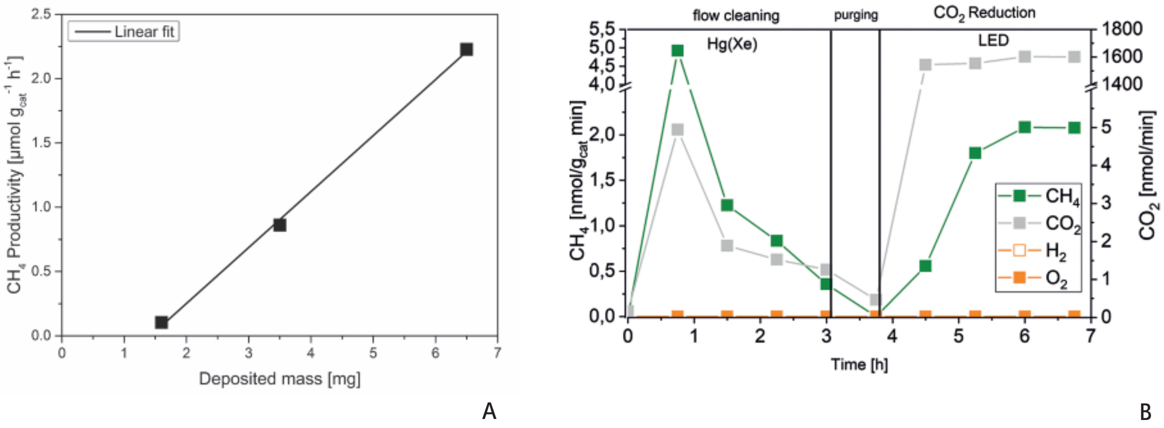

Figure 2. A) CH_4 productivity of different P25-TiO_2 films; **B)** Approximation of the AQY of P25 in photocatalytic CO_2 reduction: Removal of carbonaceous impurities with Hg(Xe) lamp (0 to 3 h), purging with He (3 to 3.75 h) without illumination. Photocatalytic CO_2 reduction with 2 W 365 nm LED (3.75 to 6.75 h).

consumes O_2 or O-derived species under reaction conditions, e.g. by replenishment of oxygen vacancies. This, in turn, implies that the light-induced formation of CH_4 from CO_2 over P25-TiO_2 is not based on a true catalytic cycle but a stoichiometric reaction.

To allow us a reliable conclusion on the applicability of P25-TiO_2 as photocatalyst material in the conversion of gas phase CO_2 to CH_4, we furthermore experimentally determined reactivity descriptors from heterogeneous catalysis (productivity) and photochemistry (apparent quantum yield) in cooperation with the group of Prof. J. Strunk at the Leibniz Institute for Catalysis in Rostock.[4] The highest observed productivity, estimated in batch mode from TiO_2 films of different thickness deposited on glass substrates (Figure 2 A), was 2.2 µmol CH_4 g_{cat}^{-1} h^{-1} for an average film thickness of 20 µm which is far below commercial viability. The apparent quantum yield (AQY), expressing the number of consumed charge carriers per incident photons, was determined from 50 mg P25-TiO_2 powder in continuous flow under steady methane formation conditions (Figure 2 B). The obtained AQY of 6.1×10^{-4} % demonstrates that the P25 exploits only a minute fraction of the incident light energy for the conversion of CO_2 to CH_4. When taking into account AQY values of thermodynamically less demanding photocatalytic reactions, it seems that although P25 is in principle able to function as photoabsorber it lacks the catalytic functionality for CO_2 reduction. Considering the overall results from our mechanistic studies on P25-TiO_2,[2-6] we believe it is safe to conclude that this material is not suitable as photocatalyst in the heterogeneous gas phase conversion of CO_2.

Fundamental studies on binary manganese oxides in oxidation catalysis

After refining the TPO and TPR parameters and conducting reference measurements on commercial binary manganese oxides in the highest available purity, we were able to verify the capability of these techniques to also identify nanocrystalline or amorphous manganese oxide phases. This was achieved by investigating samples of unknown MnO_x-composition prepared by the group of Prof. M. Behrens at the University Duisburg-Essen via precipitation of Mn(II)- and Mn(III)-acetate. The thermochemical characterization revealed that a sample which exhibited a powder diffraction pattern of pure, albeit only slightly crystalline Mn_3O_4 actually contained just 4.4 wt% crystalline Hausmannite, while the rest of the sample consisted of 12.6 wt% amorphous Mn^{2+} (MnO) and 83 wt% amorphous Mn^{3+}-species (Mn_2O_3).

The catalytic reference study, i.e. the total oxidation of CO to CO_2 and the partial oxidation of 2-propanol to acetone, was carried out with all four binary bulk oxides. For both reactions the apparent activation energies E_A were determined, as well as the reaction orders of CO, 2-propanol and O_2. The results imply that the higher valent manganese redox couple Mn(III) / Mn(IV) shows a higher activity in total oxidation reactions while the lower valent redox couple Mn(II) / Mn(III) is more suitable for selective oxidation reactions, e.g. 2-propanol oxidation to acetone.

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Synergistic Organometallic Catalysis

Starting date

01 September 2019.

Involved

Wei-Chieh CHANG (Ph.D. student, since February 2020), Carsten HINDEMITH (Laboratory assistant, since February 2020), Soumyashree JENA (Ph.D. student, since January 2020), Christophe WERLÉ (Max Planck Research Group Leader, since September 2019).

Background

Since modern society mainly relies on fossil fuels to provide either energy or basic chemical resources, aiming for sustainable energy or chemical industry systems before the depletion of fossil resources is necessary. Strategies, following the principles of *green chemistry,* are essential to this transition. In this context, catalysis still represents the most powerful methodology yet available to reduce the energy intensity of industrial chemical processes as well as their environmental burden, while simultaneously fulfilling the economic constraints dictated by the market and industrial production.

However, the quest for chemically efficient syntheses of valuable compounds with the recovery and reuse of catalysts, lower waste production, and minimal physical

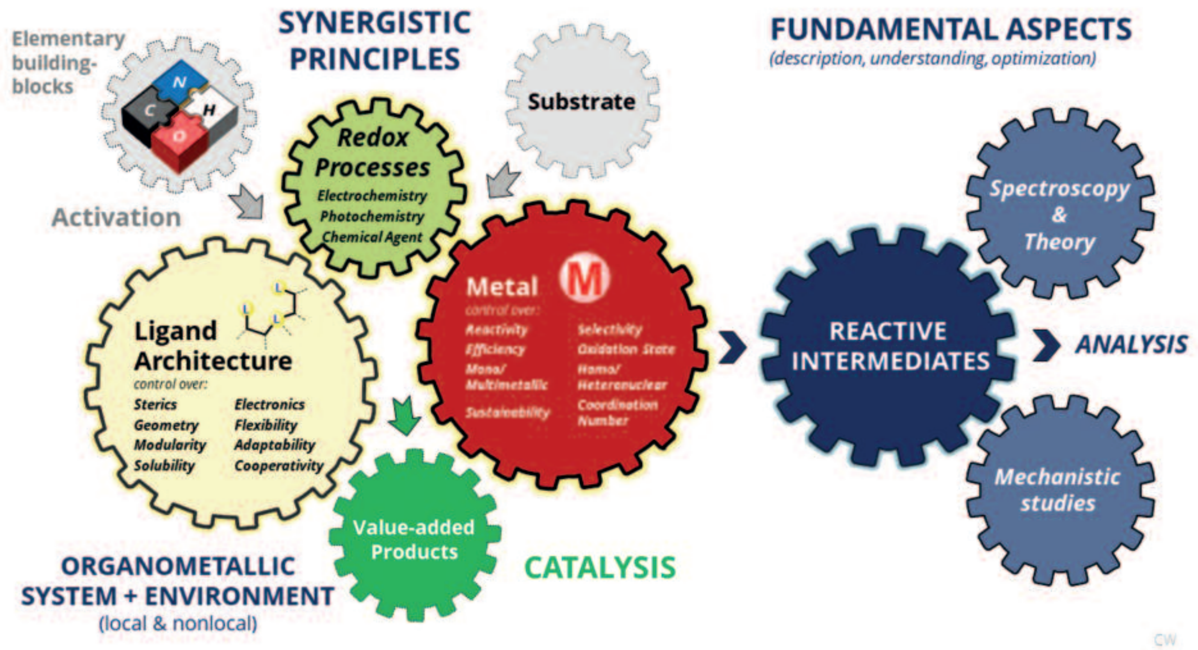

Figure 1. Synergistic Redox Catalysis – An intimate interplay between an organometallic system with its environment.

separations is a significant challenge for homogenous catalysis. In order to succeed, it is necessary to develop catalysts with optimum *selectivity*, *modularity, adaptability, efficiency,* and *sustainability*. Because of the variety of transformations, they can achieve, catalytic systems involving transition metals can play this role. In this approach, the spotlight is on the transition-metal itself – the reactivity takes place at the metal center. The ligands are considered “spectators” that remain unchanged throughout the catalyst lifetime. The steric and electronic properties of the ligands, however, do affect the properties of the catalyst. Furthermore, since the number of transition metal/ligand combinations is limited, a paradigm shift is necessary to design and develop more tunable catalysts for challenging transformations.

Objectives

The efficient and sustainable formation of C–C, C-N, C-O bonds, constitute an ongoing challenge in organic chemistry. Transition-metal catalysts have revolutionized the way such bonds are created. The popularity of these methods stems from the wide range of substrates and diversity of tolerated functional groups. Our group wants to push the boundaries further and develop greener alternatives in an atom economic way.

To succeed, we believe in the necessity of developing a knowledge-based systematic approach in the understanding and description of catalytic systems as function of their local and nonlocal environment. By this mean, new reactions and processes essential to convert the current energy systems into scalable, sustainable systems can be developed.

Our methodology encompasses everything from fundamental organometallic chemistry to the use of green energy to activate elementary building-blocks opening new pathways in the reliable syntheses of affordable and environmentally friendly fuels and base chemicals through what we call *Synergistic Redox Catalysis* (Figure 1).

Specifically, we target the elaboration, design, and development of synergistic organometallic systems capable of using green energy as the promotor to form carbon-carbon and carbon-heteroatom bonds between two synthetically challenging reaction partners, with an emphasis on late-stage C-H functionalization.

Our expertise resides in the synthesis of (multi-metallic) transition-metal complexes supported by novel ligand architectures and their characterization by both spectroscopy and computation.

We are particularly interested in the isolation and characterization of reactive intermediates present during catalysis. These transient species are the keys to understanding bond making and breaking reactions, allowing for further optimization of the catalytic cycles.

Future directions

Our research group aims to enlarge the potential of molecular catalysts. We believe that the synthetic protocols and the molecular insight from our work will encourage further investigations into the dynamic field of *synergistic catalysis*. More specifically, in the prospect of finding greener alternatives to existing catalytic methodologies, using sustainable energy.

Integration and future collaborations

Our research group is integrated into an interdisciplinary and international environment jointly between the Max Planck Institute for Chemical Energy Conversion and the Ruhr-University Bochum. We aim to pave the way for fruitful long-term collaborations between the two institutions. Initial forays are currently ongoing with Prof. Dr. Wolfgang Schuhmann (Lehrstuhl für Analytische Chemie; Ruhr-University Bochum), a worldwide-recognized expert in fundamental and applied electrochemistry.

Funding and acknowledgments

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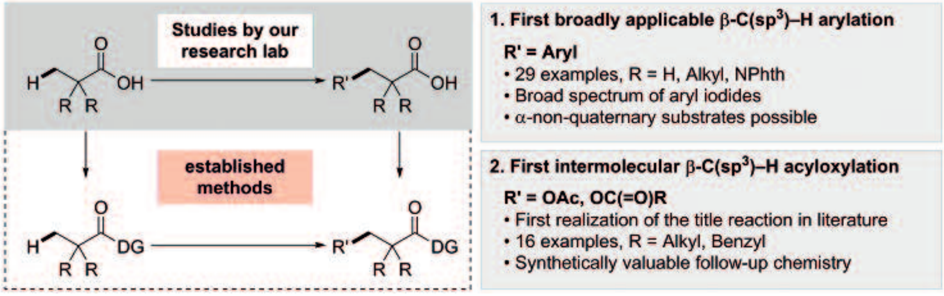
Introduction

Organic molecules have played a central role in many of the scientific advances that have so dramatically improved our quality of life and life expectancy over the last centuries. It is thus not surprising that a variety of scientific disciplines studies and employs such molecules in many different contexts from life sciences to engineering. As a consequence, the advance in these research fields is intimately linked to the availability of organic molecules with an ever growing degree of complexity. This implies that basic research towards the synthesis of compounds that would otherwise be challenging or even impossible to prepare bears the potential to stimulate important advances across all those disciplines that require such organic molecules. To this end, the van Gemmeren research lab uses transition metal catalysis as a key technology, especially methods for the activation and subsequent functionalization of C–H bonds. These methods inherently offer the opportunity to shorten synthetic routs and avoid waste production, but remain challenging due to the high chemical stability of C–H bonds and the large number of chemically distinct C–H bonds present in a typical organic molecule. These aspects impose particular demands with respect to reactivity and selectivity to the catalysts utilized. The most well established strategy to this end is the use of directing groups (DGs), which bind the catalyst before the C–H activation step that thus becomes intramolecular. This reduces the activation barrier and controls the regioselectivity of the process. The use of DGs has over the last decades enabled a large number of highly useful transformations, but also bears inherent disadvantages. Most notably, many DGs do not occur naturally in the substrate and therefore have to be introduced and removed, such that the potential of C–H activations to shorten syntheses is not fully exploited. In the research group Catalyst Controlled Selective Transformations and Ligand Design" we investigate catalysts aimed to realize the full potential of C–H activation technologies by using native functional groups as DG or achieving C–H activation without the need for DGs.

The Direct C(sp^3)–H Activation/ Functionalization of Carboxylic Acids

The functionalization of aliphatic carboxylic acids is highly attractive due to the ubiquity of these compounds in biologically active molecules and as synthetic intermediates. Since the use of free carboxylic acids as DGs is highly challenging,[1,2] the majority of established protocols has relied on the introduction of stronger exogenous DGs. Over the last years we have pioneered the development of ligand-enabled catalyst systems that allow for the use of the free carboxylic acid in C–H activation. Our first study in this field allowed us to report the first broadly applicable method for the β-C(sp^3)–H arylation of aliphatic carboxylic acids (Scheme 1).[3] In contrast to all previous studies, α-non-quaternary substrates could be used without requiring an excess of the carboxylic acid substrate. This advance was



Scheme 1. Methods for the direct C(sp^3)–H Activation/Functionalization of Carboxylic Acids.

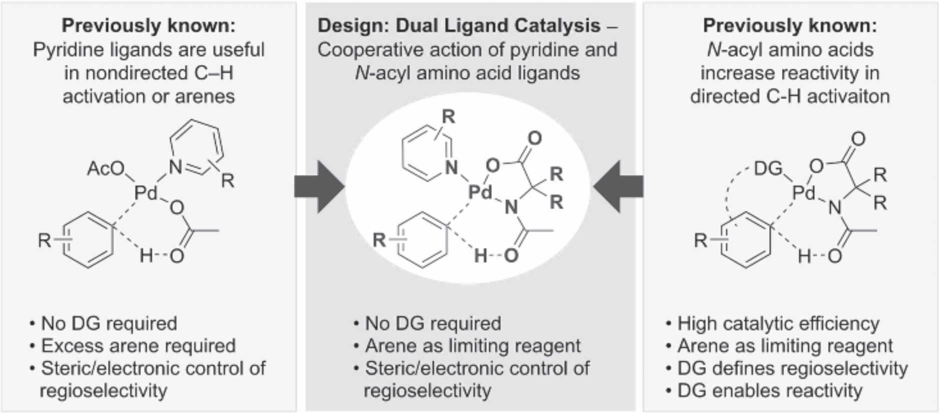


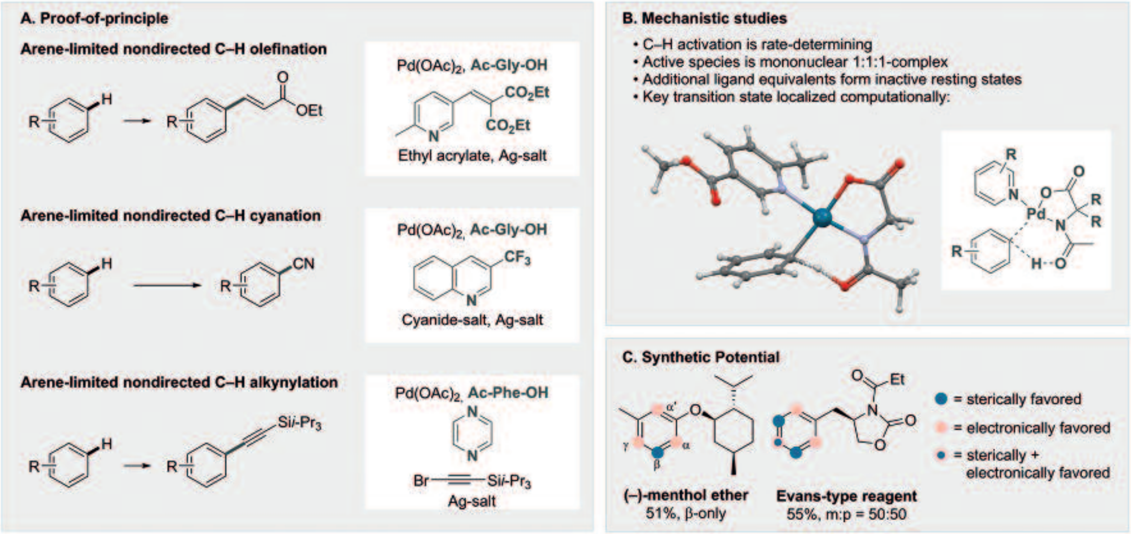
Figure 1. Design of dual ligand-enabled catalysts for nondirected C–H activation.

enabled by the identification of *N*-acetyl-β-alanine as suitable ligand. In a second study, we could recently achieve the first intermolecular C–H acyloxylation of free carboxylic acids.[4] In this case, the careful control of anions and Lewis acids present in the reaction mixture was found to be the key to success. We discovered that using the sodium-salt of our solvent hexafluoro-*iso*-propanol as a "traceless" base enabled the desired reaction. The utility of this protocol was further demonstrated by converting the products obtained into otherwise challenging to obtain 1,4-dioxygenated compounds.

The Nondirected C(sp^2)–H Activation/ Functionalization of Arenes

Although palladium-catalyzed C–H activations of arenes without the use of directing groups were known for a long time, such reactions were studied much less than related reactions with DGs. For a long time it was only possible to induce such reactions when a large excess of the arene substrate – typically as solvent – was employed, which limited the synthetic utility of nondirected C–H activations by palladium.[5] The van Gemmeren research group studies palladium catalyzed reactions aiming at the use of the arene substrate as the limiting reagent. Building upon the established use of pyridine-type ligands in nondirected C–H activations and the use of *N*-acyl-amino acid ligands in directed C–H activations, we hypothesized that the complementary use of both ligand classes could enable such a reactivity (Figure 1).

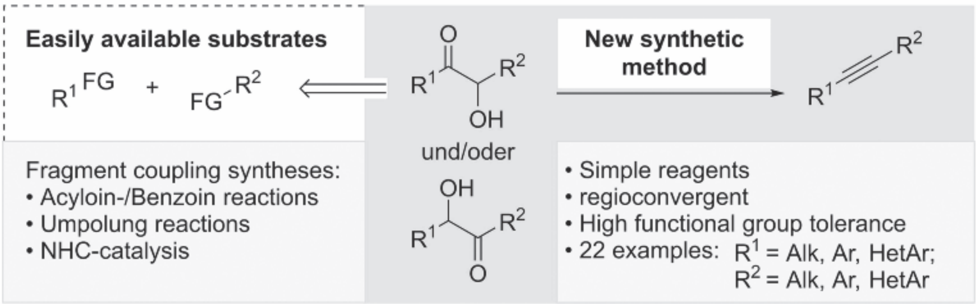
Based on this design principle, we could already develop several highly useful transformations. In our proof-of-principle publication, we succeeded in conducting the oxidative olefination in an arene-limited fashion for the first time since the discovery of this reaction by Fujiwara and Moritani in 1967 (Scheme 2). The use of the arene as limiting reagent renders this reaction attractive in the context of late-stage modification.[6] In a further application of our catalyst design, we have developed a direct C–H cyanation of arenes.[7] A third application, the inverse Sonogashira reaction using our catalysts, which proceeds with steric control of the regioselectivity, is submitted for publication.[8] Finally, we are currently preparing a manuscript for submission, in which we will report extensive mechanistic studies on our catalyst system.



Scheme 2. The Nondirected C(sp^2)–H Activation/Functionalization of Arenes.

Methods for the Synthesis of Alkynes and Olefins

Alkynes and Olefins are central functionalities in a plethora of organic molecules. In this context, we are interested in developing novel synthetic approaches towards such molecules, in which they can be accessed from other starting materials then the ones required by previous methods, thereby allowing novel strategies in synthesis planning. We have recently developed a method that converts acyloins directly into internal alkynes (Scheme 3). [9] The protocol exclusively relies on simple, commercially available reagents and is suitable for the generation of otherwise challenging to access substitution patterns. The practical utility of this method becomes apparent when considering the large number of methods available for the synthesis of acyloins, many of which build the central C–C bond. Overall, we have thus enabled a two-step synthesis of internal alkynes, in which the central bond is built up *de* novo from two fragments.



Scheme 3. New Synthetic Method for the Direct Conversion of Acyloins into Alkynes.

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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 Bin Hu was recruited as doctoral student in June 2016. Currently, the group consists of three PhD students (Daniel Waffel: VCI/Fonds scholarship, Julia Büker: scholarship of Evonik Stiftung) and one postdoc (Dr. Guixia Zhao: Humboldt research fellowship). In addition, Weiwen Dong had contributed funded by the IMPRS-SurMat, who received her PhD in 2016. Scientifically, the Max Planck Fellow group performs fundamental research in the area of heterogeneous thermal redox and photoredox 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. Heterogeneous catalysts usually consist of many phases and components, often present as nanoparticles or as X-ray amorphous layers on bulk supports. For many catalysts the chemical reactivity of supported metallic or oxidic nanoparticles is influenced by strong interactions with the support.

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 glycerol, phenol and 5-hydroxymethylfurfural (HMF), whereas oxidation catalysis comprises the selective oxidation of alcohols and the challenging C-H bond activation of hydrocarbons. Photoredox catalysis mainly focuses on the selective anaerobic oxidation of alcohols under visible light. 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 (photo)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

First, the hydrodeoxygenation (HDO) of glycerol was systematically studied over a series of co-precipitated Cu/ZrO_2 catalysts at 200 °C and 25 bar H_2 pressure [1]. These catalysts exhibited high activity and selectivity of 95% for the terminal C-O bond cleavage to 1,2-propanediol while preserving the C-C bonds. The reaction was found to occur through the dehydration of glycerol to acetol followed by its hydrogenation to 1,2-propanediol. The conversion of glycerol was observed to be linearly correlated with the specific copper surface area (Figure 1, left), suggesting metallic copper is the active site. The apparent activation energies amounting to 106 and 105 kJ mol^{-1} for Cu/ZrO_2 and pure metallic Cu, respectively, of the HDO pathway provide further evidence for metallic Cu acting as the active site [2]. Hydrogen was assumed to be not only required for the fast hydrogenation of the intermediate acetol, but also for the removal of adsorbed atomic oxygen originating from water dissociation to create empty sites for dissociative glycerol adsorption.

Furthermore, the selective hydrogenation of HMF and phenol was investigated over Pd nanoparticles supported on N-doped mesoporous carbon and on carbon nanotubes. By means of a systematic comparison it was found that N-doping not only enhances their catalytic activity but also increases catalyst stability and product selectivities. For example, the selective hydrogenation of phenol

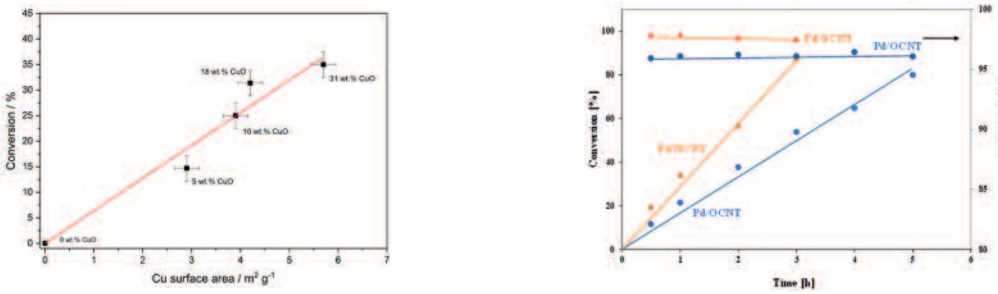

Figure 1. Correlation of glycerol conversion with the specific Cu surface area (left); Comparison of phenol hydrogenation over Pd/NCNT and Pd/OCNT at 60 ᵒC and 1 bar H_2 (right).

to cyclohexanone was compared over Pd/NCNT and Pd/OCNT using H_2 or formic acid as hydrogen donor at 60 ᵒC. In the presence of H_2, the reaction rate over Pd/NCNT was almost 2 times larger than that over Pd/OCNT (Figure 1, right). When using formic acid as hydrogen donor, the N-doping effect was even more significant leading to a 5-fold increase in phenol conversion. Separate decomposition experiments revealed that formic acid decomposed not only to CO_2 and H_2 but also to CO over Pd/OCNT causing the deactivation of the catalyst.

Catalytic Oxidation

Oxidation reactions are investigated with molecular oxygen as the preferred oxidant as well as with alternative oxidants such as hydrogen peroxide and *tert*-butyl hydroperoxide (TBHP) as oxygen donor. Employed catalysts include mixed transition metal-based spinel and perovskite oxides, metal-organic frameworks (MOFs) and noble metal-based catalysts such as Au-Pd/CNTs. 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 (i.e., alcohols like 2-propanol, benzyl alcohol and cinnamyl alcohol, olefins like styrene and cyclohexene, and aromatic hydrocarbons like toluene) and the oxidant (i.e., O_2 vs. peroxide such as H_2O_2 and TBHP).

Spinel and perovskite oxides are frequently applied in high-temperature gas-phase oxidation reactions because of their high structural stability and chemical versatility, whereas their application in liquid-phase oxidation reactions under mild conditions has been rarely reported. We aim at obtaining a comprehensive basic understanding of the processes at the solid-liquid interface for metal oxide catalyzed oxidation reactions within the SFB/TRR 247. The SFB 247 consists of three research areas: synthesis, analysis and catalysis. The core of the SFB is a comparative study, that is, well-characterized catalysts are applied and systematically compared in thermal, electro-, and photocatalysis. The comparative study will deliver generic reactivity trends that allow the establishment and validation of (real) structure–activity–correlations. In our subproject A1, our goal is to deliver activity and selectivity patterns in a reaction matrix of thermal catalysis. Samples are provided by the groups of Malte Behrens, Stephan Schulz and Christof Schulz at the University of Duisburg-Essen as well as by Harun Tüysüz group at the MPI für Kohlenforschung, whereas in-depth characterization is performed at the MPI CEC.

A series of $Co_{1+x}Fe_{2-x}O_4$ spinel oxides was synthesized using SBA-15 as hard template. The $Co_{1+x}Fe_{2-x}O_4$ samples were first applied in the aerobic oxidation of 2-propanol at 160 °C in the liquid phase (Figure 2, left). The reaction rate increased significantly with increasing Co content, suggesting Co ions are the active site. Kinetic studies over Co_3O_4 revealed an apparent activation energy of 94 kJ mol^{-1} and reaction orders of 0 and 0.7 for O_2 and 2-pro-

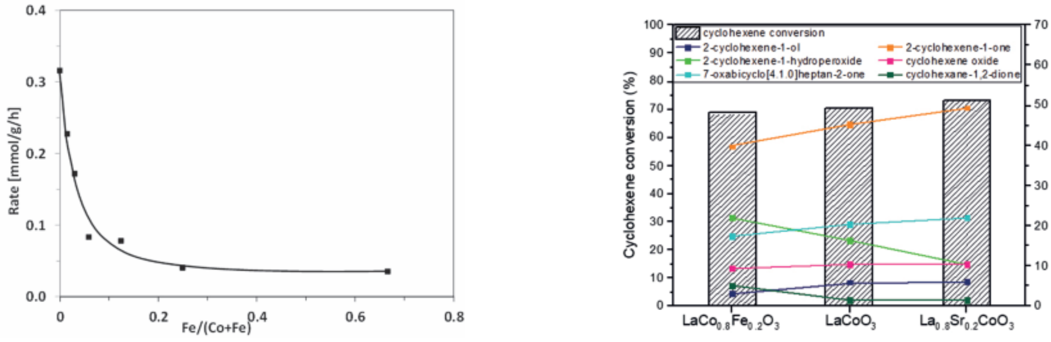

Figure 2. Effect of Fe/(Co+Fe) ratio in $Co_{1+x}Fe_{2-x}O_4$ on the reaction rate for 2-propanol oxidation at 160 °C and 5 bar O_2 **(left)**; Influence of Fe and Sr substitution in $La_{1-x}Sr_xCo_{1-y}Fe_yO_3$ on cyclohexene oxidation at 80 °C and 10 bar O_2 **(right)**.

panol, respectively. Similarly, synergistic effects between Co and Fe for the aerobic oxidations of benzyl alcohol, cinnamyl alcohol and styrene were not observed, while a low content of Fe doping was found to be beneficial for the oxidation reaction using TBHP as oxidant. In addition, two series of $La_{1-x}Sr_xCo_{1-y}Fe_yO_3$ perovskite oxides were synthesized by flame-spray synthesis [3]. The $La_{1-x}Sr_xCo_{1-y}Fe_yO_3$ perovskite oxides were tested for the aerobic oxidation of cyclohexene at 80 °C and 10 bar (Figure 2, right). The incorporation of Fe at the B site of $LaCo_{1-y}Fe_yO_3$ (y=0.2, 0.3, 0.4) showed no benefit in terms of cyclohexene conversion and product selectivity. The hydroperoxide decomposition was even inhibited. On the contrary, the substitution of Sr at the A site of the perovskite $La_{1-x}Sr_xCoO_3$ (x=0.1, 0.2) revealed an increased cyclohexene conversion which points to the presence of more oxygen vacancies on the catalyst surface. Furthermore, the enhanced hydroperoxide decomposition resulted in a higher selectivity to the main product 2-cyclohexene-1-one, whereas the remaining product selectivity was stable.

MOFs were also synthesized and applied in the aerobic oxidation of alcohols. On the one hand, we successfully synthesized CuPd mixed-metal HKUST-1 featuring Cu–Pd and/or Pd–Pd dimers via incorporation of Pd^{2+} into the pristine Cu-MOF by using a novel two-step synthesis [4]. The CuPd-MOFs were systematically characterized, and the results demonstrate consistently that the metal-node engineering occurs via introduction of Pd in a controlled fashion yielding mixed-metal HKUST-1 with a homogeneous distribution of Pd and Cu cations while retaining the structural integrity. These CuPd-MOFs exhibit superior activity and selectivity for the aerobic oxidation of benzyl alcohol to benzaldehyde, and the highly dispersed Pd^{2+}–cus sites are identified as isolated single active sites. On the other hand, a series of novel Pd-NPs@DE-HKUST-1(Cu/Pd) catalysts containing both micro- and mesopores through the incorporation of the defect-generating linker 2,6-pyridyldicarboxylate (pydc) was synthesized [5]. The Pd NPs were formed by partial reduction of the Pd^{2+} sites of the pristine mixed-metal DE-HKUST-1(Cu/Pd) with methanol. The size regime and the spatial distribution of the Pd NPs was controlled by the amount of framework-incorporated pydc. The samples exhibit superior catalytic activity in the aerobic oxidation of cinnamyl alcohol as compared to the parent HKUST-1.

The aerobic oxidation of toluene was performed over a series of supported Au-Pd nanoparticles on different CNTs at 190 °C and 10 bar O_2. Au was not active for this reaction, but the addition of Pd significantly enhanced the conversion, demonstrating a clear synergistic effect for the Au-Pd catalysts as compared with the monometallic species. Strong support effects for Au-Pd/CNTs were observed following the order of CKCNT (KOH and steam co-treated CNTs [6]) > NCNT > OCNT. Mechanistic studies revealed that the reaction proceeds via a free radical mechanism. The reaction was retarded at a conversion of < 10%, and the main reason was found to be the formation of 2-methylquinone, which is a radical scavenger.

In addition to these batch reactions, a continuous-flow microreactor with segmented flow, having many advantages like higher interfacial area, better mass / heat transfer, safe and easy operation, has been also utilized for systematic kinetic studies. For example, the turnover frequency for benzyl alcohol oxidation was found to be 3-5 times larger in the continuous-flow reactor than that in the batch reactor due to the improved mass transfer.

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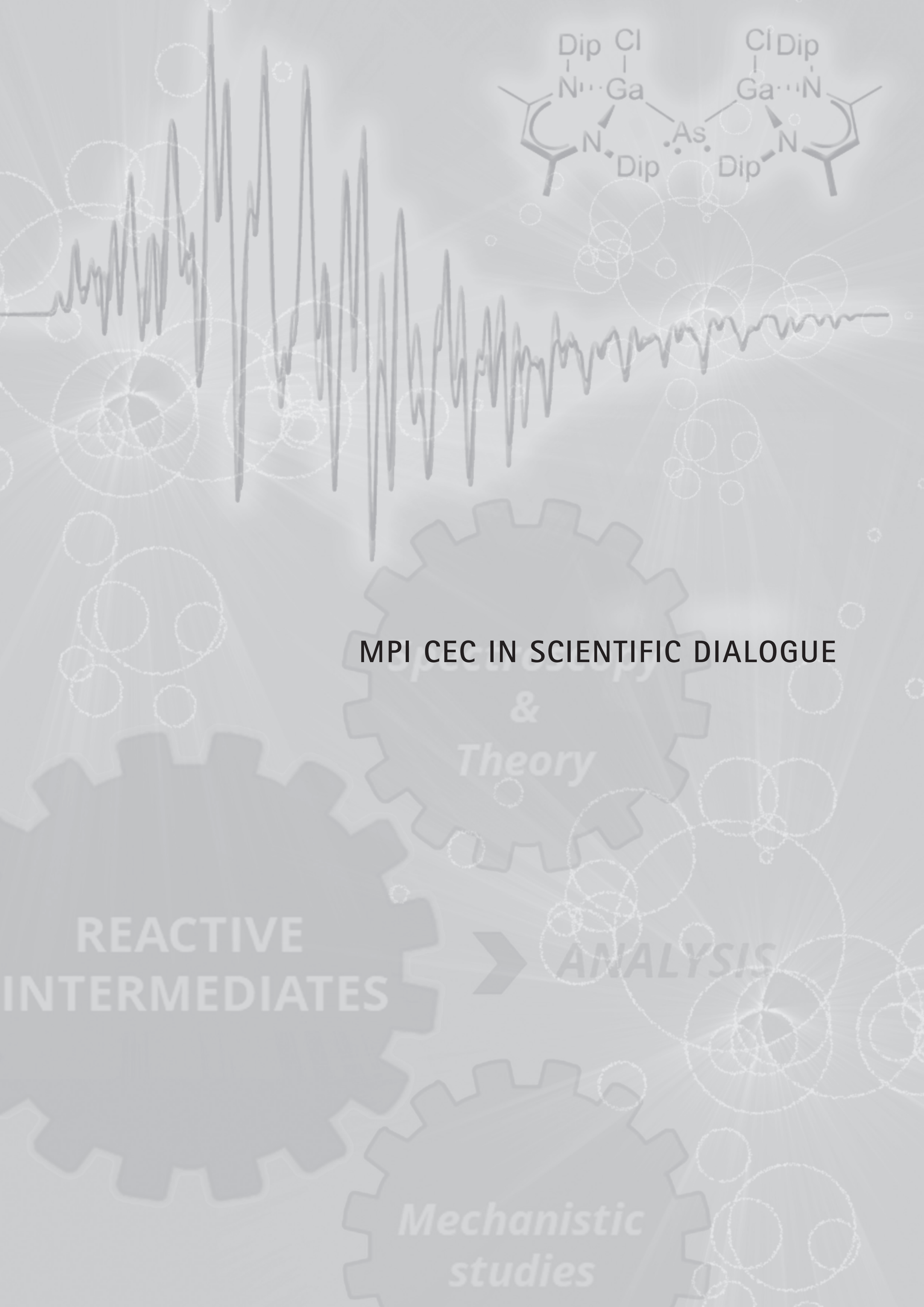
MPI CEC IN SCIENTIFIC DIALOGUE



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; support codes 03EK3037 to 03EK3043) and contains 7 subprojects with 18 partners in total from industry and academia (Figure 1). Included in the project are also two kind of laboratories for the partners of all subproject: 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 cleaned up and provided for proof of concept investigations.

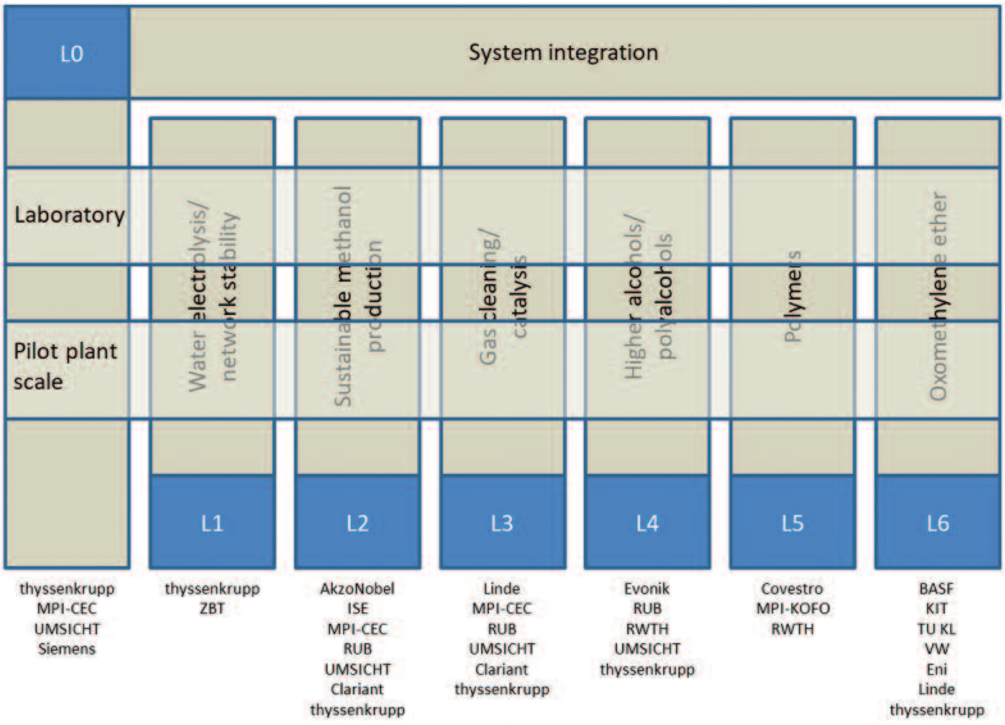


Figure 1. Structure of the Carbon2Chem® project including subprojects and participating partners.

The main tasks of the MPI CEC within the project are building up a special Carbon2Chem® laboratory in collaboration with Fraunhofer Institute UMSICHT and its operation (L0), characterization of the three metallurgical gases (coke oven gas, blast furnace gas and basic oxygen furnace) (L0) as well as the materials used for gas cleaning (L3) and studies on methanol synthesis (L2). This work is located in the Catalytic Technology group.

Carbon2Chem® Laboratory

From the two laboratories, which are operated within in the project, MPI CEC is - in collaboration with Fraunhofer UMSICHT - responsible for the general laboratory including building up the required infrastructure and operation of the lab. 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. 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 gas mixing system is given in Figure 2. 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 in subsequent flow set-ups also with complex gas mixtures instead of the usually investigated one chosen component.

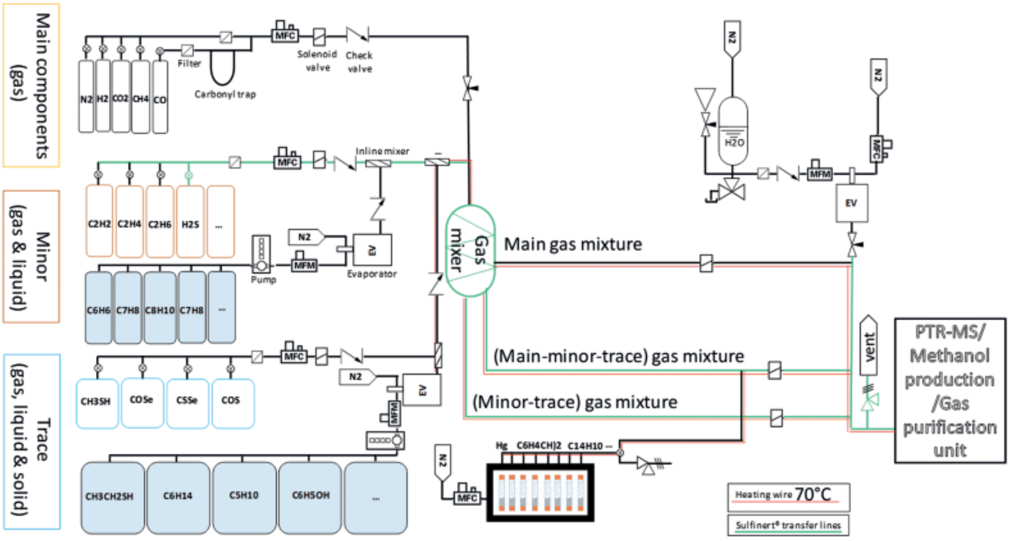


Figure 2. Scheme of the gas mixing system.

Gas Analysis

The activities regarding gas analysis focused on the design and construction of two containers (Lab-container and supply-container, Figure 3) for the online and on-site characterization of trace compounds, the so-called VOCs (Volatile Organic Compounds), in the three metallurgical gases at the steel mill plant of the company Thyssen Krupp Steel Europe in Duisburg. The characterization of these VOCs 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 of the gas-cleaning unit. For the characterization of trace compounds a high-end process mass spectrometer, the so-called Proton-Transfer-Reaction Quadrupole interface Time-Of-Flight Mass Spectrometer (PTR-QiTOF-MS) was used [2].

This mass spectrometer was a prototype and, therefore, the whole method development had to be adapted to the analysis of industrial gases, since up to date this technique had found mainly application in the determination of VOCs in air and environmental science. As before analysis a strong dilution with nitrogen was compulsory due to saturation of the detector of the PTR-QiTOF-MS, possible gas impurities even in the purest gas available (nitrogen 6.0, 99.9999% purity) could be present and

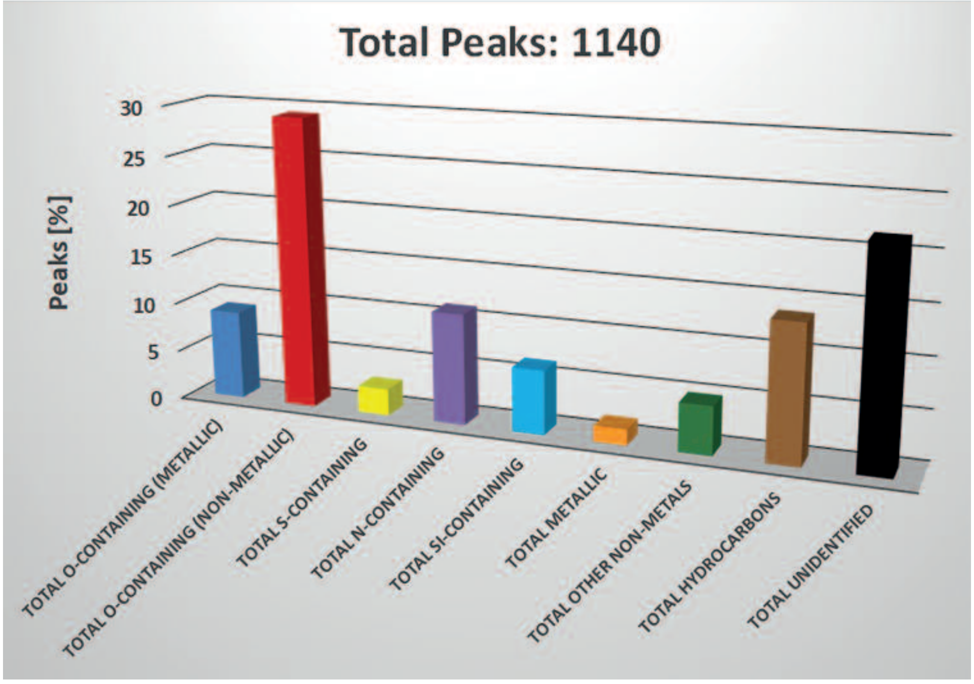


Figure 3. Total number of peaks identified in nitrogen 5.0 under dry conditions using H_3O^+ as primary ion.

lead to misestimations, which have a big impact on the design of required purification systems. It was found that the normal procedure of subtracting the background from the sample measurement in PTR-instruments would lead to wrong estimations, because the background shows a humidity dependency [3]. Furthermore, a total of 1140 peaks were identified in the mass spectrum of nitrogen 5.0 where around 80% could be assigned (Figure 3). Nevertheless, even if those remain unidentified with the method introduced, it still can be established if a peak is an instrument artefact or a gas impurity. Besides the characterization of the real gases, further optimization is performed with the gas mixing system in the Carbon2Chem® lab. With this single compounds or complex gas mixtures are investigated, so that the substances found in the HüGaProp-Container in the three 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. Based on this a database of mass spectra under dry and humid conditions is built up.

Methanol synthesis

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 [4]. In principle, two basic scenarios for the utilization of the steel mill exhaust gases are possible (Figure 4). 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 cleaning 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. This subproject within Carbon2Chem® addresses these two important questions and is investigating the influence of trace compounds as well as intermitting conditions on the stability of the catalyst.

Actual results show, that small amounts of nitrogen compounds as well as oxygen only act as reversible poisons. On the other hand, long-term measurements with 500 ppm oxygen in the synthesis gas lead to an increased deactivation of the catalyst. 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.

Based on this, a judgement on the catalyst lifetime with respect to concentrations of trace components will be possible. Additional investigations on the impact of intermitting conditions during methanol synthesis showed an unexpected high stability of the catalyst under these conditions. 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.

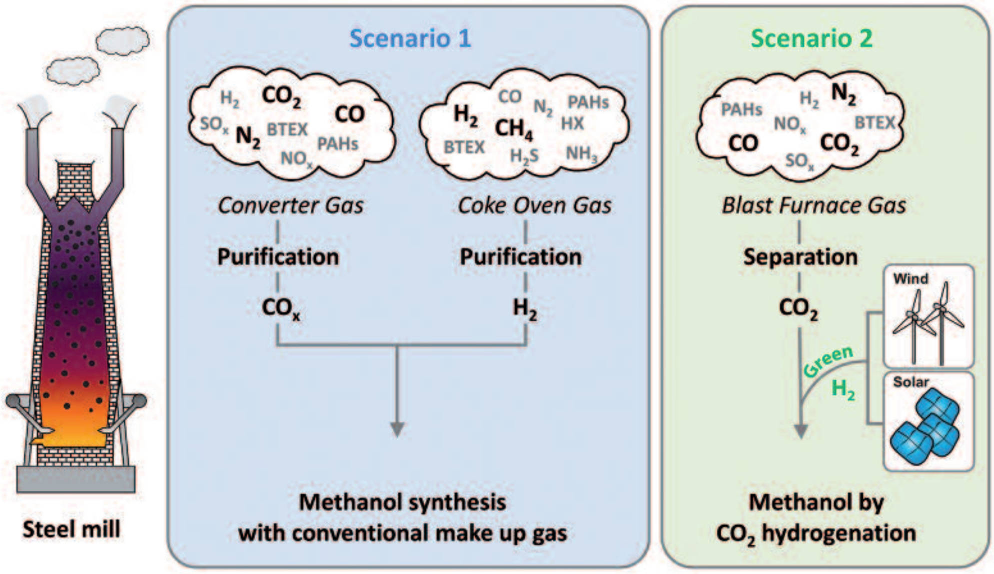


Figure 4. Possible utilization of steel mill exhaust gases to synthesize methanol. Purification and blending of coke oven gas and basic oxygen furnace gas (scenario 1) or CO_2 separation of blast furnace gas in combination with sustainably produced H_2 (scenario 2) [4].

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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 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.

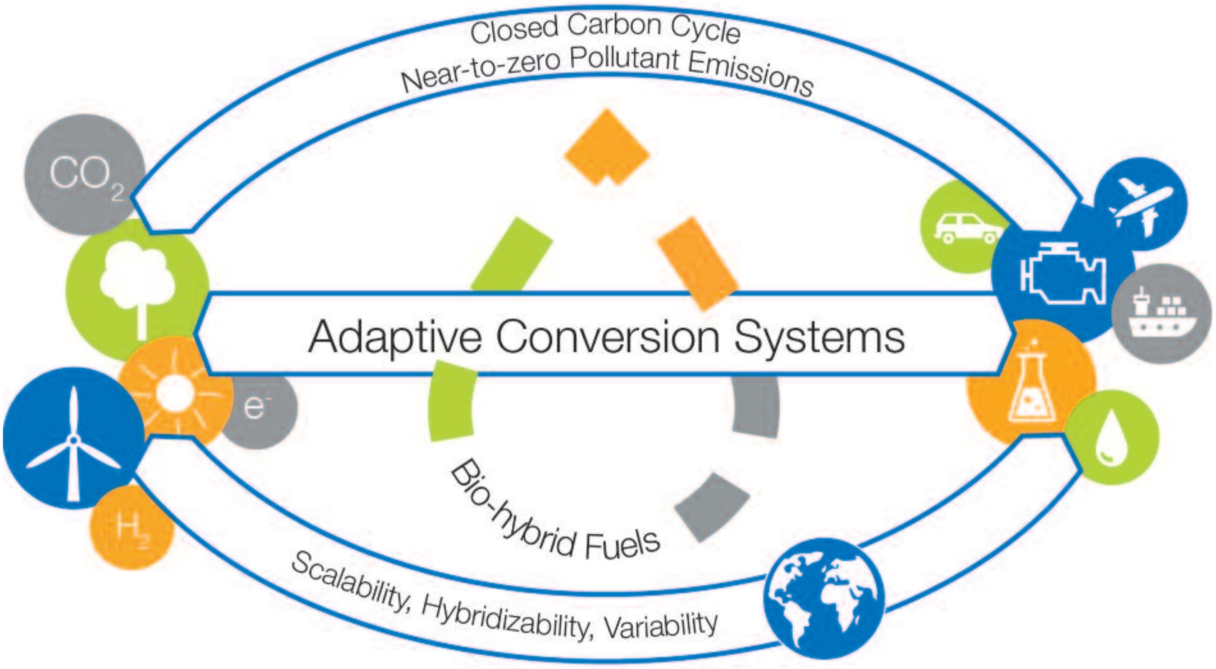
In order to enable highly efficient and clean combustion for sustainable mobility, fundamental knowledge and scientific methods are generated as basis for the development of adaptive production and propulsion systems based on renewable energy and alternative carbon sources under dynamic boundary conditions. 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 to changes in the mobility sector.

Research towards future fuels and their production of the FSC 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 taken into account in order to design flexible and economic value chains. For the reconversion of chemically stored energy, emission-minimised, molecularly controlled combustion systems are investigated. 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 FSC span between two dimensions: the 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 University and non-University academic landscape is reflected scientifically as well as structurally. Further groups involved at the MCC are the departments of Profs. Schlögl and Schüth. One strategic measure of FSC is the development of joint career paths between the partners. In this context, a MPG Research Group of the CEC is established in the field "*Magnetic Resonance for Catalysis and Materials*" in Aachen with a tenure track option for a chaired W3 professorship at RWTH Aachen University (recruitment process ongoing).



CLUSTERS OF EXCELLENCE

E-CONVERSION

Fundamentals of Energy Conversion Processes

Maxime Boniface, Katharina Krischer, Barbara Lechner, Hubert Gasteiger, Roland Fischer, Ian Sharp, Axel Knop-Gericke, Thomas Lunkenbein, Robert Schlögl

The Max Planck Institute of Chemical Energy Conversion (MPI CEC) represented by the Department of Heterogeneous Reactions is an associated partner of the cluster of excellence "e-conversion". This cluster was jointly initiated by the Technical University (TUM) and the Ludwig Maximillian University (LMU) of Munich. During the funding period of this excellence initiative extensive knowledge-transfer between the universities and associated partner institutes exists. In general, the cluster tackles the complementary investigations of solid-solid and solid-liquid interfaces that are involved in processes related to efficient energy conversion, such as photovoltaics, electrocatalysis and batteries. As such it focuses on establishing a sound understanding on recombination, overpotential and resistivity and their effect on the performance of functional materials on the micro- and nanoscale. The MPI CEC supports this cluster by its expertise in operando X-ray spectroscopy and electron microscopy.

The MPI CEC participates in the characterization of strong-metal support interaction (SMSI). For supported metal nanoparticles, the SMSI effect is expressed by embedding these nanoparticles by a partially reducible support during reductive activation. In electrochemical processes this overgrowth can enhance the selectivity towards the hydrogen oxidation reaction (HOR) compared to nanoparticles that are, for instance, directly supported on the carbon electrode. A superior HOR selectivity on the anode side would be desirable during startup or shutdown in order to avoid the oxygen reduction reaction (ORR) that would immediately lead to the degradation of the adjacent carbon electrode. As the concept of SMSI is well-established for gas-phase reactions almost nothing is known on its formation in liquid phase reactions.

The MPI CEC and research groups of the Munich universities aim to unravel details on the formation mechanism of the SMSI state in the liquid phase by operando X-ray spectroscopy and electron microscopy using supported Pt nanoparticles in a stepwise project outline. In particular, this study tries to identify particle size and support effects. First, a reference system has to be established that allows to study the SMSI formation in the gas phase. At this stage the deposition method of monodisperse nanoparticles as well as oxidic supports of variable nature onto the substrates used for the operando measurements should be developed. For the deposition of monodisperse particles different techniques will be studied such as sputtering, soft landing and deposition from the liquid phase (TUM). It has to be verified to which extent the operando substrates can be decorated with thin films of reducible and non-reducible oxides (Al_2O_3,TiO_2, ZnO) by atomic layer deposition (ALD; TUM) while the coverage of the electrical contacts should be avoided (Figure 1). Second, the particle size and support dependency of SMSI will be studied in the presence of H_2 and H_2/H_2O gas mixtures. The obtained results may act as a reference. Third, the study will be transferred to the liquid phase using a home built electrochemical cell for electron microscopy and X-ray spectroscopy. In addition, a home built quasi in situ electrochemical cell will help to bridge the resolution limitation of electron microscopic investigations in condensed matter.

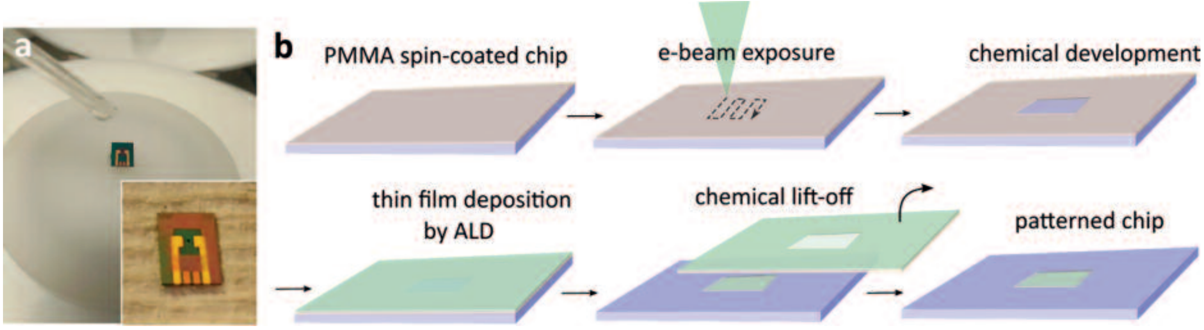


Figure 1. a) Photograph of an in-situ chip prior to PMMA coating. **b)** E-beam lithography workflow.

COLLABORATIVE RESEARCH CENTRE

CRC/TRANSREGIO 247

Heterogeneous Oxidation Catalysis in the Liquid Phase

The Collaborative Research Center (CRC) 247 is a joint research institution of the University Duisburg-Essen, Ruhr-Universität Bochum, the Fritz Haber Institute of the Max Planck Society, the Max Planck Institute (MPI) for Kohlenforschung, and the MPI of Chemical Energy Conversion. As such, it promises to deliver a sound understanding of heterogeneous oxidation reactions in the liquid phase. In comparative studies involving multinary spinels and perovskites, catalytically relevant features shall be identified that are common for photo-, electro-, and thermal catalysis. To master the complexity of this challenge, a broad portfolio of complementary local and integral techniques are being applied by different groups that deliver insights into relevant structural arrangements beyond the ideal crystal structure and related metastability. In addition, a dedicated pool of operando techniques will unravel the presence of reaction induced chemical dynamics in the temperature regime below 200 °C. Subsequently, the obtained results will be correlated to theory to obtain a realistic model of liquid-phase oxidation reactions. The CRC 247 is built on three hypotheses:

(1) Structural features beyond the ideal crystal structure (i.e. real structures) can be correlated with catalytic activity.
(2) By combing theory and operando techniques the nature and evolution of the working catalysts can be determined.
(3) The systematic combination of photo-, electro-, and thermal catalysis delivers trends that can be used to decipher relevant elementary steps and the full reaction mechanism.

The departments of Heterogeneous Reactions and Inorganic Spectroscopy of the MPI Chemical Energy Conversion, as well as the department of Molecular Theory and Spectroscopy of the MPI Kohlenforschung are part of the analytical section within the CRC 247 and tackle in close collaboration important structural (operando) analysis conducted by electron microscopy, X-ray spectroscopy, and theoretical modelling. Their individual contributions to the CRC 247 are part of this report.

Advanced TEM and in situ X-ray Spectroscopy – Department of Heterogeneous Reactions/CEC

Thomas Götsch, Franz-Philipp Schmidt,
Alexander Klyushin, Axel Knop-Gericke,
Thomas Lunkenbein, Robert Schlögl

Within the CRC 247, the department of Heterogeneous Reactions of the MPI Chemical Energy Conversion is focusing on complementary advanced transmission electron microscopy (TEM) and in situ X-ray photoelectron spectroscopy (XPS) studies of spinel- and perovskite-type catalysts in order to untangle their real and working structures. The realization of this project is also based on the methodological development of TEM grid reactors dedicated for the reaction under study, i.e. 2-propanol oxidation or the oxygen evolution reaction. In the following, two cases are presented that may act as an illustrative example of the ongoing research:

Case I: Co_3O_4 in 2-propanol oxidation reaction

During temperature cycling, the spinel-type cobalt oxide suffers from deactivation in the low temperature regime in the gas-phase oxidation of 2-propanol.[1] To understand

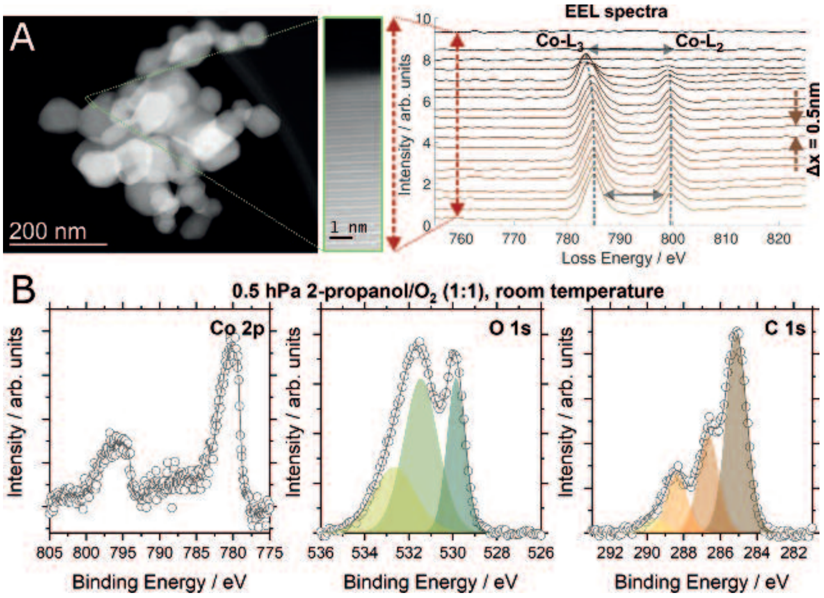


Figure 1. A) STEM-EELS scan across the surface of a Co_3O_4 particle. **B)** In situ XPS data of the same material during 2-propanol oxidation.

the chemistry behind this deactivation, we combined (scanning) transmission electron microscopy ((S)TEM) analysis with near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) investigations. Figure 1A shows high-resolution STEM-electron energy loss spectroscopy (EELS) data that probe differences between the electronic structure in the bulk and at the surface of the material. These results reveal that the spectra at the surface of the Co_3O_4 particles are more CoO-like compared to the bulk.

In Figure 1B, some XPS spectra acquired during a 2-propanol oxidation run (1:1 2-propanol/O_2, 0.5 hPa) are shown that reveal the presence of adsorbed carbonaceous species as seen in the C 1s spectrum (component just below 287 eV), whereas the Co 2p spectrum seems to be slightly reduced under these conditions.

Case II: Transmission electron microscopy for liquid phase (electro-)catalysis

While operando TEM in the gas phase has proven to be a valuable asset in the characterization of heterogeneous catalysts, problems arise when transitioning to the liquid phase. Besides safety issues when applying high pressures, also beam damage is multiplied compared to the gas phase. Thus, in order to be able to map out these regions in the parameter space using TEM, identical location imaging techniques have to be used where the same particles are viewed at different stages of catalytic treatments.

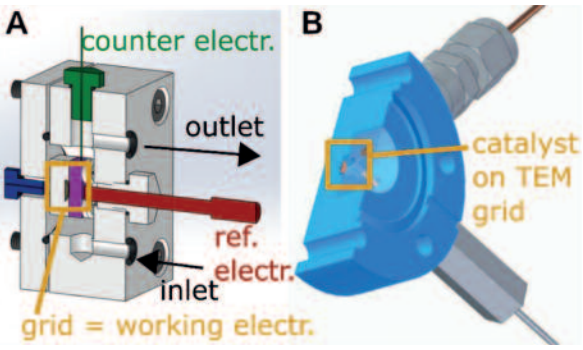


Figure 2. A) Quasi in situ electrochemical cell and **B)** quasi in situ high pressure liquid phase reactor (up to 20 bar).

Similar to a previously designed quasi in situ reactor for gas phase heterogeneous catalysis,[2] we are developing tools to perform quasi in situ studies on electrochemical systems (oxygen evolution, electrochemical alcohol oxidation reaction, Figure 2A) and high-pressure liquid phase heterogeneous catalysis (oxidation reactions, panel B). These developments will prospectively allow us to extend our capabilities of contributing to the central questions of the CRC.

Advanced X-ray Emission Spectroscopy of Heterogeneous Oxidation Catalysts – Department of Inorganic Spectroscopy/CEC

Olaf Rüdiger, Minmin Chen, Serena DeBeer

An alternative to surface sensitive techniques like XPS for investigating active sites in heterogeneous catalysts is the use of element selective core spectroscopies. In this regard, we are using X-ray emission spectroscopy (both resonant and non-resonant) to analyze spinel and perovskite systems, both ex situ and under operando conditions. Spinel systems contain one Co^{2+} in a tetrahedral site and two Co^{3+} in a octahedral symmetry. In addition, Fe-doped spinel materials present higher catalytic currents. The involvement of each site in catalysis, as well as the role of the Fe, is still not well understood. To investigate these questions, we are currently running two type of experiments: 1) in the soft X-ray regime, 2p3d resonant inelastic X-ray scattering (RIXS) is a complex experiment sensitive not only to oxidation state but also to local symmetry (Oh vs. Td). 2) Using hard X-rays, Kβ lines (resulting from 3p to 1s transitions on the photoabsorber) are often useful electronic structural fingerprints, as the strong 3p-3d exchange present in open shell transition metals renders this spectral region dependent on the number of unpaired d- electrons. This means that Kβ lines provide a measure of both spin and oxidation state. To higher energy are the so-called valence-to-core (VtC) XES features, which provide information about the identity and protonation state of neighboring ligands.

1) In a typical 2p3d RIXS experiment, we start measuring XAS spectra around the metal L-edge, to select the excitation energy to be used in the emission spectra. In figure 3, we show the example of the Co_3O_4 spinel compared to the $CoFe_2O_4$ inverse spinel. The inverse spinel contains only high spin (HS) Co^{2+} in an octahedral site, while the spinel has a mixture of high spin Co^{2+} tetrahedral and low spin (LS) Co^{3+} in octahedral geometry. The RIXS spectra from the spinel sample are more complex since they are a result of the presence of two different species. In this experiment, one starts at a $2p^63d^n$ ground state, excites to a $2p^53d^{n+1}$ intermediate state, and arrives at a $2p^63d^{n'}$ final state. In this way we can interrogate the formally parity (as well as spin) forbbiden d-d transitions of a catalyst. The first peaks observed at low energy transfer correspond to d-d excitations, while at higher excitation energies and energy transfer charge-transfer states are observed. Nevertheless, the multiplicity of states results in complex spectra that will require careful analysis and simulation. In this direction we work closely with the department of Molecular Theory and Spectroscopy at the MPI-Kohlenforschung where efficient quantum chemistry methods are developed.

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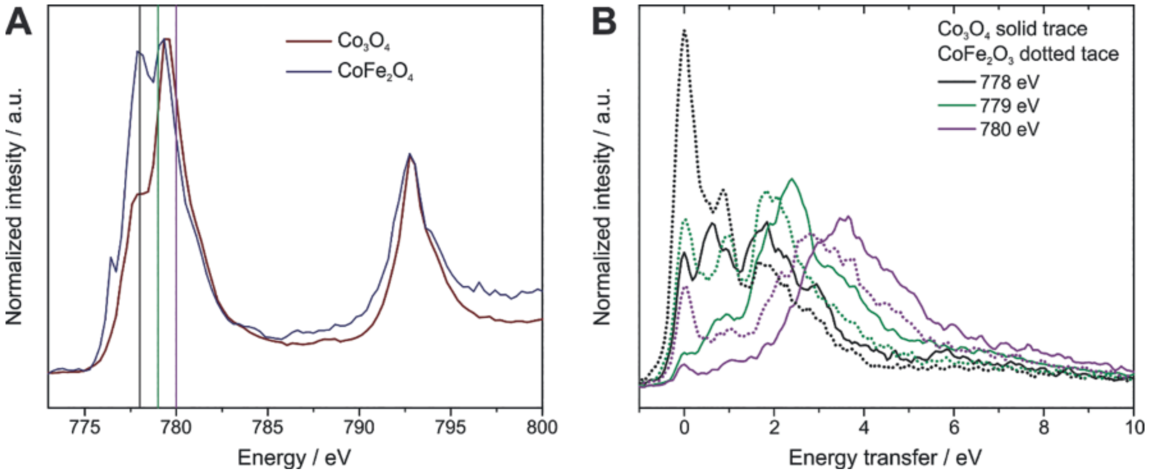

Figure 3. A) Normalized XAS Co L-edge spectra of powder Co_3O_4 and $CoFe_2O_4$. The vertical lines indicate where the RIXS spectra from panel (B) have been collected. **B)** RIXS spectra of the same samples at three different excitation energies.

These methods are grounded in wavefunction based theories and are able to compute a large variety of XAS, VtC-RXES and RIXS spectra of classes of chemical systems ranging between molecules and 'real-life' molecular and solid systems.

We have developed an operando spectroelectrochemical cell to measure at beamline BL07LSU at Spring-8. Operando measurements did not show changes with the applied potential on the different spectral signatures. This is in contrast to what we have observed on electro-deposited amorphous Co oxides or previous experiments using a similar setup on NiO.[1]

2) Non-resonant Kβ XES experiments in the hard X-ray regime can provide information about the spin state and oxidation of the metal of interest, while valence-to-core measurements report on the nature of the bound ligands. These measurements can be carried on using the in-house instruments at the CEC. In collaboration with the group of Harun Tüysüz from the MPI-Kohlenforschung, we are investigating boron doped Co spinels calcined at different temperatures. The resulting materials showed different catalytic performances with a maximum activity for the samples calcined at 300°C. In Figure 4A we compare the non-resonant Kβ mainline from these samples with pristine Co_3O_4 and CoO. The increased number of unpaired electrons in CoO (HS Oh Co^{2+}) results in a clear splitting of the mainline into the Kβ' (7637 eV) and $K\beta_{1,3}$ (7651 eV), while the pristine Co_3O_4 has a much lower fraction of HS Co^{2+} and as a result the Kβ' is less pronounced. The starting material (boron doped $Co(OH)_2$) is also HS Co^{2+} and therefore shows a similar spectrum to CoO. The calcined materials are more similar to the Co_3O_4 indicating that there has been a significant conversion to LS, probably Co^{3+} after the calcination. More information can be obtained on a synchrotron where the use of monochromatic beam can provide additional information. If we scan the incident energy while measuring the intensity at the emission spectrometer fixed at the energy value where the Kβ line has its maximum, we obtain a high-energy-resolution fluorescence detected spectra (HERFD). This technique obtains more well-defined spectra than traditional K-edge XAS, especially on the pre-edge region, where the peaks tend to be smeared by core-hole lifetime broadening from the 1s electron-hole (that for Kβ-HERFD is dependent on a narrower 3p electron-hole). In Figure 4B, we can see that the calcined samples present an edge position and shape more similar to Co_3O_4 than to CoO, which is indicative of the formation of the spinel domains.

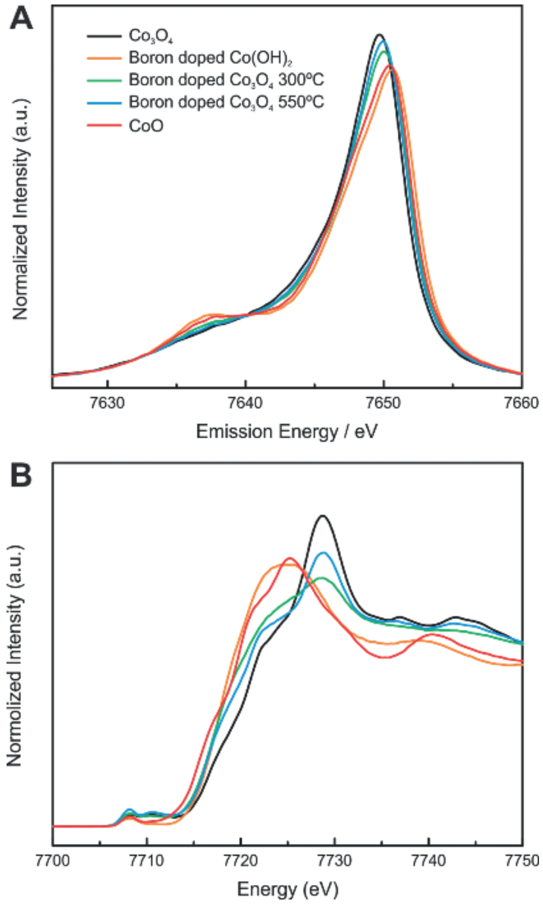

Figure 4. A) Kβ XES spectra of pristine Co_3O_4, CoO and boron doped samples calcined at different temperatures. **B)** Corresponding HERFD XANES spectra of the same samples measured at the Kβ maximum.

The sample calcined at 300°C probably has a more distorted structure which may be related to its increased activity. Interestingly, CoO and $Co(OH)_2$ do not present the second pre-edge feature at 7712 eV, usually assigned to charge transfer processes to the ligand. These materials are the ones with the worst catalytic properties, so it is tempting to relate this band to its catalytic activity. We are planning future beamtimes (already accepted proposals at CHESS-PIPOXS and Diamond Light Source-I20) to measure 1s3p RIXS and investigate this pre-edge region in detail. In addition to that, we are measuring non-resonant $K\beta_{2,5}$ or valence-to-core in our in-house spectrometer to investigate the ligands around the Co. In this technique, we measure the relaxation of an electron from the 2s or 2p orbitals of the ligand to the 1s hole of the metal. By doing this, we can investigate if boron is substituting any oxygen atoms in the structure, something that is not possible to discriminate by EXAFS.

Similarly to what we have observed in the soft X-ray regime, we did not observe significant changes on the spectral signatures during spectroelectrochemical experiments when measuring the spinel Co_3O_4 catalysts. On the other hand, when measuring electrodeposited Co oxide, we observe clear changes with the potential (see O. Rüdiger report). Our current interpretation is that the conductivity between particles on the film is low, as a result, only a minor fraction of the material is doing electrocatalysis and any spectral changes resulting from the applied electrode potential are masked by a much larger fraction of the sample that is not in direct electron transfer with the electrode. We are currently working in two strategies to overcome this limitation: i) Use thin films of Co_3O_4 synthesized on the electrode surface instead of nanoparticle dropcasting; ii) Combining Co_3O_4 with a conductive material in a similar manner to what we did with NiO supported on graphene.[1]

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Multiscale Methods for Theoretical Spectroscopy of Oxide Surfaces under Electrochemical Conditions – Department of Molecular Theory and Spectroscopy/KoFo (JWS)

Dimitrios Manganas, Tiago Gouveia,
Serena DeBeer and Frank Neese

Within the CRC 247, the department of Molecular Theory and Spectroscopy at the MPI Kohlenforschung is participating in a joint project together with the Computational Materials Chemistry group from Uni-Bochum. The goal of this project is to develop and validate multi-method and multi-scale computational protocols, which in the framework of CRC 247 are used to investigate the spectroscopic response at the surface of operating catalysts (Figure 5). In the first funding period, the target of the project is two-fold. It focuses on electronic structure method development aiming to 1) deliver accurate geometric structure descriptions of solid systems under complex environmental conditions and 2) properly compute the X-Ray and resonance Raman spectroscopic properties for antiferromagnetic solids. Hence the project is profited by strongly established collaborations within various experimental groups of CRC 247.

As an example, in collaboration with the Department of Inorganic Spectroscopy at the MPI-CEC in the framework of the joint work space (JWS), project B8 contributes to understanding the complex information content of in-situ X-ray spectroscopies (XAS, XES, XPS, RIXS). This is a multistep process that requires developing and validating multimethod theoretical spectroscopy protocols on systems with increasing structural complexity, in terms of coordination environment, oxidation and spin states as well as environmental conditions. In fact, by employing various wavefunction based theories it has been possible to unravel the XAS, XES, and RIXS intensity mechanisms in a variety of chemical systems ranging from molecules to solids [1-3].

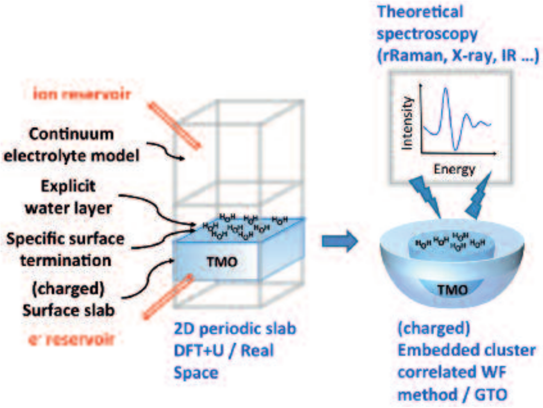

Figure 5. The multiscale-multimethod approach that is used to unravel the spectroscopic response of oxide surfaces.

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INTERNATIONAL MAX PLANCK RESEARCH SCHOOL ON REACTIVE STRUCTURE ANALYSIS FOR CHEMICAL REACTIONS (IMPRS-RECHARGE)

The International Max Planck Research School on Reactive Structure Analysis for Chemical Reactions (IMPRS-RECHARGE) has been established in 2015 (spokesperson Frank Neese) and has seen a very successful first funding period. The extension proposal was approved for a second running period from 2021 to 2026 upon the successful evaluation of the school in 2019. 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 school brings together students from three universities (Bonn, Duisburg Essen, and Bochum) as well as the two institutes on the Mülheim Chemistry Campus (see Table 1).

MPI für Chemische Energiekonversion	MPI für Kohlenforschung	Ruhr-Universität Bochum	Universität Duisburg-Essen	Rheinische Friedrich-Wilhelms-Universität Bonn
Inorganic Spectroscopy Prof. Dr. S. DeBeer **Molecular Catalysis** Prof. Dr. W. Leitner **Heterogeneous Reactions** Prof. Dr. R. Schlögl	**Homogeneous Catalysis** Prof. Dr. B. List **Organometallic Chemistry** Prof. Dr. A. Fürstner **Molecular Theory and Spectroscopy** Prof. Dr. F. Neese **Organic Synthesis** Prof. Dr. T. Ritter **Heterogeneous Catalysis** Prof. Dr. F. Schüth	**Chair of Physical Chemistry II** Prof. Dr. M. Havenith **Chair of Organic Chemistry II** Prof. Dr. W. Sander **Chair of Industrial Chemistry** Prof. Dr. M. Muhler Prof. Dr. W. Kleist **Chair of Analytical Chemistry** Prof. Dr. W. Schuhmann	**Faculty of Chemistry** Prof. Dr. M. Behrens Prof. Dr. S. Schulz **Faculty of Engineering** Prof. Dr. C. Schulz	**Mulliken Center for Theoretical Chemistry** Prof. Dr. T. Bredow Prof. Dr. S. Grimme Prof. Dr. B. Kirchner

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

Structure and Student Distribution

The IMPRS-RECHARGE accepts applications throughout the year, and installed an online application portal (provided by the Gesellschaft für wissenschaftliche Datenverarbeitung mbH, Göttingen) in 2017, enabling improved management of incoming applications. The personal documents of the applicants are stored at a highly secured GWDG-server.

The IMPRS accepted students from 13 different countries. At the start of the IMPRS RECHARGE, there were only two female participants. Meanwhile, the percentage of female participants has risen the 41%. The IMPRS has also achieved a high degree of geographical diversity with nearly 50% of the participants being of non-German origin.

Table 2 shows the admission number per year, and the distribution of gender and nationality. Figure 1 depicts the geographical distribution and Figure 2 the allocation of students to the partner institutions.

Students	2015	2016	2017	2018	2019	Total
Accepted	9	5	2	12	1	29
Gender Distribution						
Female	2	0	1	8	1	12
Male	7	5	1	4	0	17
Student's Nationality						
National	5	2	1	8	1	17
International	4	3	1	4	0	12
EU	2	0	0	1	0	3
Non-EU	1	4	1	3	0	9

Table 2. Students characteristics in terms of gender and nationality.

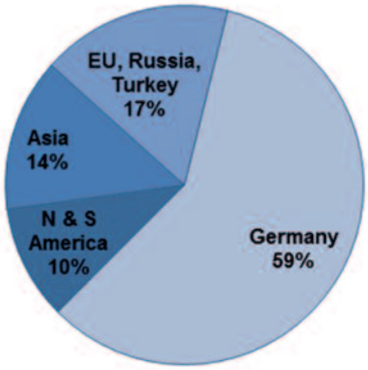


Figure 1. Geographical distribution

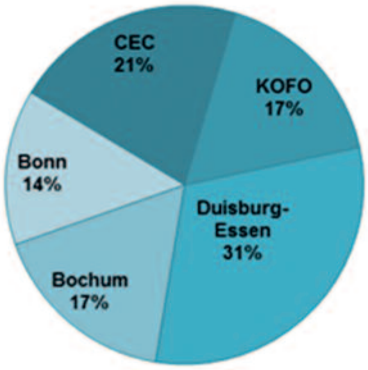


Figure 2. Distribution to partner institutions

Doctoral Program

Besides the students' scientific research culminating in the doctoral/PhD thesis, the students are obliged to complete an additional training program (see Table 3) that combines the excellent research conditions of the partners with an intensive interdisciplinary teaching program. All academic school members and a number of external experts are involved in this program.

In addition to close and direct interaction with the supervisor, doctoral students are supposed to meet regularly with their individual thesis advisory committee (TAC).

Students, who successfully completed the additional RECHARGE curriculum and as well obtained the doctoral/PhD degree at one of the partner universities, receive a separate IMPRS-RECHARGE certificate.

Block Courses

The block courses are carried out as a lecture series and impart the necessary background knowledge on theoretical methods, physical background of spectroscopy and some basic insight into the related chemistry of catalysts and reactions.

Introduction to RECHARGE: Theory and Experiment (basic course 2018)

- Spin Hamiltonian Formalism for Transition Metal Complexes
- Ligand Field Theory
- Introduction into Solid State Chemistry
- Nanoparticles
- Organometallic Electrocatalysis
- Chemical Reaction Engineering
- Catalysis. A Concept?
- Electron Correlation. Accuracy in Electronic Structure Models
- Day of Catalysis:
  - Organocatalysis
  - Synthetic Approaches for the Production of Solid Catalysts
  - Late-Stage Functionalizations
  - Advances in Metal Carbene Chemistry
  - Theoretical Studies of Transition Metal Catalysis and Biocatalysis
- Electrochemistry
- Metal Organic Reaction Mechanisms
- Organic Reaction Mechanisms
- Introduction to Band Structure Theory: A Chemists View ...
- Periodic Models of Solids and Surfaces (I and II)

	1st Year	2nd Year	3rdYear	Final Oral Presentation
Block Course	Basic	Basic - Physical Methods	Advanced - Catalytic Reactions	
	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 3. Curriculum structure.

*The summer schools entitled "Theoretical and spectroscopic methods in Inorganic Chemistry" and "Catalysis and Energy: from Synthesis to Application" are organized in a biannual rhythm.

Physical Methods in Homogeneous and Heterogeneous Catalysis (basic course, physical methods 2019)

- Absorption Spectroscopy
- XAS/XES Spectroscopy
- IR Spectroscopy
- Electrochemistry
- X-ray Spectroscopy Applied to Homogeneous Catalysis
- EPR Spectroscopy
- Electron Microscopy
- (Resonance) Raman Spectroscopy
- Diffraction / Sorption / SAXS
- Diffraction Methods
- XPS Spectroscopy
- Mössbauer Spectroscopy
- Characterization of Heterogeneous Single-site Catalysts
- Magnetism
- NMR Spectroscopy

Advanced Courses on Catalytic Reactions (advanced course 2017)

- Chemical Vapor Deposition
- Heterogeneous CO_2 Conversion
- Methane Chemistry
- Introduction to the Synchrotron Radiation Facility BESSY II
- Introduction to ISISS and EMIL
- Photocatalytic Activation of CO_2
- Bridging Heterogeneous Catalysis on Metals and Homogenous Catalysis in Molecules – Phenomena, Methodology and Theory
- Ammonia Synthesis
- CO_2 Harvesting

Student-organized Events

The doctoral students regularly organize international conferences. They independently perform all tasks that are related with the organization of conferences, including selection of scientific topics, speakers, budget planning, and observance of financial regulations.

The first symposium "Catalysis for Sustainable Chemical Energy Conversion" was performed at the Universität Duisburg-Essen, September 17-21, 2017.

The second symposium "Catalysis towards Greener Chemistry" was carried out at the Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, May 20-23, 2019.

International networking activities between the IMPRS-RECHARGE and the 2MIB (Molecules, Materials, Instrumentation and Biosystems) doctoral schools of Paris-Saclay University were particularly initiated by the symposium in 2017 that led to the "First French / German Joint Symposium on Materials for Catalysis and Energy Applications". The event was hosted at the Université Paris-Sud, Orsay (France), October 10-11, 2019.

Furthermore, teams of students regularly organize retreats on topics of own choice.

Discussion Meetings

Discussion meetings provide an informal opportunity for the students to present and discuss recent research results, to meet-up with new students and to organize coming activities. The meetings are organized roughly every three to four month.

Soft Skills Courses

Another major objective of the IMPRS is the improvement of the soft skills of its students. 'Scientific writing' was course topic in 2017 (performed by Dr. Melanie Conrad, Golin Wissenschaftsmanagement) and in 2018 (performed by Mark Buchanan and Justin Mullins, Write-About Science). A further 2018-topic was 'presentation skills' (performed by Julie Stearns, ImpulsPlus). In 2019 the topic was 'career planning after graduation'. MPI alumni were invited to talk about their current professional background and how they decided on their professional path in academia or non-academia. This subject was deepened in panel discussions with the alumni. Lectures on the topics „How to win a Job Hunting" (by Rob Thompson, RTTA) and „Research Career in Industry" (by Dr. Anna Prodi-Schwab, Evonik) completed this event. This career day was open to all interested early stage scientists at Mülheim Chemistry Campus.

Publications of the IMPRS-students

The scientific output of the students is steadily growing (see Figure 3), and many of the papers are published in excellent journals.

Furthermore, the students are very active as participants in national and international conferences.

Doctoral Theses

John, L.: Computational insights and catalyst syntheses for the electrochemical CO_2 reduction, Universität Duisburg-Essen, 2018.

Van Stappen, C.: Fundamental and practical spectroscopic studies towards understanding the electronic structure and reactivity of nitrogenases, Ruhr-Universität Bochum, 2019.

Cibura, N.: Fundamental studies on catalytic properties of manganese oxides in oxidation reactions, Universität Duisburg-Essen, 2019.

Dzialkowski, K.: Dispersionswechselwirkungen in schweren Gruppe 15 Elementverbindungen, Universität Duisburg-Essen, 2019.

Froese, C.: Mechanistic studies on the synthesis of higher alcohols over bimetallic catalysts, Ruhr-Universität Bochum, 2019.

Özcan, F.: Development of coprecipitated late 3d transition metal based catalysts for energy conversion related applications, Universität Duisburg-Essen, 2019.

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

Figure 3. Scientific progress – measured by number of publications and first-author papers.
*The number of 2019-publications includes already accepted articles that will be published in 2020.

KOPERNIKUS PROJECT

POWER-TO-X

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

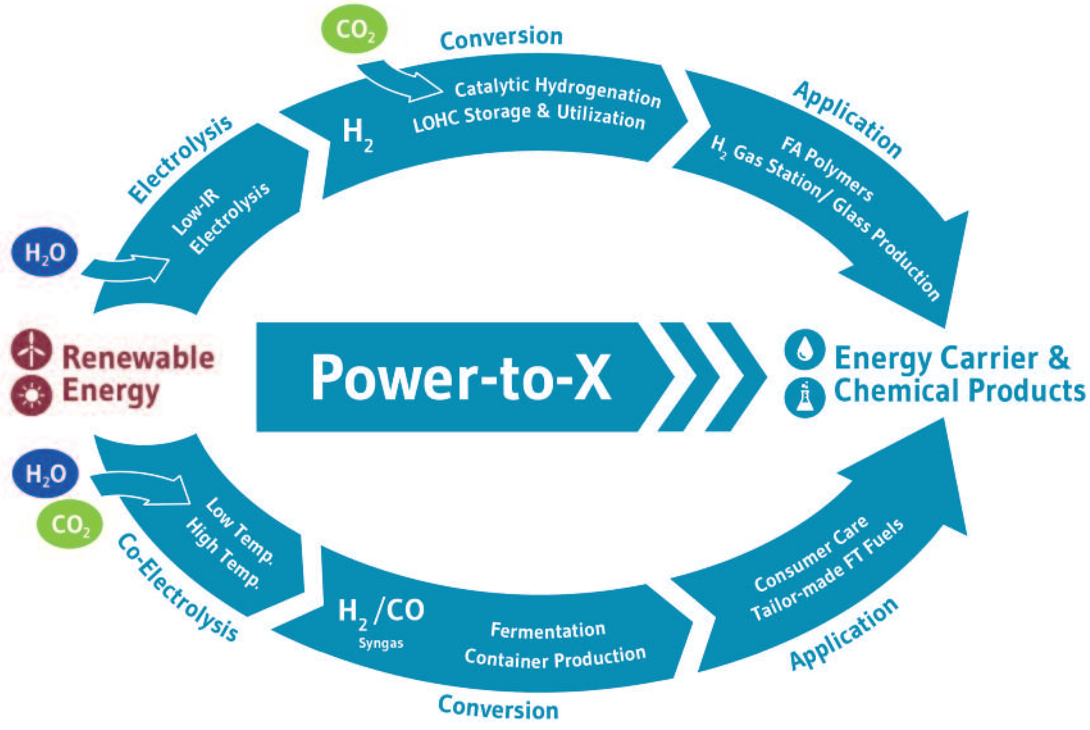
The „Kopernikus Projects for the Energy Transition" are funded as large scale national platforms with a 10 years horizon by the BMBF to develop technological and economic solutions for the conversion of the energy system in collaboration between academia, industry, and society. The project "Exploration,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

The aim of the 1st phase (2016-2019) of the Kopernikus project P2X was to research the technological basis for solutions to convert renewable energy into energy carriers and chemical products for applications in the key industrial markets of energy, mobility and transport, and chemistry. As a result of the successful project work, it was possible to closely interlink the fields of action and application in terms of content and structure and thus identify promising options for the 2nd phase (2019-2021) of the „validation".

Selected technologies that were examined in the first phase are now integrated within the two technology pathways „hydrogen as an energy vector" and „synthesis gas as an energy vector". These technology pathways start 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. This allows validation of the individual technologies within defined value chains. CO_2 (from industrial sources or direct air capture) serves as the carbon source. Reduction of greenhouse gas emissions in comparison to the corresponding petrochemical value chains defines the central evaluation criterion.

The research work focusses on the knowledge-based validation of the technology components based on promising applications in order to prepare their demonstration and implementation in the 3rd project phase. The selected areas of application include polymers (e.g. paints, foams and adhesives) and special chemicals (e.g. for consumer care) for the chemical sector. Synthetic fuels conforming to standards (kerosene, petrol or diesel fuels) are addressing the mobility sector. The LOHC technology is envisaged for hydrogen logistics to use H_2 as fuel and as heating gas in the glass industry, addressing the sectors mobility and energy utilization, respectively .

In order to achieve these ambitious goals of the second project phase, 14 research institutions, 6 associations and societies, as well as 26 industrial companies throughout Germany are participating within the project consortium. Existing large-scale projects and infrastructures associated through the partners and beyond are envisaged as synergistic platforms in the further development. Communication to the general public and international networking are additional strategic measures for the second phase.



MANGAN

The BMBF-funded cluster Project "MANGAN", initiated in 2015, aims to elucidate the capability of manganese-based compounds as catalysts for the electrochemical oxygen evolution reaction (OER). In particular, the question that the MANGAN project seeks to answer is whether manganese-based compounds can replace existing noble metal based catalysts for electrochemical water splitting and which boundary conditions have to be fulfilled to do so. The variety of stable oxidation states and structures makes manganese an interesting candidate for this fundamental study. Despite the application-oriented question, it is not the attempt of the MANGAN project to develop a device but rather to achieve a fundamental understanding of boundary conditions and potential structure-function relationships of manganese-based catalysts for OER.

Consortium and Project Coordination

The MANGAN project is a consortium of experts from various fields approaching the central questions from different directions. The MANGAN cluster consists of 25 research groups organized in 15 sub-projects focusing on different research aspects to cover the full systemic complexity of water splitting. These aspects cover various synthesis approaches, theoretical modeling, the development of electrode materials, and the application of high-end characterization techniques. The project partners are located at the Fritz Haber Institute of the Max Planck Society, the Helmholtz-Zentrum Berlin, the Max Planck Institutes for Chemical Energy Conversion and Iron Research, the technical universities of Aachen, Berlin, and Darmstadt, as well as the universities of Bielefeld, Bochum, Erlangen-Nürnberg, Freiburg, Gießen, Mainz, and Duisburg-Essen. In addition, BASF is involved as industrial partner. The Max Planck Institute of Chemical Energy Conversion contributes to the project by research on carbon based electrode materials and the incorporation of manganese oxides in carbon matrices (Saskia Heumann) and the development of site-specific spectroscopy methods for catalyst characterization (Serena DeBeer).

Figure 1. Logo of the MANGAN cluster project.

Moreover, the MPI-CEC coordinates the MANGAN cluster project. The coordination project is located in the department Heterogeneous Reactions and is in regular contact with the individual project partners. It organizes biannual project meetings for scientific discussion, as well as workshops and video conferences. In addition, the International Bunsen-Discussion-Meeting on Fundamentals and Applications of (Photo) Electrolysis for Efficient Energy Storage in April 2019 was co-organized by the MANGAN coordination. The coordination project maintains the project webpage and the database, comprising the experimental results of the individual project partners. Further activities of the coordination project are the development of a standardized measurement protocol and the evaluation of the data obtained within the project. The latter will serve as basis to draw a conclusion regarding the applicability of Mn base compounds for OER as well as to achieve a comprehensive overview of the development and characterization of such catalysts.

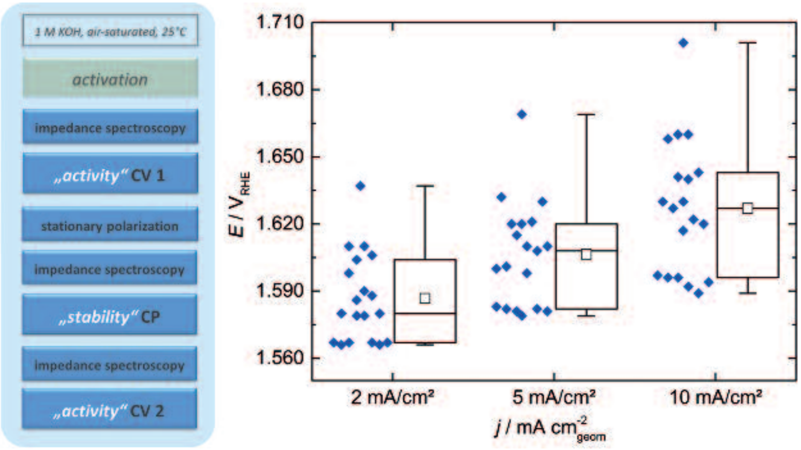


Figure 2. Left: Sequence of measurements to obtain comparable key performance indicators (KPI) describing the activity and stability for each catalyst. **Right:** Potential to reach 2, 5, and 10 mA/cm$^2_{\text{geom.}}$ (KPI for the initial activity) of a commercially available nickel cobalt oxide reference measured by different project partners. The range in which 50% of the obtained results can be found (box), the data ranges (whiskers), the average values (open squares) and the median values (line) are shown next to the data.

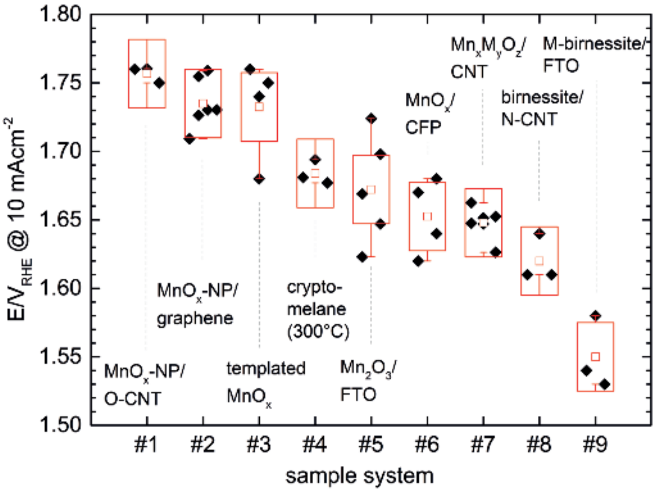


Figure 3. KPI (potential at 10 mA/$\text{cm}^2_{\text{geom.}}$ in "CV 1") for selected Mn oxides (MnO_x) on different substrates.
The box indicates a 50 mV window for comparison to the variation of KPI measured for references shown in Figure 2. (CNT: carbon-nano-tubes, CFP: carbon fiber paper, FTO: fluorine tin oxide, NP: nanoparticle, M: transition metal).

Development of a Standardized Measurement Protocol

A systematic electrochemical analysis of catalysts for the oxygen evolution reaction gives need to develop an appropriate experimental standard. To ensure the comparability of results obtained by the individual groups, identical rotating disc electrode (RDE) setups were distributed amongst the MANGAN partners and a standardized protocol was developed. This protocol defines the electrode preparation, the experimental conditions as well as the experimental settings and measurement steps. In a defined sequence (Figure 2, left), the activity and stability of the catalysts are tested and quantified by key performance indicators (KPI). These indicators serve as basis for a comparison of different investigated compounds.

Importantly, the application of a standardized experimental protocol in this large-scale consortium allowed revealing the limits of the RDE technique for electrochemical characterization. This was achieved by performing a series of measurements on an identical reference catalyst (commercial nickel cobalt oxide) distributed amongst the project partners. Although, the experimental conditions, the electrochemical setup, and the sample preparation procedure were held identical, a deviation of a few 10 mV for the individually determined KPI quantifying the initial sample activity of the individually reference material could be observed (Figure 2, right). This suggests that the results obtained by the RDE technique have to be handled with care in terms of the quantification of catalyst performance. In a subsequent study, further parameters that influence the RDE results – such as binder materials and catalyst ink preparation – were identified. Crucially, all results were communicated and discussed amongst the project partners at all times, to ensure the awareness of possible error sources.

Database

The evaluation of the database established within the framework of the MANGAN project is one of the main outcomes of the project. The data of all investigated materials – independent of their catalytic performance – are summarized in this database and will be made accessible to the scientific community. Beside measurements following the developed protocol for the electrochemical characterization, the project partners were allowed to alter experimental conditions to avoid too strong restrictions in the optimization process of promising candidates for OER. In any case, all parameters are documented together with electrochemical results and complementary analysis. By this, a comprehensive set of different Mn based compounds and their electrochemical activity towards OER could be obtained (Figure 3). Although, certain Mn based compounds exhibit a comparable good activity with respect to the reference, the stability of most systems appeared as a limiting factor. And while a first analysis suggests layered or tunneled structures and the interplay of Mn^{III} and Mn^{IV} sites as beneficial for OER, an unambiguous structure-function relationship cannot be determined. Importantly, the variety of approaches within the consortium and the regular discussion of results including all partners allowed deducing general insights on the influence of parameters on the development of oxygen evolution half-cells. This includes beside the choice of the catalyst itself also the electrode material, electronic properties, and catalyst dynamics during operation. In the end, the interplay of all components of the oxygen evolution half-cell will determine the overall performance. In addition to the publication of the database, this leads to the second outcome of the project, which will be a comprehensive perspective on OER catalyst design and characterization.

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The MAXNET Energy Research Consortium

The MAXNET Energy originates from the MAXNET Enerchem initiative of the MPG, which was launched in 2005 with the goal to build a scientific network of different collaborators in the context of the topic "energy research". With great emphasis on nanotechnology and through joint efforts, several institute projects with special relevance for social development and a sustainable energy industry were initiated. Already in the early phase of Enerchem topics such as energy storage, as well as energy transport and chemical conversion were formulated as central aspects. Consequently, in the years between 2005 and 2013 a variety of topics ranging from hydrogen storage and batteries to CO_2 conversion, electrochemistry and photo-electrochemistry at five sites of the MPG (FHI, KoFo, MPI FKF, MPIP and MPIKG) were initiated (Figure 1), aiming at shortening the path between basic research and application to guarantee fast progress.

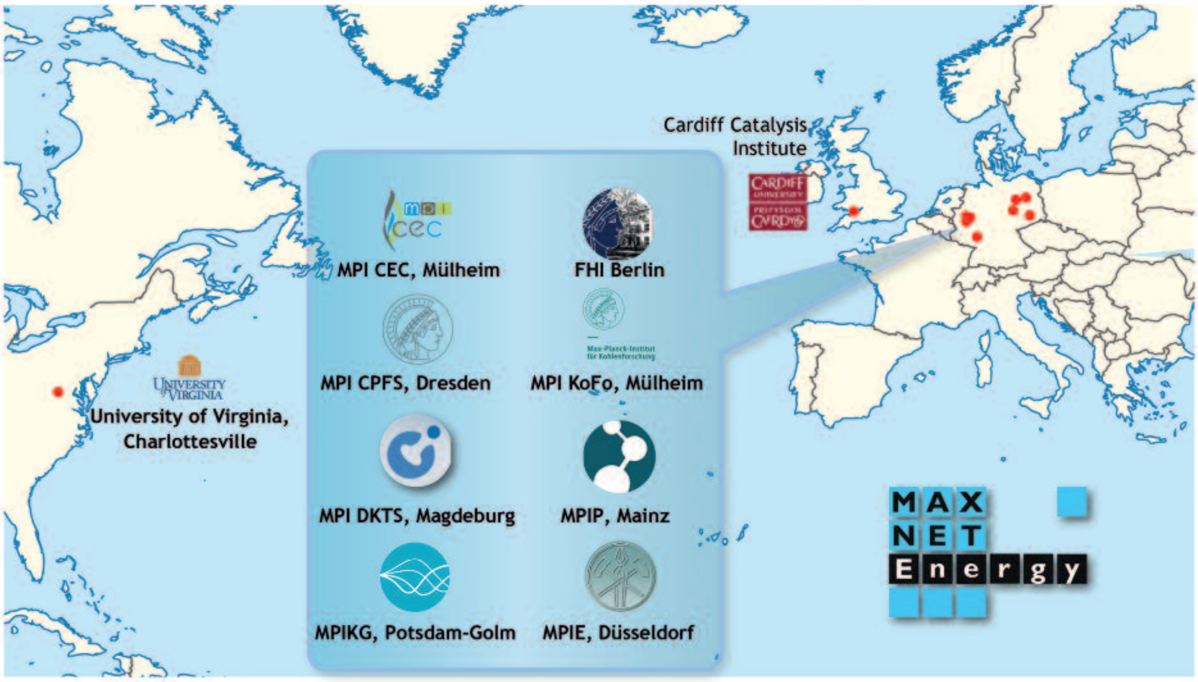

Figure 1. The MAXNET Energy consortium

The MAXNET Energy Research Consortium originates from the idea to conduct fundamental science in order to fill the knowledge gaps in key technologies for the transition to a sustainable energy economy. A prominent example is energy storage, which is required to convert the fluctuating renewable-energy supply into a high density and long-term storable form. An approach that has many advantages is to store the energy in chemical bonds, which can, for example, be achieved by electrocatalytic water splitting and storage or further conversion of the obtained hydrogen. While water electrolysis may be considered as a technological problem that has been solved long ago, existing solutions cannot easily be applied in large scale, as they require expensive and rare materials which often suffer from degradation. To circumvent such problems, detailed understanding generated from fundamental research is necessary in order to bring forth new solutions in cases where development stagnates in parameter optimization of already established solutions.

The realization that we did not yet have to our disposal all those technologies that could enable a systemic closed supply of the fluctuating renewable energy resources such as wind and solar energy within Germany, Europe or worldwide has been the main motivation. However, to ensure the wide application of renewable energy, energy storage should be considered as a central aspect and the special role of chemistry and basic research should be emphasized. With the Enerchem initiative, the MPG laid the foundation, so that energy research could be established as one of the main research topics of the MPG through basic research and close networking within the MPG.

With the founding of the MPI for Chemical Energy Conversion 2012 and the initiation of MAXNET Energy initiative in 2013, the MPG not only demonstrated its long-term commitment to cutting-edge research on the topic of energy, but put this core issue on an institutional basis. Figure 2 gives an overview of the past development over time.

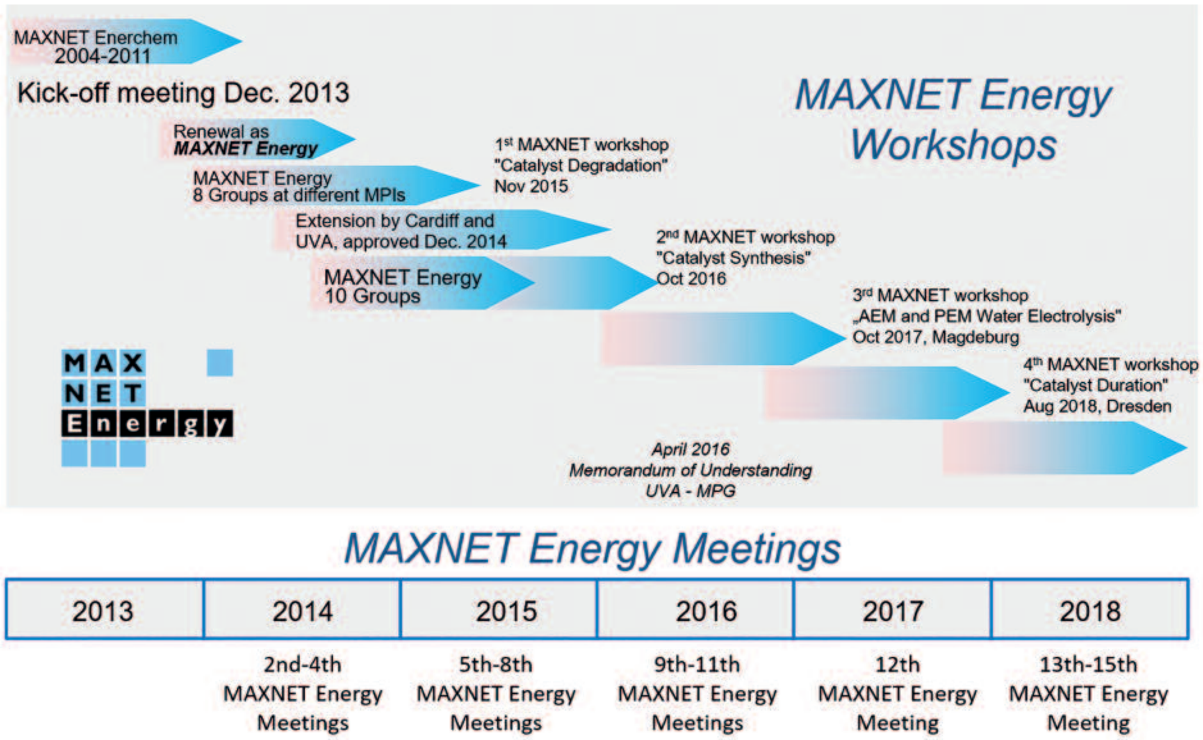

Figure 2. Evolution of the MAXNET Energy Initiative over time. In the experience of this history, the initiative now plans for the future a strong focus with a core team and an instrument of flexible cooperations to process relevant aspects beyond the core activity. In the historical development, the focus changed from a development of nanostructured materials for various applications of energy storage towards the focus on OER.

The storage of energy in the form of chemical bonds via water splitting is the central aspect of MAXNET Energy. However, the main focus has not been on the system or its operation, but on the generation of knowledge in the field of fundamental electrocatalytic processes. For water splitting, e.g. the availability of efficient, durable and cheap catalyst materials, especially for the **oxygen evolution reaction (OER)** is a great challenge. Due to the enormous complexity of the dynamic processes at the electrode, only processes that have been developed in recent years have been able to provide deeper insights into these crucial processes at the atomic level. Exactly in this field lies the core competence of the MPG – only through the generation of basic knowledge can there be development leaps in different areas of research.

MAXNET Energy and its collaborators are committed to fill these gaps. By using selected systems that can be potentially scalable, catalyst materials are tested under loads with methods that allow the material dynamics of the interfaces to be investigated. From this, theory questions are developed in order to model the electrochemical reactions so that better insight for the re-selection of cheap materials is achieved.

To achieve the above, the unique two dedicated modes of operation in MAXNET Energy i.e. the collaborative „joined mode“ and the cooperative „shared mode“, will bring together expertise, samples, materials, resources and methods from different groups to solve a central problem. A good example of this is the development of an electrochemical flow cell (**Figure 3a**), which is known as the central test platform and is jointly available to all project partners. Thus, electrochemical characterization of different catalyst materials under controlled and uniform conditions has been made available for all participants.

Two more aspects facilitate synergy within the consortium: On the one hand, there is the necessity for comparability of results, which is achieved by setting global standards and defining common procedures. On the other hand there is an added value for each group as it can access a broad variety of techniques and machinery together with the top experts in the corresponding field.

An example of the above is the multi-parameter diagram shown in Figure 3b which became collaborative with the MANGAN project (review of protocols in 21 laboratories of electrochemistry) and was designed to provide a scientifically helpful assessment for the potential of different catalyst materials. In the numerous discussions about the working direction of MAXNET has always been argued that one has to develop highly active systems that through internal nanostructuring will receive an activity. In contrast to the literature, we have shown that catalyst performance is a multi-component problem. Therefore, a multi-parameter system has been defined which characterizes the electrocatalytic activity of a material in such detail that meaningful comparisons became possible.

To achieve this, the development of the aforementioned electrochemical flow cell coupled to an ICP-OES (Inductively Coupled Plasma – Optical Emission Spectrometer) was very helpful for the in-depth characterization of different materials, especially in terms of their stability.

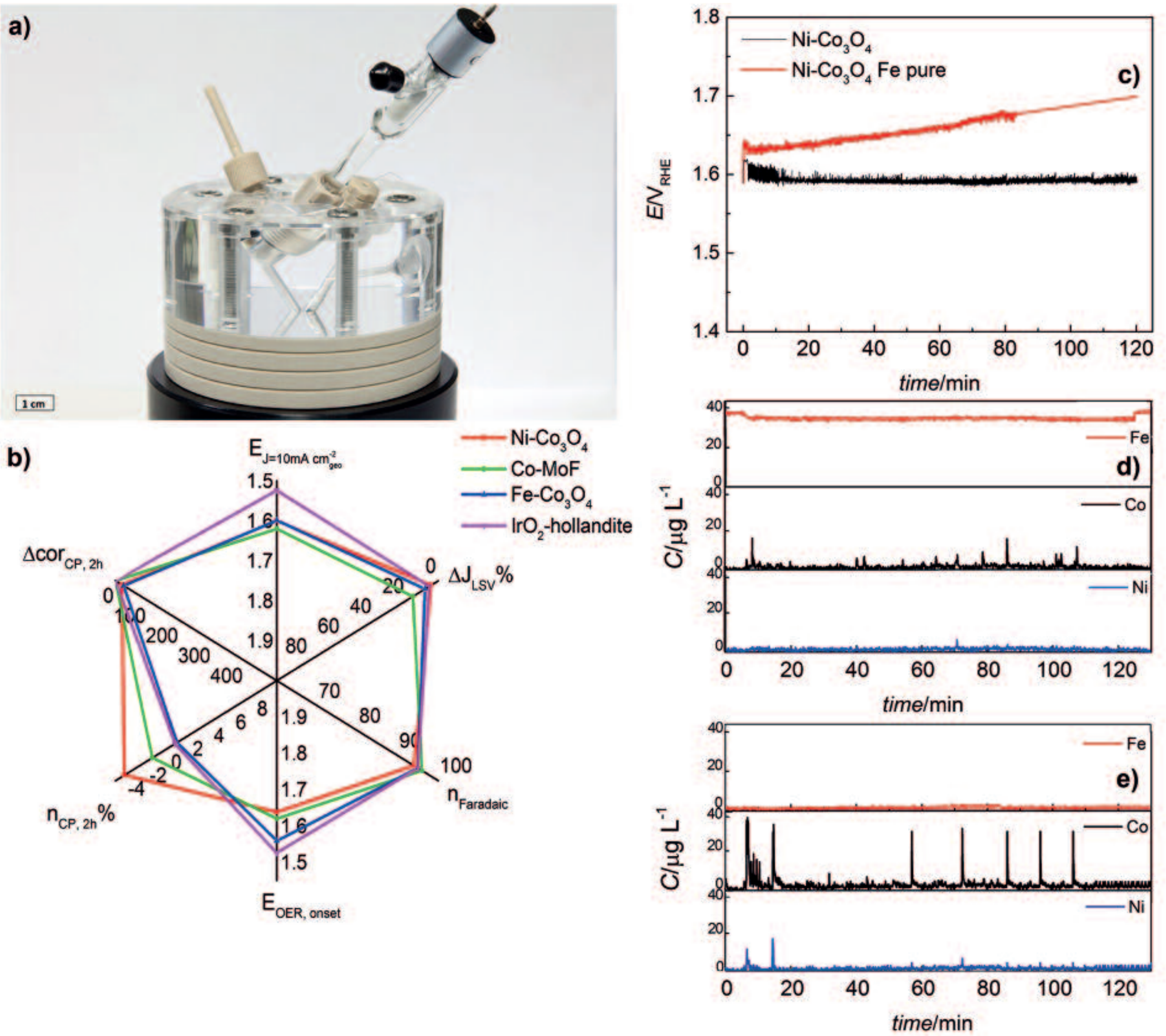

Figure 3. a) The MAXNET electrochemical flow cell was developed by close cooperation of the AG Mayrhofer with the AG Schlögl and was used in all projects. **b)** The multi-parameter graph compares 4 parameters of stability (side arms) with 2 parameters of activity (top, bottom). **c–e)** An example of a NiCo-oxide reference system (in 1M KOH) shows the influence of Fe impurities on the catalyst's stability and dissolution behavior.

It has found applications in various cooperations, e.g. with the MPI for Coal Research, the MPI for Chemical Physics of Solids, Cardiff University and others. In addition to the detection of degradation products, we are in particular also concerned with the influence of external parameters. Such a case was the quantification and the in-depth understanding of the influence of Fe impurities, which naturally occur in commercial KOH, on the activity and stability of OER catalysts (**Figure 3c–e**).

MAXNET Energy is coordinated at the MPI CEC and has been cited in many peer-reviewed journal publications.

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The objective of the REDIFUEL project is to generate a sustainable and innovative synthetic drop-in synthetic diesel (EN 590 conform) which can compete with currently used fossil based fuels. The concept is a three step process as shown in Figure 1.

Starting from variable biomass, first synthesis gas (CO and H_2) is generated. Using Fischer-Tropsch reaction, the synthesis gas is converted to various alkanes and alkenes. While the alkanes will make up most of the final fuel blend, part of the alkenes will be converted to alcohols. In the final REDIFUEL fuel mixture between 20 %-30 % of the fuel matrix will be made up by those alcohols of various chain lengths.[1] The alcohols act as high value additives in the proposed synthetic fuel. It was proven that they show enhanced combustion behaviour and decrease the amount of pollutants.[2,3]

Those alcohols are generated by converting C5-C10 olefins into C6-C11 alcohols. The hydroformylation/hydrogenation reaction is very effective for this transformation.[4] In the hydroformylation reaction carbon monoxide and hydrogen are added to an olefin double bond, generating aldehydes elongated by one carbon atom. In the second step the aldehydes are hydrogenated to alcohols. The reaction has nearly 100% atom efficiency and can be run under mild conditions. Both steps in the hydroformylation/hydrogenation reaction need to be catalysed. The most commonly used and very effective ones are homogeneous transition metal catalysts, e.g. catalysts based on rhodium or cobalt.[5]

The catalyst is crucial for the overall yield and also the product distribution.[6] Therefore an effective catalytic system is the starting point and influences the overall effectiveness of a future process to generate those alcohols.

The overall goal of this task is to develop an active and cost efficient catalytic system for the hydroformylation/hydrogenation process. To convert olefins to alcohols, two catalysed reaction steps are necessary. The first one is the hydroformylation reaction, that yield linear (*n*-) and branched (*iso*-) aldehydes. The aldehydes can be further hydrogenated in a second step to the desired alcohols (hydrogenation step).[7]

To accomplish this sequence of reactions there are two distinctively different approaches (Figure 2).

The first one consists of a two-step approach (Figure 2 right) where first the hydroformylation is carried out with a homogeneous catalyst, then the products are separated from the catalyst and are subsequently hydrogenated to alcohols in a second step. This approach is a common practice in industry. Nevertheless, up to date the process for the effective hydroformylation of longer chain olefins (C5+) is still a challenge because for long chain olefins

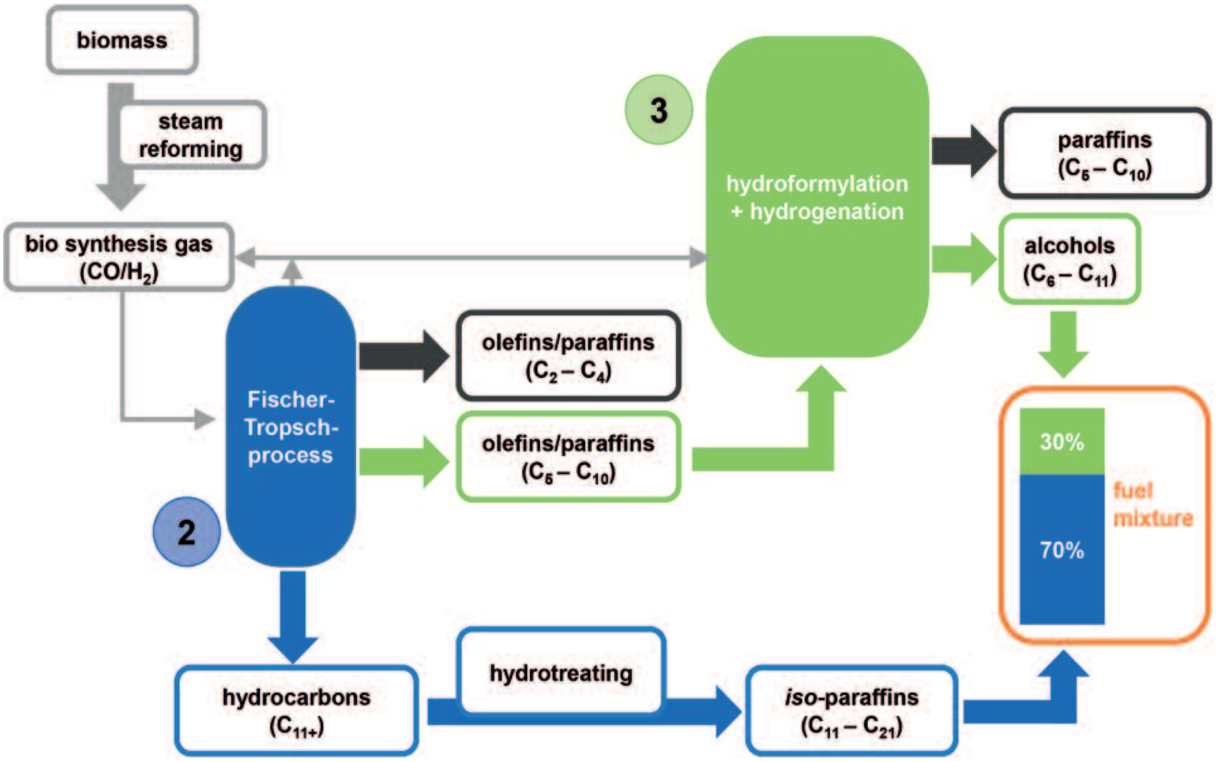

Figure 1. Process Concept of the REDIFUEL Project.

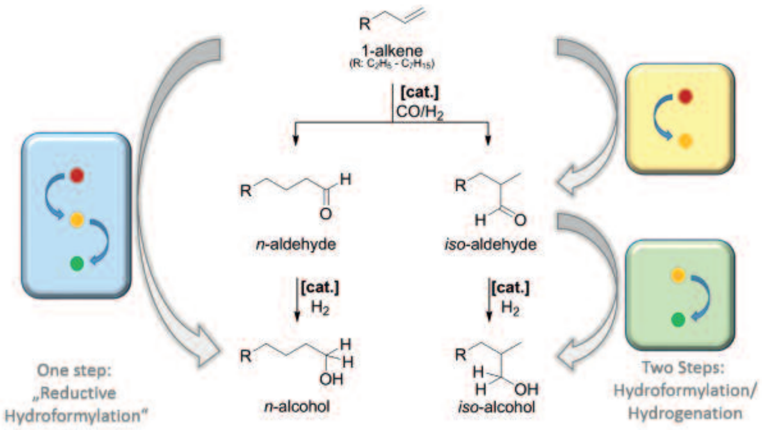

Figure 2. The two different approaches for the hydroformylation/hydrogenation reaction.

the reactivity in liquid/liquid biphasic systems, usually used for catalyst recycling, decreases drastically. Additionally, complex mixtures like that originating from the Fischer-Tropsch process in the REDIFUEL project have not been investigated so far and pose a further challenge.

The second approach is a one-step reaction (Figure 2 left) in which both reactions occur at the same time. A reaction in which several catalysed reactions are run in a single step is also known as tandem catalysis. Tandem catalysis fulfils many principles postulated for a green chemistry because expensive and resource consuming separation steps for the intermediate products can be circumvented. Although known since the 1960 s, the tandem-catalytic approach, also known as reductive hydroformylation, has not gained very much attention since.[7]

Cost effective and active catalysts for this kind of reaction are scarce and new kind of catalysts need to be developed to fulfil the requirements for a sustainable process.

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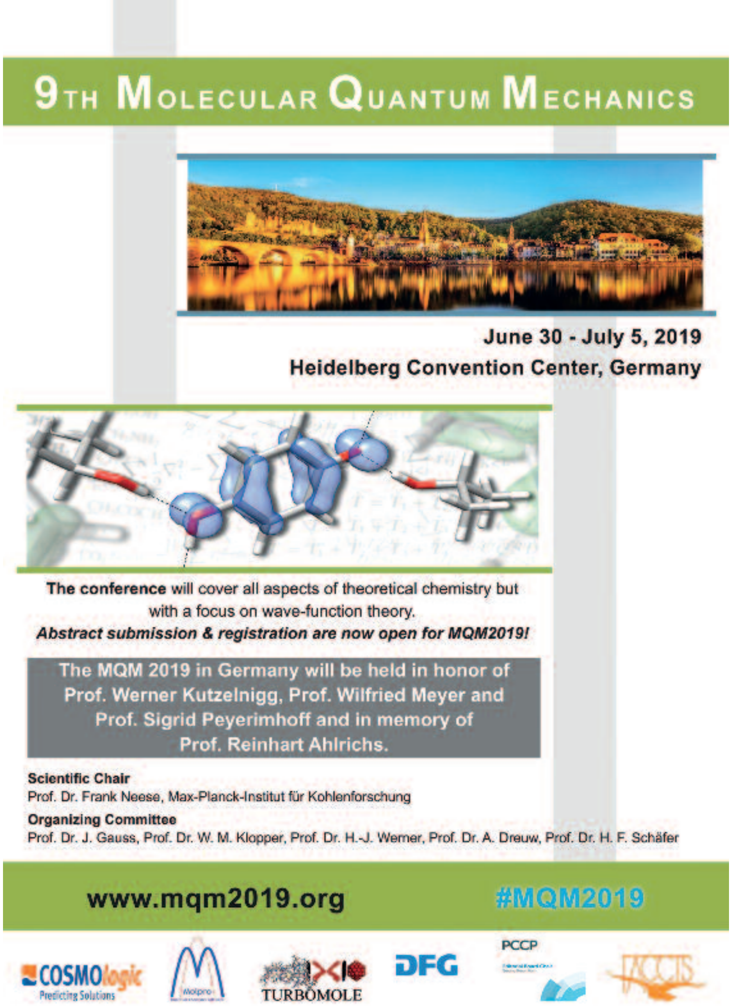
The Research Communications team is responsible for press and public relations, for all graphic design tasks as well as photographs and the documentation of the institute's activities.

The team strives to serve as an interface between the institute and the public, and to create awareness for the important role of basic research in the field of chemical energy conversion. It promotes the perception of the research among the community, press, government, corporate partners, prospective students, alumni and internal stakeholders. Therefore, the team informs journalists with press releases, provides background knowledge and also invites them to visit the institute.

Events

The organization of various scientific and also public oriented events is another major part of the team's work.

In 2018, the CEC and KOFO PR department jointly organized a large international conference on Quantum Chemistry, the 9th Molecular Quantum Mechanics conference (MQM 2019), which took place in Heidelberg. The event was chaired by Prof. Frank Neese (now director of the MPI für Kohlenforschung) and welcomed around 400 scientists from all over the world.



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Other considerable events the Research Communications team plans and coordinates are the Frontiers Award lecture series and the Ernst Haage symposium including the Ernst Haage Award ceremony. Since 2018 the Ernst Haage Prize is jointly awarded by both institutes.

Besides these recurring scientific events, the CEC also frequently opens its doors for school classes and other visitor groups. Together with two Mülheim institutions – the Hochschule Ruhr West and the Haus Ruhrnatur – the institute annually provides a group of school students with the opportunity to participate in a three-day vacation program including scientific experiments and tours of the laboratories. Additionally, the communication team organizes a Girls' Day every year, which aims to interest girls in scientific and technical professions.

The MPI CEC also takes part in big regional science events, such as the „WissensNacht Ruhr" or the „NRW Tag", and displays excerpts of its research to public.

The Research Communications team, furthermore, regularly updates and improves the website and frequently generates content to be provided there, as well as taking care of all posters and printed media of the institute.

Social Media

The PR team regularly posts news about the institute on our facebook page. The content is tailored to a rather broad audience here.

We also set up a twitter account (@mpicec_press) which is mainly used to share scientific content such as publications and research results. It serves (our) scientists to share knowledge, news, publications or job postings. Since the establishment of the institute's account, many scientists followed and set up their own account which we highly welcome. A further expansion of the social media presence is planned.

Another important aspect is the execution of internal communication activities, to provide transparency and keep all employees informed about the institute's proceedings. This is mainly done through the intranet, emailing, and a screen in the foyer.

Impressum

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