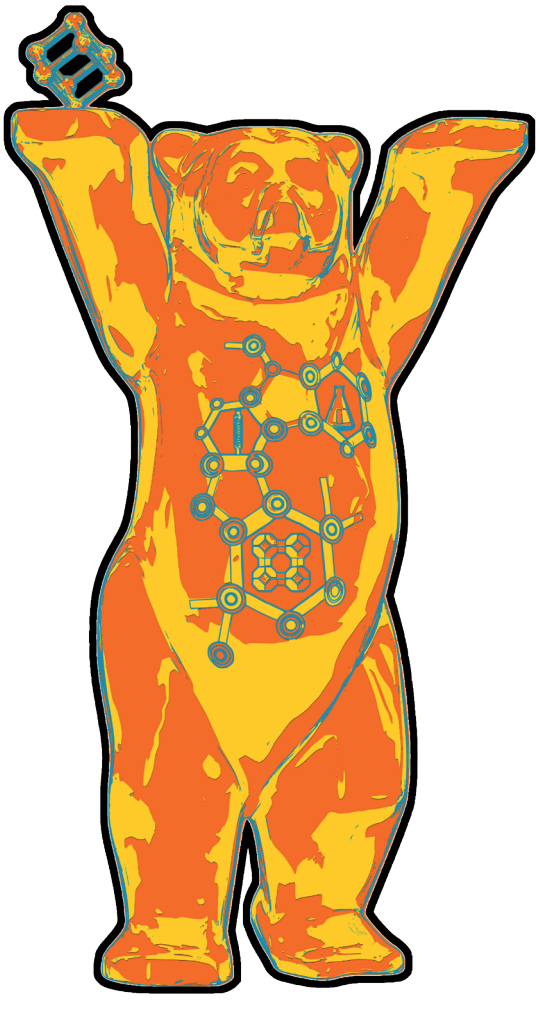

UniCat & BIG-NSE
10th Anniversay

"Unifying Concepts in Catalysis: Status Quo and Challenges"
Symposium at TU Berlin, 12-14 July 2017

Welcome

A Decade of Excellent Catalysis Research in Berlin and Potsdam

We are looking back at a decade in the life of the Cluster of Excellence UniCat and its graduate school BIG-NSE. Catalysis research is an interdisciplinary field per se. The same has been true for the cluster from the very beginning: scientists from chemistry, biology, physics, and chemical engineering work closely together.

We view it as a great success story because, over the past ten years, in collaboration with four universities and two Max Planck Institutes, we have been able to push forward with an extremely challenging research topic, namely to uncover similarities and differences of chemical and biological catalysis.

We have produced a wealth of publications in high-impact scientific journals with an increasing number of joint publications of several UniCat groups, that would have never been possible without this research network. The boundaries between the different subject areas of chemistry, biology, and physics have been almost dissolved. Perhaps most notable is that we could establish a common language and many new scientific (and personal) friendships.

At UniCat, close cooperation between all subject areas is not only a matter of course but also a necessity. This begins with the PhD and master students, who regularly visit the different laboratories, and ends with the principal investigtors (PI), who get together on a regular basis and look into fields outside their core expertise.

People need to know each other, especially the young people. From the very beginning, we looked very far ahead and founded the graduate school BIG-NSE as an integral part of the Cluster of Excellence. Highly talented and motivated students from almost any discipline and country have been welcome to earn their doctorate in one of the UniCat research groups.

In the BIG-NSE, scholarship holders spend their first three months entirely together. That leaves its mark. From the very beginning, we seek to form a tight-knit network between the different disciplines based on the bottom-up principle.

Our cooperation with the company BASF SE, with whom we operate the joint laboratory BasCat, is another success of the UniCat cluster. The goal is to establish a direct connection between innovative fundamental research and industrial application to foster a transfer of fundamental science to applications. In BasCat our central aim is to establish new methods ranging from synthesis to operando analysis and modeling in the field of heterogeneous catalysis.

Since early 2017, the Inkulab, which is another spin-off by UniCat, has been providing entrepreneurs from the fields of chemistry, life sciences, and nanotechnology with free laboratory workstations and a start-up incubation program.

However, in the coming years, the field of green chemistry will experience enormous growth due to environmental needs and the foreseeable shortage of fossil resources (‘Chemiewende’). Not only for these reasons, the ‘Chemiewende’ of-

fers many opportunities for young entrepreneurs specializing in sustainable chemistry towards ecological production.

We will boost such activities in the near future through the foundation of a larger entrepreneurial center, the so-called Chemical Invention Factory (CIF). Thanks to the State of Berlin and the Berlin University of Technology (TU Berlin), its realization in a new building on its Charlottenburg Campus has already been approved.

Unifying Concepts in Catalysis: Status Quo and Challenges

We wish to welcome all participants to our symposium “Unifying Concepts in Catalysis: Status Quo and Challenges” here on the campus of the TU Berlin.

We are proud of presenting 10 years of catalysis research and feel extraordinarily lucky of engaging the renowned scientists Petra de Jongh, Linda Broadbelt, Tobin Marks, Doug Rees, Marc Fontecave, Steven Boxer, and Frank Neese.

In addition, the program includes talks by leading UniCat researchers, a poster session on Wednesday, experience talks with former BIG-NSE students on Friday, and a festive reception on Thursday evening.

We warmly welcome all of you to Berlin, which is a dynamic and creative capital where tradition and innovation coexist in a climate of freedom; an ideal place to get inspired and encouraged to take on challenges.

We wish you all an enjoyable and memorable event!

Matthias Driess
Chair of UniCat

Peter Hildebrandt
Vice Chair of UniCat

Martin Oestreich
Chair of BIG-NSE

Index

Program

Wednesday 12 July

09:00	**Prof. Dr. Christian Thomsen** *Opening address*
09:05	**State Secretary Steffen Krach** *Greeting remarks*
09:15	**Prof. Dr. Matthias Driess** *Introduction*
10:00	**Prof. Dr. Petra de Jongh** *Supported coinage metal catalysts - particle size and support effects*
	Coffee break
11:05	**Prof. Dr. Joachim Sauer** *Activation of small molecules on oxide surfaces - theory and experiment*
11:50	**Prof. Dr. Linda Broadbelt** *Reaction pathway discovery and analysis: bringing biological and chemical catalysis together*
	Lunch
14:00	**Prof. Dr. Reinhard Schomäcker** *Design of OCM catalysts and reactors guided by fundamental research results*
14:45	**Prof. Dr. Tobin Marks** *Catalytic transformations built on the interplay of main group and transition elements*
	Coffee break
15:50	**Prof. Dr. Robert Schlögl** *Dynamics of active sites in heterogeneous catalysis*
	Poster session with snacks and drinks

Thursday 13 July

09:00	**Prof. Dr. Doug Rees** *Ironing out the nitrogenase mechanism*
09:45	**Prof. Dr. Peter Hegemann** *Enzymatic and vectorial catalysis as the basis for optogenetics in neuroscience*
	Coffee break
10:50	**Prof. Dr. Marc Fontecave** *Catalysis for energy storage: enzymes, artificial enzymes and bioinspired materials*
11:35	**Dr. Oliver Lenz** *H_2 Activation from a bio-physical-chemical point of view*
	Lunch
14:00	**Prof. Dr. Frank Neese** *A 'theoretical spectroscopy' approach to catalysis. perspectives and opportunities*
14:45	**Prof. Dr. Kallol Ray** *Chemical activation of dihydrogen, dioxygen, water, and hydrogen peroxide*
	Coffee break
15:50	**Prof. Dr. Steven Boxer** *Electric fields and enzyme catalysis*
17:00	**Reception**

Friday

14 July

09:00 **Prof. Dr. Reinhard Schomäcker**
Introduction

09:15 **Dr. Patrick Littlewood**
Precise catalyst modifi cation by atomic layer deposition for methane dry reforming

10:30 **Dr. Jian Li**
Cell-free synthetic biology for the nextgeneration biomanufacturing

11:15 **Dr. Amandine Guiet**
Pleasures and challenges of being an associate professor in France: a personal review

Lunch

13:30 **Dr. Heiner Schwarz**
Clariant's idea-to-market innovation process – catalyst development for N_2O emission reduction in nitric acid plants

14:15 **Dr. Florian Heims**
A chemist transforms into an engineer – my experiences as Continental Trainee

15:00 **Dr. Bartlomiej Krawczyk**
From academia to industry: my personal experience

Coffee break

16:00 **BIG-NSE alumni panel discussion**

17:20 **Awarding ceremony BIG-NSE graduates**

18:30 **Get-together**

Supported coinage metal catalysts - particle size and support effects

Petra E. de Jongh

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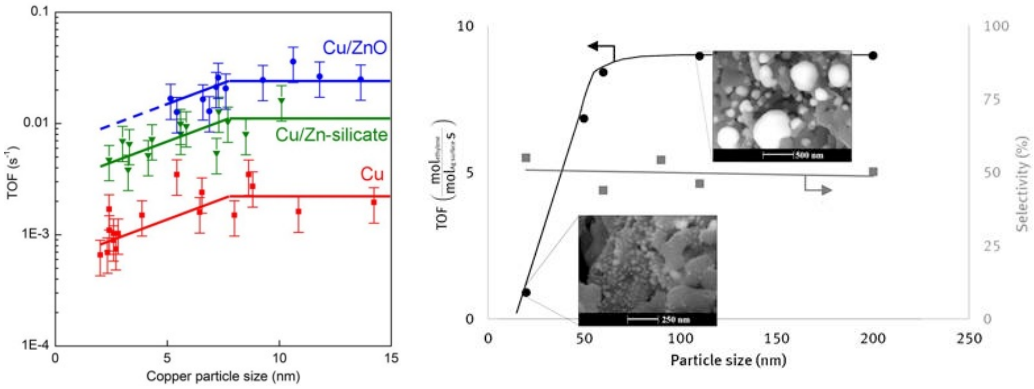
Heterogeneous catalysts often consist of supported metal particles. As the catalytic activity is associated with the surface of the metal particles, in general small metal particles are used, to optimize the specific metal surface area. Interestingly this does seldomly means that the smallest possible particles are the best; in the vast majority of cases an optimum particle size is found.



Surface-specific activity (TOF) versus particle size for (left) copper nanoparticles on different supports used in the methanol synthesis at 260 °C, 40 bar; (right) Ag/α-Al_2O_3 catalysts for ethylene epoxidation at 200 °C (left axis) and selectivity at 2.8% conversion (right axis) of in a flow of 25 mL min-1 of 8.5% oxygen and 30% ethylene in helium.

I will highlight recent work of our group regarding particle size and support effects specifically concerning the coinage metals.I will go into detail regarding recent results particle size and support effects for supported Cu catalysts for methanol synthesis.[1-3] In a second example will also discuss the particle size effects, most notable on activity and selectivity, of supported Ag catalysts for ethylene epoxidation.[4] If time allows a last example will concern support effects using Au nanoparticles for the selective hydrogenation of butadiene.[5]

[1] Prieto, de Jong(h) et al., *Nature Mater* **2013**, *12*, 34.
[2] van den Berg, de Jong(h), et al., *ACS Catal.* **2015**, *5*, 4439.
[3] van den Berg, de Jong(h) et al., *Nature Comm.* **2016**, *7*, 13057.
[4] van Reijen, de Jong(h) et al., *submitted*.
[5] Masoud, de Jong(h) et al, *ChemCatChem* **2017**, accepted for publication

Activation of small molecules on oxide surfaces - theory and experiment

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With the raw material shift in chemical industry to natural gas, there is renewed interest in the oxidative coupling of methane (OCM). Within UNICAT we followed a dual strategy. From the applications point of view we were searching for an improved catalysts (NEWCAT) with tests performed in a miniplant (see lecture by R. Schomäcker). From the fundamental point of view we wanted to understand the mechanism in detail. For this we have chosen the simplest catalysts for this reaction among a large number of complex solid oxides, namely Li-doped MgO.[1] Early, Lunsford proposed that the active sites are $O^{\bullet-}$ radicals neighbored to Li^+, with $Li^+O^{\bullet-}$ formally replacing $Mg^{2+}O^{2-}$, and that the C–H bond is activated by homolytic splitting involving hydrogen atom transfer to the $O^{\bullet-}$ sites.

The activation barriers reported for the rate-determining step of Li-doped MgO, hydrogen abstraction at $Li^+O^{\bullet-}$ sites, varied widely between 85 – 90 kJ/mol for CH4/CD4 isotope exchange and C_2 hydrocarbon formation to 139 – 147 kJ/mol for H abstraction by surface sites in mikrokinetic simulations. UniCat work[2] yielded 90 – 160 kJ/mol with strong variations during the run. Our quantum chemical calculations yielded surprisingly low energy barriers for H abstraction at terraces and steps of Li-doped MgO, between 7 ± 6 and 27 ± 6 kJ/mol.[3] This suggested that the $Li^+O^{\bullet-}$ site may not be the active site or that the rate determining step may be not H abstraction from the C-H bond. Support for this conclusion came from temperature programmed reaction experiments, which showed that on both Li-doped MgO and pure MgO catalysts conversion of CH_4 and O_2 starts at about 410 °C and formation of C_2 species at about 540 °C. We conclude that the reaction pathways are the same for both materials and that the same active sites are present. The role of Li is just in restructuring the surface towards creation of more steps, corners, edges and kinks,[3] as has been also shown by surface science on MgO films.[4]

Further quantum chemical calculations showed that CH_4 binds heterolytically on $Mg^{2+}O^{2-}$ sites at steps and corners, and that the homolytic release of methyl radicals into the gas phase will happen only in the presence of O_2 which picks up the electron and forms a superoxo surface species. Evidence for the activation of oxygen in the presence of electrons on MgO and CaO surfaces also came from experiments on powder catalysts[5] and thin films.[6]

In the new mechanism suggested[3] the role of the oxide is not to provide and receive back electrons, but just to bring together the reactants allowing them to exchange electrons directly between themselves.

[1] S. Arndt, G. Laugel, S. Levchenko, R. Horn, M. Baerns, M. Scheffler, R. Schlögl, R. Schomacker, *Catal. Rev. Sci. Eng.* **2011**, *53*, 424-514, Catal. Rev.-Sci. Eng.

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[3] K. Kwapien, J. Paier, J. Sauer, M. Geske, U. Zavyalova, R. Horn, P. Schwach, A. Trunschke, R. Schlögl, *Angew. Chem., Int. Ed.* **2014**, *53*, 8774-8778.

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[5] P. Schwach, M. G. Willinger, A. Trunschke, R. Schlögl, *Angew. Chem., Int. Ed.* **2013**, *52*, 11381-11384.

[6] Y. Cui, X. Shao, M. Baldofski, J. Sauer, N. Nilius, H.-J. Freund, *Angew. Chem., Int. Ed.* **2013**, *52*, 11385-11387.

Reaction pathway discovery and analysis: bringing biological and chemical catalysis together

Linda J. Broadbelt

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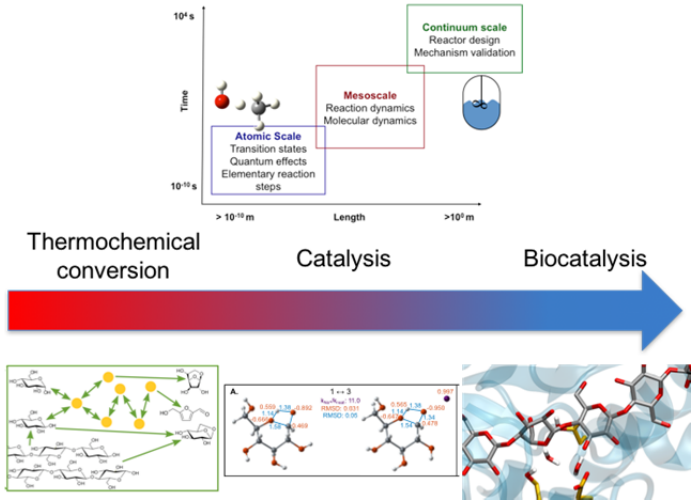
Reaction pathway analysis is a powerful tool to design novel routes to chemicals, identify optimal processing conditions, and suggest strategies for catalyst design. We have developed methods for the assembly of kinetic models of substantive detail to be built that enable the atomic scale to be linked with the process scale as illustrated in Figure 1. We have applied our methodology to a wide range of different problems, including production of silicon nanoparticles[1], biochemical transformations[2-3], polymerization and depolymerization[4-5], and tropospheric ozone formation[6].

While the chemistries we have studied are seemingly very disparate, applying a common methodology to study them reveals that there are many features of complex reaction networks that are ubiquitous, and a kinetic modeling framework can be a tool that unifies understanding of chemical and biological catalytic systems. This talk will focus on mechanistic modeling of a range of conditions for converting hydrocarbons derived from renewable sources, starting with quantitative analysis of chemical catalysis by native inorganic constituents and transitioning to mechanistic understanding of how enzymes achieve exquisite selectivity for similar conversion processes, leading to the potential for the design of novel biochemical pathways.



Reaction pathway analysis links scales ranging from the atomic scale to the continuum scale and can be applied to a wide variety of topicals areas, ranging from thermochemical conversion of biomass to selective catalysis by Nature's catalysts

[1] A.J. Adamczyk, L.J. Broadbelt, *J. Phys. Chem. A*, **2011**, *115(11)*, 2409-2422.
[2] D. Wu, Q. Wang, R. S. Assary, L. J. Broadbelt, G. Krilov, *Journal of Chemical Information and Modeling*, **2011**, *51(7)*, 1634-1647.
[3] M. Moura, J. Finkle, S. Stainbrook, J. Greene, L.J Broadbelt, K.E.J. Tyo, K.E.J., *Metabolic Engineering* **2016**, *33*, 138-147.
[4] R. Vinu and L.J. Broadbelt, *Energy Environ. Sci.* **2012**, *5(12)*, 9808 – 9826
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[6] S.S. Khan, L.J. Broadbelt, *J. Atmos. Chem.* **2009**, *63(2)*, 157-186.

Design of OCM catalysts and reactors guided by fundamental research results

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The oxidative coupling of methane is considered as a dream reaction since it comprises the challenge to catalyze the formation of the desired C_2 products to an extend that the reaction feed, methane, is able to escape the thermodynamically more favored deep oxidation to CO_x. Despite this serious challenge, surprisingly a large number of materials were reported in the literature over the last three decades to fulfill this task, unfortunately with mediocre performance.[1] The broad spectrum of described catalyst materials suggests a rather simple mechanism of this reaction.

On the other hand, numerous of efforts have still not been successful in improving the performance, especially the selectivity, to an economically viable level. The reason for this behavior is the occurance of dozens of elementary reactions, partly at the catalyst surface, partly in the gas phase combine in a complex network with several selectivity controlling junctions. Fundamental theoretical and experimental studies have revealed the essential role of structural defects or redox active elements of the catalyst in providing electrons for the oxygen activation[2,3] The rate and extend of oxygen reduction results in oxygen species with different activity and selectivity against methane and higher hydrocarbons. This finding may be considered as a change in paradigm of the discussion of the selective oxidation of hydrocarbons, be-cause so far the activation of C-H bond was considered as the key step of such reac-tions. The predominant involvement of structural defects of simple basic oxide catalysts causes their strong deactivation behavior under the harsh reaction conditions of OCM. Fortunately, there are stable analogues available like La_2O_3 and $Mn/Na_2WO_4/SiO_2$.

The ascending learning curve about the mechanism of OCM over different catalysts paved the way to improve the catalytic performance of $Mn/Na_2WO_4/SiO2$ by reducing its number of inselective active sites while the number of selective ones were simultaneously in-creased.[4] The knowledge about the desired and undesired gas phase reactions guided the development of reactor concepts for suppressing the unselective overoxidation. [5] Finally, the observation of the catalyst ability to store oxygen and the improvement of the oxygen storage capacity enabled the implementation of the Chemical Looping Technology with a potential for industrial application.[6] Detailed techno-economic analysis were done for several reactor and process concepts and the results were validated on mini plant scale. The lessons learnt about OCM established a technology platform for the development of further complex catalytic processes with single or multiple active sites, such as direct oxidation of methane to methanol or the utilization of CO_2 as C_1-building block in multi-step synthesis processes.

[1] S. Arndt, G. Laugel, S. Levchenko, R. Horn, M. Baerns, M. Scheffler, R. Schlögl, R. Schomäcker, *Catal. Rev. Sci. Eng.* **2011**, *53*, 424-514.

[2] P. Schwach, N. Hamilton, M. Eichelbaum, L. Thum, T. Lunkenbein, R. Schlögl, A. Trunschke, *Journal of Catalysis* **2015**, *329*, 574–587.

[3] K. Kwapien, J. Paier, J. Sauer, M. Geske, U. Zavyalova, R. Horn, P. Schwach, A. Trunschke, R. Schlögl, *Angew. Chem., Int. Ed.* **2014**, *53*, 8774-8778.

[4] M. Yildiz, Y. Aksu, U. Simon, K. Kailasam, O. Goerke, F. Rosowski, R. Schomäcker, A. Thomas, S. Arndt, *Chem. Commun.* **2014**, *50*, 14440–14442

[5] H. Schwarz, M. Geske, C.F. Goldsmith, R. Schlögl, R. Horn, *Combustion and Flame* **2014**, *161*, 1688–1700

[6] V. Fleischer, P. Littlewood, S. Parishan, R. Schomäcker, *Chemical Engineering Journal* **2016**, *306*, 646–654

Catalytic transformations built on the interplay of main group and transition elements

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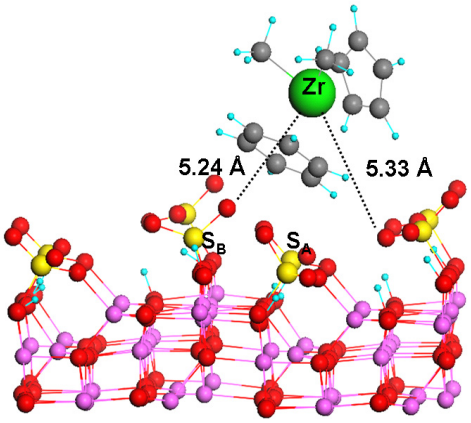
When chemisorbed upon specific metal oxide and carbonaceous surfaces, the reactivity of many types of organometallic molecules is dramatically enhanced. High activities for diverse catalytic olefin and oxygenate transformations are illustrative consequences of such altered reactivity. This lecture focuses on the intricate covalent and non-covalent multi-center interactions that modulate these catalytic processes, focusing on polymerization, hydrogenation, and dehydrogenation processes. Specific topics include: 1) Catalytic chemistry and cooperativity effects in multinuclear organo-group 4 catalysts in homogeneous solution, 2) Catalytic chemistry of organo-group 4 catalysts anchored on/activated by oxide surfaces versus those in homogeneous solution, 3) Definitive structural characterization of these catalysts on “super-acidic” sulfate oxide surfaces, and the scope of their catalytic properties, 4) Catalytic oxygenate chemistry of group 6 oxo complexes bound to activated carbon.



XAS, NMR, and DFT derived model of an organozirconium arene hydrogenation catalyst on sulfated alumina

It will be seen that the information obtained from these studies leads to design rules for next-generation homogeneous and supported catalysts, and to novel and useful polymerization[1,2] and hydrogenation/-dehydrogenation catalysts, including those for the detoxification of gasoline[3,4] or hydrogen production from bioalcohols.[5,6]

[1] S. Liu, A. Motta, A.R. Mouat, M. Delferro, T.J. Marks, *J. Amer. Chem. Soc.* **2014**, *136*, 10460–10469.

[2] M. M. Stalzer, M. Delferro, T.J. Marks, *Catalysis Letters* **2015**, *145*, 3-14 (Review)

[3] W. Gu, M.M. Stalzer, C.P. Nicholas, A. Bhattacharyya, A. Motta, J.R. Gallagher, G. Zhang, J.T. Miller, T. Kobayashi, M. Pruski, M. Delferro, T.J. Marks, *J. Am. Chem. Soc.* **2015**, *137*, 6770–6780.

[4] M.M. Stalzer, C.P. Nicholas, A. Bhattacharyya, A. Motta, M. Delferro, T.J. Marks, *Angew. Chem. Int. Ed.* **2016**, *55*, 5263–5267.

[5] T.L. Lohr, A.R. Mouat, N.M. Schweitzer, P.C. Stair, M. Delferro, T.J. Marks, *Energy Environ. Sci.* **2017**, in press. DOI: 10.1039/C6EE03739A.

[6] A.R. Mouat, T.L. Lohr, E.C. Wegener, J.T. Miller, M. Delferro, P.C. Stair, T.J. Marks, *ACS Catalysis* **2016**, *6*,6762–6769.

Dynamics of active sites in heterogeneous catalysis

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The concept of active sites is fundamental to all varieties of catalysis. It is thus worthwhile to explore its validity in heterogeneous catalysis that seems at first glance to operate on a different definition than used in molecular catalysis.

In the standard model of heterogeneous catalysis active sites are high-energy sites generated during synthesis and activation. They stay active and unchanged in structure during the life of the catalyst and are assumed to be constant in function and number in kinetic formalisms.

In many fundamental and applied reaction studies, some doubt about this simplified definition arouse and several authors postulated “dynamical” active sites without being very precise what this term should mean exactly other that some interaction between catalyst and reactants may induce a change of the structure of active sites with respect to the initial state of the catalytic material. The fact that all catalysts “de-activate” with time is a simple and strongly supporting argument for this assumption.

If we leave the notion that a translational surface structure defined by reconstruction of the underlying bulk structure defines the active site structure then we can widen the term “active site” to the structure of an ensemble being supported on an active phase. This ensemble may exchange ligands as in molecular catalysis if we account fragments of surfaces as “ligands”. Such a notion automatically makes interfacial catalysis to “nano-catalysis” as practical fragments of surfaces will be of nanoscopic dimension.

Catalytic activity may then be induced by structural fluctuation of the ensemble of atoms. In this fluctuation, temporarily high energy configurations may occur that act as active sites in a catalytic process. They would after action fall back into the pool of ensemble sites. No special mechanism for re-activation of the high-energy sites would be required as in our conventional formalism of cyclic operation of a structurally identical active site.

The concept will be illustrated by several examples applying in-situ techniques to identify and count such dynamical active sites. It becomes clear that this widening of the active site concept in heterogeneous catalysis is supported by the progress of in-situ observation and the study of models both in experiment and by theory. The value of such a widened comprehension of the term active site is that the conceptual boundary between interfacial and molecular catalysis is reduced to the material realization of ligands but not to a different function of active sites.

Ironing out the nitrogenase mechanism

Douglas C. Rees

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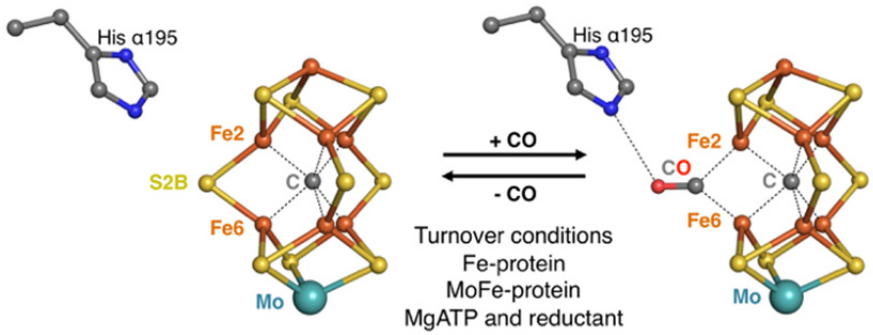
Nitrogenase, the enzyme solely responsible for replenishing the nitrogen cycle from atmospheric dinitrogen, catalyzes the ATP-dependent reduction of dinitrogen to ammonia. Nitrogenase consists of two component metalloproteins, the molybdenum iron (MoFe-) protein and the iron (Fe-) protein. The MoFe-protein contains the active site FeMo-cofactor, while the iron (Fe-) protein, the only known electron donor that supports dinitrogen reduction, binds and hydrolyzes ATP.

The mechanistic questions related to how nitrogenase overcomes the kinetic stability of the NN triple bond to fix dinitrogen under ambient conditions have intrigued chemists for the past century. We have applied a structure-based approach to examine how nitrogenase uses the metalloclusters and ATP-dependent electron transfer to reduce dinitrogen and other substrates under ambient conditions.



Turnover-dependent CO inhibition and reactivation of the nitrogenase FeMo-cofactor

A key to establishing the mechanism of substrate reduction by nitrogenase is the ability to trap and characterize liganded forms of the MoFe-protein. Substrates and inhibitors bind to the FeMo-cofactor only in reduced states generated under turnover conditions. Our studies have established that turnover-dependent binding of CO to the FeMo-cofactor can be accompanied by the reversible displacement of the S2B belt sulfur atom.[1]

Using selenocyanate, we have further demonstrated catalysis dependent, site-selective incorporation of selenium into the same S2B position of the FeMo-cofactor identified as the CO-binding site.[2] Through a series of crystal structures, the exchangeability of all three belt-sulfur sites of FeMo-cofactor was demonstrated, providing direct insights into unforeseen rearrangements of the metal center during catalysis.

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Enzymatic and vectorial catalysis as the basis for optogenetics in neuroscience

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In Biology, many processes as energy consumption, as well as synthesis, assembly, and targeting of macromolecules, transport of ions, replication and stress responses etc. are catalyzed by more or less complex catalysts.

In the past 10 years our group studied photocatalysed ion transport across membranes mediated by light-gated ion channels or light driven ion pumps from microalgae. We have studied the principles photocatalysed vectorial transport (vectorial catalysis) by employment of biochemical, electrical, spectroscopic and structural techniques or incorporation of synthetic artificial chromophores in collaboration with several UniCat members (P. Hildebrandt, A. Zouni, P. Scheerer, R. Bittl, N. Budisa etc).

We engineered many different transporters respective absorption, kinetics, ion selectivity and converted active into passive transporters that are in total widely used as instruments for the analysis of neuronal networks in the neurosciences (for example in Neurocure) founding the basis for the new field of Optogenetics. We also began to study natural and engineered light-gated enzymes as Histidin-Kanase-Rhodopsins (HKRs), light-activated phosphodiesterases (LAPDs, designed by Andreas Möglich) and photo-activated cyclases with BLUF or rhodopsin-type photosensory domains.

Catalysis for energy storage: enzymes, artificial enzymes and bioinspired materials

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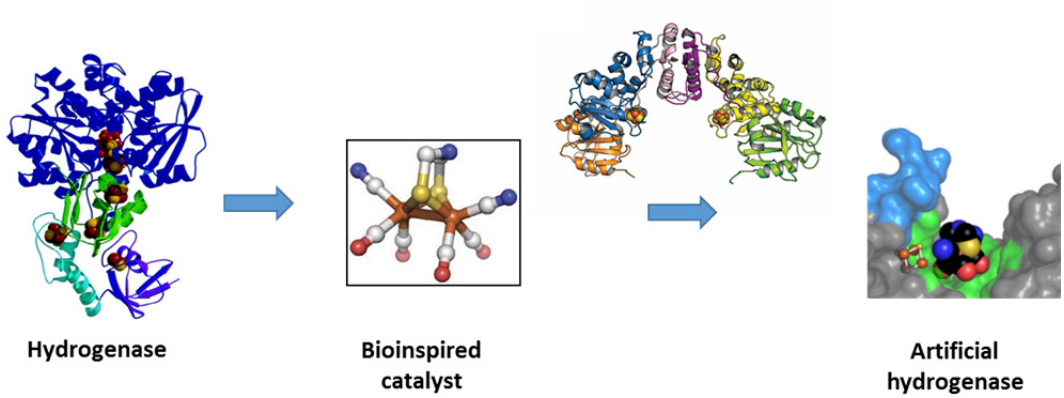
The development of renewable energies, such as solar energy, requests new efficient technologies for storing them in the form of energy-dense chemicals. One example is hydrogen, derived from water, which can be used as an energy vector. Another example is carbon-based compounds, such as carbon monoxide, formic acid, methanol and hydrocarbons, derived from reduction of CO_2. To achieve this goal one needs to optimize cheap and stable metal-based catalysts for decreasing the energy barriers associated with the multi-proton and multi-electron processes at work.

Natural enzymes (hydrogenases, formate dehydrogenases and CO dehyrogenases, photosystem II, laccase) provide a unique source of inspiration. The bioinspired chemistry rational approach can be usefully exploited to generate novel classes of catalysts, not only homogeneous but also heterogeneous. [1,2] Artificial enzymes combining a protein host and a synthetic catalyst is another fascinating approach still very little explored.[3] These strategies will be illustrated using a variety of examples for proton reduction, CO_2 reduction and water oxidation.



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H_2 activation from a bio-physical-chemical point of view

Many coworkers and collaborators, and Oliver Lenz

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A great variety of chemical compounds catalyzing the reduction of two protons to form dihydrogen have been synthesized and characterized, but most of them require considerable overpotentials, and the reaction is unidirectional [1]. Reversible H_2 oxidation yielding two protons and two electrons is mediated only by few compounds, which have been synthesized by using the architecture of nature's H_2-activating catalysts – hydrogenases – as an inspiration [2,3].

Hydrogenases perform reversible H_2 oxidation at high turnover frequencies, low overpotential and mild conditions. Their catalytic center usually contains either two iron atoms or one iron and one nickel, in addition to cyanide and carbon monoxide ligands which are bound to iron [1]. The research performed within UniCat concentrates on a special class of [NiFe]-hydrogenases that catalyzes H_2/H^+ cycling in the presence of high O_2 concentrations, which is a rare trait and relevant for biotechnological application [4].

In a highly collaborative effort, we were able to solve the first crystal structure of an O_2-tolerant membrane-bound [NiFe]-hydrogenase [5]. Genetic engineering, biochemical, crystallographic, spectroscopic, and computational techniques were used to identify a novel iron-sulfur cluster species that changes its geometry and chemical composition in a redox-dependent manner, thereby confering protection against deleterious effects of O_2 [6].

For another type of [NiFe]-hydrogenase, catalyzing the H_2-mediated reduction of the cofactor NAD^+, vibrational spectra have been re-interpreted to develop a model for O_2 tolerance based on the reversible sulfoxygenation of the catalytic center [7]. On the basis of this model, a bioinspired, heterobimetallic S-oxygenated [NiFe] complex has been synthesized as a structural and spectroscopic model compound. Its detailed characterization revealed properties similar to those of the enzyme [8], demonstrating a successful interplay of biology, chemistry, and spectroscopy to unravel peculiar characteristics of certain biocatalysts and fundamentalfunctional concepts.

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A 'theoretical spectroscopy' approach to catalysis: perspectives and opportunities

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The talk will explain and highlight how one can use a combination of highlevel spectroscopy and quantum chemistry to gain insight into the structure and mechanism of transition metal based catalyst.

Chemical activation of dihydrogen, dioxygen, water, and hydrogen peroxide

Kallol Ray

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Small molecule activation constitutes one of the main frontiers of inorganic and organometallic chemistry, with much effort directed towards the development of new processes for the selective and sustainable transformation of abundant small molecules such as dioxygen (O_2), water (H_2O), hydrogen peroxide (H_2O_2) or protons (H^+) into high-value chemical feedstocks and energy resources. Because nature mostly uses metal ions to activate these relatively inert molecules and modulate their reactivity, much inspiration for the field has come from bioinorganic chemistry.

This talk will focus on some of the recent highlights from the Cluster of Excellence UniCat on homogenously catalyzed bioinspired activation of small molecules, as well as stoichiometric reactions that further our understanding towards such ends. It will cover many aspects of small molecule activation including: organometallic chemistry, (electro)catalysis, photochemistry, spectroscopy, synthesis, and detailed mechanistic studies involving trapping of reactive intermediates.

The demonstrated examples will help to emphasize the continuous effort of UniCat in uncovering the structure-reactivity relationships of biomimetic model complexes, which may allow vital insights into the prerequisites necessary for the design of efficient catalysts for the selective functionalization of unactivated C–H bonds, O_2/H_2O/H_2O_2 activations, or H^+ reductions by using cheap and readily available first-row transition metals under ambient conditions.

Electric fields and enzyme catalysis

Steven Boxer

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The contribution of electrostatics to differentially lower the energy of the transition state in enzyme-catalyzed reactions has been widely debated. The vibrational Stark effect (VSE) provides a method for obtaining quantitative information on the electric field projected onto a vibrational probe bond. If this bond is placed where charge is separated going to the TS, it can provide a measure of the *functionally relevant* electric field.

This approach depends on a combination of vibrational Stark spectroscopy (vibrational spectroscopy in an external electric field), vibrational solvatochromism, MD simulations, and measurements of IR or Raman spectra in complex environments. Each part of this analysis involves approximations that can be tested and refined. This approach has now been used to study several enzymes, including the reinterpretation of data already in the literature, and can be extended to the analysis of time-dependent changes probed by vibrational spectroscopy and chemical catalysts as well.

Extensions of this approach to libraries of enzymes that have either evolved naturally or been evolved in the laboratory using directed evolution will be discussed to test whether the electric field observable correlates with natural selection.

Precise catalyst modification by atomic layer deposition for methane dry reforming

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Atomic Layer Deposition (ALD) of metal oxides is increasingly being explored as a highly controlled method of synthesizing catalysts with precisely controlled active layers, nanoparticles, or novel core-shell/overcoat support arrangements [(1)]. It has been previously shown that a metal oxide overcoat can improve the thermal stability of transition metal heterogeneous catalysts as well as reduce their propensity to coking [(2, 3)].

In this work, alumina ALD has been used to modify a range of standard, model, inverse and commercially available nickel-alumina catalysts. These are tested for methane reforming with CO_2 (Dry Reforming, or DRM), which is becoming increasingly attractive as a source of syngas due to the abundance of its reactants and the need to diversify of carbon feedstocks in the chemicals industry. Although this has resulted in catalysts with extremely high activities and/or stabilities in comparison to their uncoated counterparts [(4)], the phase behavior and morphology of the overcoat under the harsh conditions required from DRM, or the interaction of the oxide with the active nickel phase, have not been clearly understood.

Chemisorption and reaction studies have been used to investigate the effects of changes in the alumina overcoat on catalytic activity. Using a range of microscopy and vibrational spectroscopy techniques we have shown that not just the size but the chemical environment of overcoated nickel particles is preserved under DRM conditions. Additional studies explore the effect of ALD synthesis conditions on the overcoat layer and catalysis, including the stability of inert phases formed under calcination conditions. This has allowed development of materials modified by ALD towards advanced heterogeneous catalysts with an industrial focus.

This work was made possible by an NPRP exceptional grant award [NPRP-EP X-100-2-024] from the Qatar National Research Fund (a member of the Qatar Foundation). The statements made herein are solely the responsibility of the authors.

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Cell-free synthetic biology for the next-generation biomanufacturing

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The foundational principle of cell-free synthetic biology is that precise, complex biomolecular systems can be constructed without using intact cells. Because of no cell walls, this open system allows for easy manipulation, monitoring, sampling, and optimization. Therefore, *in vitro* cell-free systems have many advantages over *in vivo* cell systems including high product yields, fast reaction rates, tolerance of toxic precursors and/or products, and highly controlled reaction conditions. Recently, cell-free synthetic systems are becoming important as platforms for enabling biosynthetic routes to proteins, novel biopolymers, and small molecule chemicals (Figure 1). In this context, we take advantage of cell-free biology to design and construct efficient platforms for the rapid and cost-effective next-generation biomanufacturing.

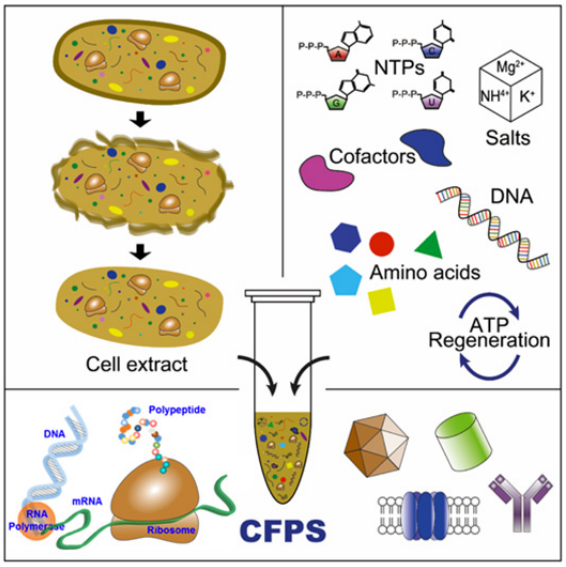

***Figure 1**. Cell-free synthetic biology for the synthesis of proteins, materials, and chemicals*

Here, I will show cell-free protein synthesis of “difficult-to-express” metalloproteins,[1] cell-free incorporation of non-standard amino acids into proteins,[2] cell-free biosynthesis of natural products,[3] as well as development of a novel *Streptomyces*-based cell-free system for the expression of GC-rich gene coded proteins.[4] Looking forward, cell-free synthetic biology will continue to open new opportunities for (i) debugging and optimizing modular construction of pathways and circuits through the use of simple, well-defined experimental conditions and (ii) carrying out molecular transformations when bioconversion yields, productivities, or cellular toxicity limit feasibility of whole-cell fermentation.

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Pleasures and challenges of being an associate professor in france: a personal review

Amandine Guiet

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10 years after the creation of Unicat and its graduate school, over 100 BIG-NSE students have graduated. After struggling to "bridge the gap in catalysis" during the PhD phase, the next challenge for the former BIG-NSE fellows is to bridge the gap between the PhD and the professional life.

After graduating in 2014 from the TU Berlin under the supervision of Professor Anna Fischer and co-supervision of Professor Matthias Driess and Professor Arne Thomas, I started to work as a temporary Associate Professor at the University of Maine in Le Mans in the “Institute of Molecules and Materials of Le Mans (IMMM)” in the group of Oxides and Fluorides. Two years later, I obtained a permanent position as Associate Professor in this group, which corresponds to a “Maître de Conference” position in the french academic ranks.

What are the pleasures and the challenges of being an associate professor in France and how did UniCat and BIG-NSE help me obtain this position?

In the first part of this presentation, the French academic system and Associate Professor functions in French universities will be introduced. In the second part, my research activity in the group of Oxides and Fluorides at the University of Maine in Le Mans will be presented. Since 2014, I have been working on a new project developed by Gwenaël Corbel, CNRS full-time Junior Researcher, entitled "copper-based antibacterial materials".

The aim of the project is to discover copper based materials able to kill resistant pathogens associated with Healthcare-Associated Infections in order to incoporate them into soft and hard surfaces in contact with the patient.

Clariant's idea-to-market innovation process – catalyst development for N_2O emission reduction in nitric acid plants

Heiner Schwarz

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Due to its high global warming potential laughing gas constitutes one of the most detrimental greenhouse gases. Nitric acid plants are the principal source for industrial N_2O emissions.[1] Thanks to Clariant's catalyst portfolio for N_2O abatement plant operators are able to drastically reduce their emissions and help protect the environment.

Installation of Clariant's secondary N_2O abatement catalyst EnviCat® N2O-S in a medium-pressure nitric acid plant.

The talk focuses the secondary catalyst technology EnviCat® N2O-S. I want to highlight several aspects of industrial catalyst development and commercialization in the framework of Clariant's Idea-to-Market process which supports the project team in development and successful commercialization of innovative products.

Apart from aspects of marketing and commercialization, we highlight the importance and challenges in catalyst engineering and creating a convincing value proposition for the customer.

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A chemist transforms into an engineer – my experience as Continental trainee

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I did my PhD in the group of Prof. Dr. Kallol Ray in the field of inorganic chemistry at the Humboldt Universität zu Berlin with the support of a BIG-NSE scholarship. During this time, it was very fascinating for me to understand the in-depth chemical and electronic structure of catalytically active transition metal complexes and to dig deep into the understanding of their reactivity. The only thing missing was the practical application of this acquired knowledge into a final, physically manifested product.

During my university time I used to equivocate on the question of friends or my family, what I exactly do, because they anyway would not understand. Since I joined Continental this has completely changed and I'm now able to explain even my grandma what I do in one simple phrase – "I develop the tires of tomorrow".

This desire to focus more on applied research and development led my way into industry and, luckily, I was offered the position of an eXplore Tires RnD Trainee at Continental in the Global Technology Center in Hanover. It was a unique possibility for me to get to know a completely new activity field, which I have never considered before, as well as to build up my network within one of the biggest automotive suppliers in the world.

After my first six months in the company as a trainee I joined the truck tires development department in my current function as a technology development engineer responsible for the development of new truck tire technologies and tire sizes. I've been learning a lot of new and interesting things about tires, their construction and how they are being manufactured. Although I deal in my position more with tire construction, mechanics and engineering than chemistry, I profit from my soft and self organization skills, which I acquired during my time as a PhD student.

From academia to industry: my personal experience

Bartlomiej Krawczyk

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My fascination with natural science started early in my life in my father's basement, which was filled with chemicals and laboratory glass (used for preparation of photography reagents). Over time pure chemistry fascination shifted towards biology resulting in an MSc. in Biotechnology. Afterwards, working on my PhD thesis, supported with a BIG-NSE scholarship, I focused on the discovery and biosynthesis of microbial secondary metabolites.

All this experience was a great foundation for my current position at Boehringer-Ingelheim where I work on drug discovery. During my talk I will give an overview of my career pathway including scientific fascinations, achievements, but also failures.

D1-1: From mechanistic studies of oxidative coupling of methane reaction to an enhancement in its performance

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Ethylene (C_2H_4) is the building block for a vast range of chemicals, from plastics to anti-freeze solutions and solvents. It is among the most often produced organic compounds of the petrochemical industry. The current market demand is more than 150 million tons per year with a global growth rate of around 3.5 % over the next 5 years[1]. It is usually produced in steam-cracking units from a range of petroleum-based feedstocks, such as naphtha.

Therefore, its production capacity and cost are strongly depending on the availability and price of crude oil. Because of the increasing demand for ethylene besides the limitation in the oil reserves, an alternative process to produce this essential compound is required. Oxidative coupling of methane (OCM), which converts methane directly into C_2 products and higher hydrocarbons (Eq-1[2]), may be the way to realize this aim. The most important advantage of this process is that it converts the less expensive methane, with its reserves exceeding those of crude oil, to highly demanded product, i.e. ethylene[3].

$$CH_4 + O_2 \rightarrow C_2H_6 \text{ or } C_2H_4 + H_2O \qquad \text{Eq.1}$$

Nevertheless, the OCM process has not yet been commercialized, as a minimum yield of about 30% towards C_2 products is required for making it economically viable. The main reason for this limitation is the occurrence of partial and total oxidation reactions, which are thermodynamically more favorable than the coupling reaction. To solve this problem the reaction should be kinetically controlled. To reach this aim, the origin of formation of CO_X was investigated theoretically and experimentally in more detail over two of the well known active catalysts for the OCM, i.e. MgO and Mn-Na_2WO_4/SiO_2.

Those studies showed that in the presence of either gas phase oxygen or nucleophilic adsorbed oxgen species, the rate of formation of CO_X is increasing.On the countrary, the strongly adsorbed $O^{-\cdot}$species are believed to lead to selective conversion of methane to C_2 products. Therefore, the yield of the reaction to C_2 components was tried to be enhanced by both ways, increasing the concentration of the selective oxygen species and decreasing the unselective ones.

The main focus of the work presented here is surveying the influence of different feasible techniques, capable of controlling the concentration of selective oxygen species on the catalyst surface, on performance of OCM. Firstly, the oxidizing agent was changed from O_2 to N_2O. The reason for this was not only the lower activity of the latter component but also the presence of just one oxygen atom in its structure. This increased the chance of formation of oxygen ion radicals, i.e. selective oxygen species, and consequently the overall selectivity towards the desired C_2 products.

Secondly, the activity of unselective adsorbed oxygen species was suppressed by saturating the reaction flow with water, since the rate of activation of water molecules with the unselective active sites of the catalyst is higher than of methane. In addition, reaction of

water results in the formation of OH radicals which themself activate methane molecules in the gas phase, resulting in higher reaction conversion.

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D1-2: Miniplant scale analysis of oxidative coupling of methane (OCM) process

Hamid Reza Godini[1], Tim Karsten[1], Stanislav Jaso[1], Steffen Stünkel[1], Son Xuan Nghiem[1], Shankui Song[1], Setarehalsadat Sadjadi[1], Erik Esche[1], Oliver Görke[2], Ulla Simon[2], Alexander Gurlo[2], Reinhard Schomäcker[3], Günter Wozny[1], and Jens-Uwe Repke[1]

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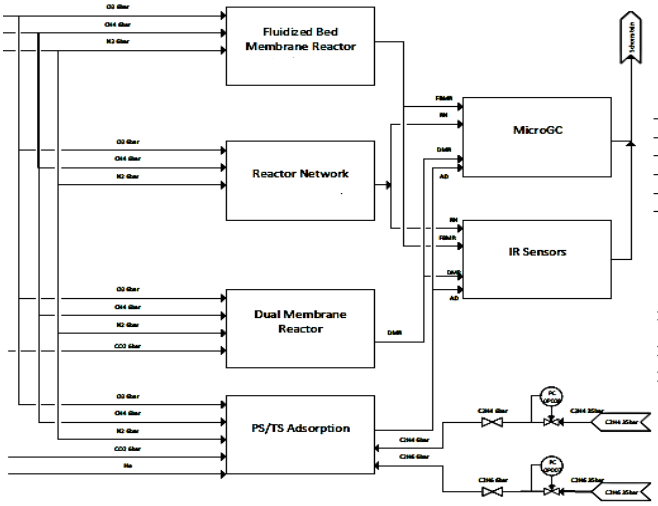
Oxidative Coupling of Methane (OCM) has been intensively investigated since 1970s. In the beginning of the UniCat project and after reviewing all available OCM literature, it was decided to construct a miniplant scale facility at TU Berlin and simultaneously investigate the performance of reactors and downstream units to address following questions:

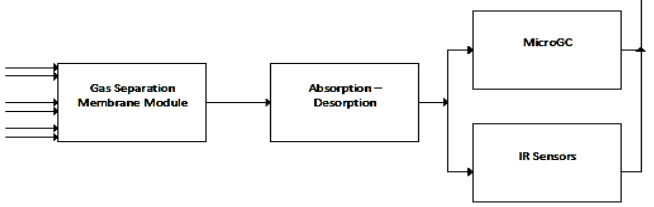
1. Catalyst stability test and validating the lab-scale reactor results by testing the catalyst in different reactor types (fixed-bed, membrane reactor, fluidized-bed and fluidized-bed membrane reactor) and scales (bigger than lab-scale) under different reaction conditions (carbon dioxide and steam as diluents) close to industrial application
2. Testing alternative downstream units for carbon dioxde separation (polymer mebrane and CO2-absorption) and ethylene separation via adsorption unit in miniplant scale
3. Analyzing the interaction of the operation and performance of the reactor and downstream units in the context of concurrent process engeenring/optimal conceptual design

Using the UniCat Mn-Na_2WO_4/SiO_2 catalyst and a miniplant membrane reactor, very promising 25.5% C_2-yield with 66% C_2-selectivity were achieved. [2] In the fluidized-bed membrane reactor, 23% C_2-yield with 49% C_2-selectivity was achieved for testing 45 gram of catalyst. Hybrid system of polymer membrane and amine absorption provided a lower ethylene loss and energy for separation of CO_2 separation.

Extensive model-based analysis using CFD, MATLAB, MOSAIC and Aspen supported the conceptual techno-economic analysis of the individual and integrated OCM with methane reforming [3] and ethane dehydrogenation processes. Kinetic analysis and tracking



Unit	Dimensions	Operating Conditions
(1) Absorption column	40 mm ID, 5 m Length	20-40 °C, 10-32 bar
(2) Desorption column	100 mm ID, 4 m Length	110-130 °C, 1-3 bar
(3) Membrane Reactor	7 mm ID, 20 cm Length	700-850 °C, 1-6 bar
(4) Fluidized-bed Reactor	40 mm ID, 80 cm Length	700-850 °C, 1-6 bar
(5) Adsorption	60 mm ID, 1 m Length	Ads. 40 °C, Des. 200 °C



Block-Flow-Diagram for the units in the UniCat OCM Miniplant at TU Berlin [1]

the reaction rate of the main OCM reactions along the reactor has also been performed in order to improve the OCM reactor design. [4] Several national and international cooperations (e.g. EU MEMERE project for OCM membrane reactor [5]) have been established as a result and in continuation of these activities.

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[5] Third European Workshop on Membrane Reactors MR4PI2017, Italy, March **2017**

D1-3: Bioinspired hydroxylation of methane

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[2] BasCat − UniCat BASF Joint Lab, TU Berlin, EW K 01, Hardenbergstraße 36, 10623 Berlin
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[4] Institute of Chemistry, HU Berlin, Brook-Taylor-Strasse 2, 12489 Berlin

The selective oxidation of methane to methanol by oxygen is a higly challenging target because of the higher reactivity of the primary oxidation product compared to methane. In nature microorganisms are able to catalyse the oxidative degradation of methane with high efficiency. Therefore synthesis and structural characterization of bioinspired methane monooxygenase (MMO) models based on Fe and Cu metal sites are of high interest for this research field. The catalytic function of particulate MMO is based on a dicopper site and Cu^{II}–O–Cu^{II} units were discussed as the ultimate oxidant. This finding has stimulated the investigation of dioxygen activation at dinuclear copper(I) complexes supported by a novel dinucleating ligand systems that stabilize such functions.[1,2]

Furthermore Cu-containing zeolites have been studied as catalysts for methane to methanol conversion. Recently, UniCat researchers have found that solid-state ion-exchanged Cu/mordenites exhibit a significantly higher activity for the partial oxidation of methane to methanol than comparable reference catalysts, i.e., Cu/mordenites prepared by the conventional liquid-phase ion exchange procedure (Figure 1).[3]

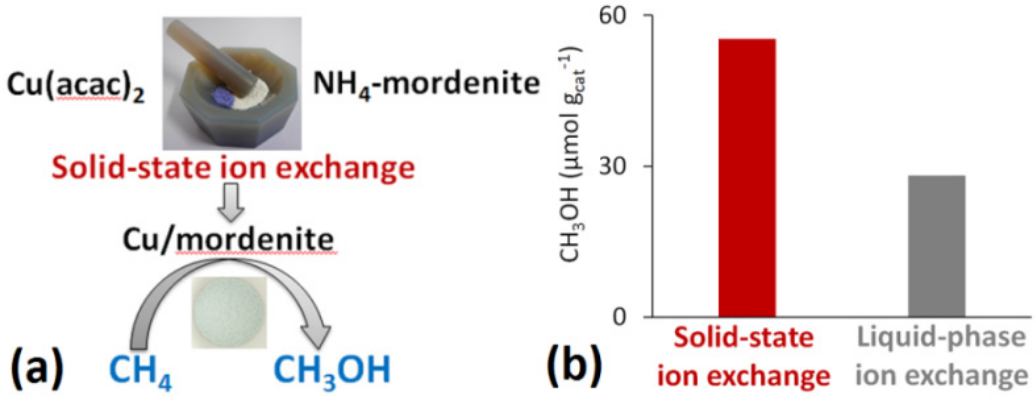

Figure 1. *(a) Procedure for Cu/mordenite preparation, (b) Methanol production over Cu/mordenites prepared using solid state and liquid phase ion exchange*

In situ ultraviolet−visible (UV-vis) spectroscopy indicates that different active clusters including dicopper and tricopper-oxo complexes are formed in the catalyst upon oxygen treatment. Notably after activation of methane, different methoxy intermediates seem to be generated at the Cu sites from which one is preferably transformed to methanol by reaction with water. The findings can guide synthetic approaches to further enhance the activity of biomimetic Cu-based catalysts for the direct conversion of methane to methanol under mild conditions.

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D2-1: Dry reforming of methane as building block of a future C1-chemistry

Patrick Littlewood[1], Elham Baktash[1], Xiao Xie[1], Michael Bernicke[1], Johannes Pfrommer[1], Torsten Otremba[1], Arne Thomas[1], Reinhard Schomäcker[1], Matthias Driess[1], G.D. Wehinger[2], T. Eppinger[2], M. Kraume[2], H.R. Godini[2], S. Xiao[2], S. Jaso[2], S. Stünkel[2], D. Salerno[2], S. Nghiem Xuan[2], S. Song[2], M. Kim, O. Görke, G. Wozny[2]

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Carbon dioxide utilization is not only politically desirable, but also economically favorable, because CO_2 is available in huge quantities and high quality. So far, only a few processes such as urea production or some power-to-gas technologies make use of substantial amounts of CO_2.

Production of syngas as a feedstock for a variety of chemical value added chains via dry reforming of methane (DRM) would be another promising option. For this endothermic equilibrium limited reaction highly active and coke resistant catalysts are required. This is especially true if the reactor is not designed and optimized as a standalone process, but as part of an integrated multi-step process in combination with oxidative coupling of methane (OCM) providing the CO_2 and heat for the reaction. Beside noble metal catalysts, nickel based catalysts show promising performance but also a strong tendency to deactivate, most typically by coking. In joint efforts different approaches were chosen within UniCat to prepare nickel catalysts, like particle formation from solid solutions[1] , single source precursors[2], or NiMn mixed metal oxides[3].

A catalyst with superior performance was obtained when nickel nanoparticles were modified with alumina by Atomic Layer Deposition (ALD)[4]. Both the high activity and stability may be explained by the occurring metal support interactions between the alumina layer and the nickel particles.

The performance and kinetic data of these catalysts were used for the design of DRM reactors with improved feed distribution for reducing the tendency towards coking [5,6], dual-membrane reactors[7] for the combination of DRM and OCM, as well as for techno-economic analysis of such integrated processes[8].

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D2-2: Transformation of carbon oxides - CO_2 activation at surfaces

Contribution from the groups of J. Sauer[1], R. Schlögl[2], H.-J. Freund[3]

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We consider carbon dioxide activation and reaction through various routes:

- Reduction by transfer of electron leading to bent CO_2
- Coupling reaction in a $(CO_2)_2^-$ dimer to oxalate by second charge transfer
- Reduction of CO_2 with H_2 to CH_3OH and H_2O
- Dry reforming of CH_4 with CO_2
- Formation of urea from oxalate and NI_3
- Reaction of CO_2 with unsaturated hydrocarbon
- Formation of acetate from CH_4 and CO_2

The following specific projects have been carried out:

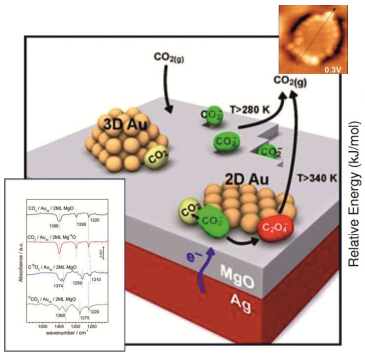

Figure 1

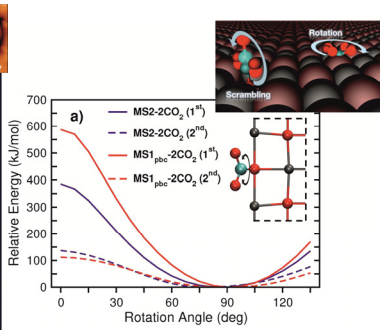

Figure 2

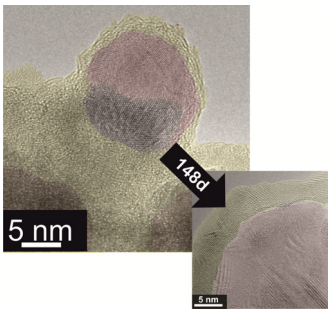

Figure 3

- Model studies involving charge control at Au nanoparticle-oxide interfaces (thin film and doped bulk samples). CO_2 activation through electron transfer to form oxalates has been identified (Fig. 1).
- Bonding of CO_2 to simple oxide surfaces, such as CaO(100) has been studied with respect to preferential adsorption sites and molecular surface exchange reactions via isotopic labelling studies (Fig. 2).
- Detailed structural TEM studies on $Cu/ZnO/Al_2O_3$ catalysts for methanol synthesis from CO_2 has been reported identifying ZnO overlayers on Cu nanoparticles as the active morphologies (Fig. 3). For dry reforming catalysis $NiMgAl_2O_4$ active morphologies have been studied indicating $NiAl_2O_4$ overgrowth of Ni nanoparticles in the active phase.

D2-3: Unifying CO_x transformations in chemistry: conversion of carbon oxides by (bioinspired) molecules

Christian Limberg[1], Matthias Driess[2], Martin Oestreich[2], Matthias Schwalbe[1]

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Interconnecting the knowledge on chemical systems where CO_x can be used as synthetic building block for value-added products is a highly desired aim in sustainable chemistry. This poster summarizes major achievements towards a unifying chemocatalytic approach in CO_x transformations, using various types of molecular entities by different UniCat groups:

1) Modelling of the active site of carbon monoxide dehydrogenase (CODH) by molecular compounds that contain nickel centers in low oxidation states and vacant coordination sites, and related studies on Ni-centered CO_x binding and transformations. [1-5]
2) New strategies for the conversion of carbon dioxide into methane by metal-free catalysis are described. Aside from exhaustive reduction of CO_2, partial reduction to intermediate oxidation levels such as formate and methanol is equally important. Utilizing reactive divalent group 14 element compounds and silylcopper(I) for CO_2 activation will also be discussed in this poster. [6-8]
3) Bioinspired tethered Ru−S complexes are presented which were found to catalyze the temperature-dependent hydrosilylation of carbon dioxide with a variety of simple monohydrosilanes chemoselectively to bis(silyl)acetals or silylated methanol, respectively. This is the first example of a catalyst system that gives access to both of the intermediate oxidation states in a controlled way. [9]
4) Remarkable new results on light-driven photocatalytic reduction of carbon dioxide without using noble metal-based photosensitizers will also be discussed. [10-11]

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[11] C. Matlachowski, M. Schwalbe, *Dalton Trans.* **2015**, *44*, 6480-6489.

D3-1/D3-4: Chemical activation of dihydrogen, dioxygen, water, and hydrogen peroxide

Kallol Ray

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Small molecule activation constitutes one of the main frontiers of inorganic and organometallic chemistry, with much effort directed towards the development of new processes for the selective and sustainable transformation of abundant small molecules such as dioxygen (O_2), water (H_2O), hydrogen peroxide (H_2O_2) or protons (H^+) into high-value chemical feedstocks and energy resources. Because nature mostly uses metal ions to activate these relatively inert molecules and modulate their reactivity, much inspiration for the field has come from bioinorganic chemistry.

This talk will focus on some of the recent highlights from the cluster of excellence (UniCat) on homogenously catalyzed bioinspired activation of small molecules, as well as stoichiometric reactions that further our understanding towards such ends. It will cover many aspects of small molecule activation including: organometallic chemistry, (electro)catalysis, photochemistry, spectroscopy, synthesis, and detailed mechanistic studies involving trapping of reactive intermediates.

The demonstrated examples will help to emphasize the continuous effort of UniCat in uncovering the structure-reactivity relationships of biomimetic model complexes, which may allow vital insights into the prerequisites necessary for the design of efficient catalysts for the selective functionalization of unactivated C–H bonds, O_2/H_2O/H_2O_2 activations, or H^+ reductions by using cheap and readily available first-row transition metals under ambient conditions.

D3-3: In-situ X-ray absorption experiments for tracking (electro-)catalysis: water oxidation by first-row transition metal oxides

Petko Chernev[1], Ivelina Zaharieva[1], Marcel Risch[1,2], Diego Gonzales-Flores[1], Rodney Smith[1,3], Stefan Loos[1], Chiara Pasquini[1], Katharina Klingan[1], Reza M. Mohammadi[1], Paul Kubella[1], Holger Dau[1]

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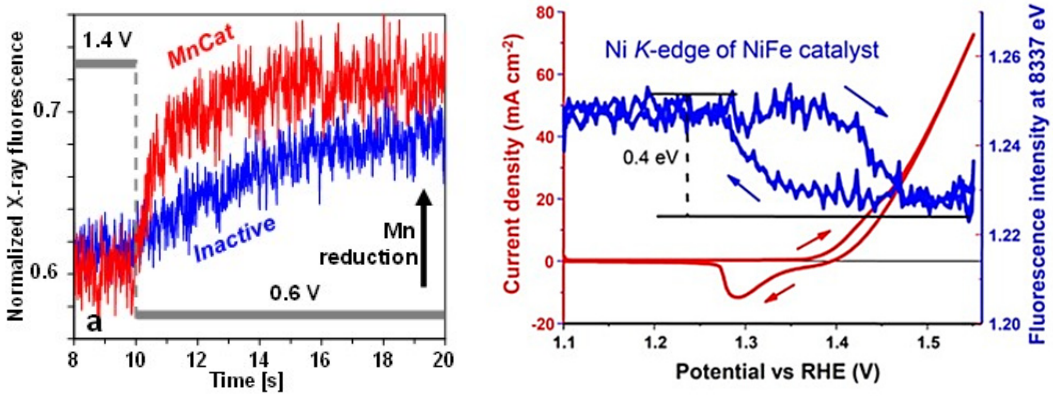
Efficient water oxidation, the anodic process of water electrolysis, will be pivotal in the 'ab-initio' production of non-fossil fuels. Water electrolysis is a process known for more than 200 years, but mechanistically water oxidation is still insufficiently understood. This has motivated the development of new experimental tools to investigate, at atomistic level, electrocatalytic water oxidation under operation conditions.



Left: After a potential jump, $Mn^{III<=>IV}$ oxidation-state changes are much faster in a catalytically active oxide than in an inactive one.[4] Right: X-ray tracking of Ni oxidation state changes during a CV, revealing $Ni^{II<=>III/IV}$ redox-state changes (versus $Fe^{III<=>IV}$).

We find that the active catalyst material on water-oxidation electrodes are often (or even always?) non-classcial, hydrated oxides where catalytic activity relates closely to redox-state changes of the metal ions. [1-4] The functional crucial redox dynamics, induced by variation of the electrode potential, were revealed by X-ray absorption spectroscopy at the respective metal *K*-edges.[2-4]

Investigations of various water oxidation catalysts have been pursued jointly with UniCat groups (of P. Strasser, M. Driess, A. Fischer, C. Limberg, A. Thomas; the above author list includes exclusively the X-ray team members from FUB).

[1] D. Gonzalez-Flores, I. Sanchez, I. Zaharieva, K. Klingan, J. Heidkamp, P. Chernev, P. W. Menezes, M. Driess, H. Dau and M. L. Montero, *Angew. Chem. Int. Ed.*, **2015**, 54, 2472-2476.

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D4-1: Towards increasing structural diversity of biologically active ribosomal peptides

Rashed Al Toma[1], Emmanuel Reyna-González[2], Vincent Wiebach[1], Anja Kuthning[1], Bianca Schmid[1], Florian Oldach[1], Stefan Grätz[1], Alexander Denisiuk[1], Nediljko Budisa[1], Elke Dittmann[2] and Roderich Süssmuth[1]

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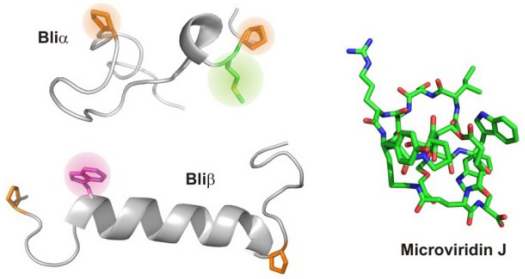
Due to their wide structural diversity and remarkable stability combined with a broad spectrum of bioactivities, ribosomally synthesized and post-translationally modified peptides (RiPPs) are of great interest for the development and use as drugs. Structure alteration of *in vivo*-produced biologically active RiPPs can be achieved by employing genetic code engineering and expansion in a rational designed manner. This includes the application of selective-pressure incorporation (SPI) and stop codon suppression (SCS) approaches for the incorporation of isostructural and orthogonal noncanonical amino acids (ncAAs) into the core peptides of the target RiPPs.[1-3]



3D Structure of lichenicidin Bliα and Bliβ and microviridin J

As an example we are presenting here the successful incorporation of various isostructural ncAAs into the core peptides of the class II lanthipeptide lichenicidin Bliα and Bliβ.[1,2] The tested ncAAs, include surrogates of Pro, Trp and Met, were incorporated by SPI approach in *E. coli*. The antimicrobial activities of the newly generated lichenicidins were tested against *Micrococcus luteus*. Bio-orthogonal chemistry (click reactions) was also applied on some of the newly generated congeners as post-biosynthetic modifications in term of further increasing their structural diversity.[1] Tricyclic microviridins were synthesized using a combination of solid phase peptide synthesis (SPPS) and enzymatic transformations. The novel method employs constitutively activated ATP grasp ligases that carry covalently attached leader peptides at their N-termini catalyzing lactone and lactam ring formation. The engineering potential of the chemo-enzymatic technology was demonstrated using synthetic peptide libraries that were used to optimize microviridin variants targeting the serine proteases trypsin and subtilisin.[4] The approach further facilitates the production of microviridins predicted in microbial genomes obviating the need of cultivation [5] and the incorporation of ncAAs for further functionalization of microviridins.

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D4-1: Deciphering fungal cyclodepsipeptide synthetases and exploring *aspergillus niger* as an expression host for secondary metabolites

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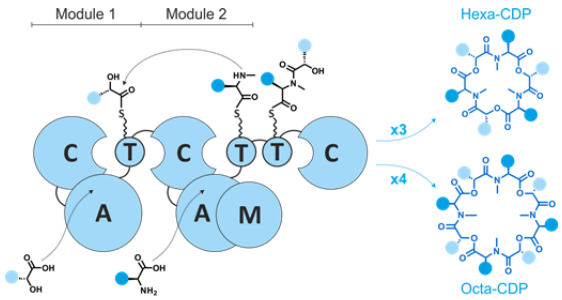
Recently, we could show that the filamentous fungus *Aspergillus niger* is an excellent host for the production of secondary metabolites (SMs) from the class of fungal cyclodepsipeptides (CDPs)[1]. We generated *A. niger* strains that express the non-ribosomal synthetases[2] enniatin synthetase (ESYN), beauvericin synthetase (BeSYN) and bassianolide synthetase (BaSYN) under control of the inducible Tet-On system and we are able to produce the corresponding SMs in titers reaching several hundred milligrams per liter. From previous experiments we know that these synthetases show a relaxed substrate specificity[3,4,5]. Thus, if alternate substrates are provided to the enzymes, novel CDP derivatives are synthesized. By a precursor-directed-biosynthesis approach, we used the generated *A. niger* strains to produce a library of novel "unnatural" CDPs and sent the purified compounds for bioactivity studies.



Biosynthesis mode of CDP synthetases

Furthermore, we aim at deciphering the architecture and synthesis mechanism of the CDP synthetases. By swapping module 1 from a fourth CDP synthetase (PF1022 synthetase (PFSYN)) with module 1 of ESYN and BeSYN, two functional hybrid synthetases were generated, that incorporate the hydroxy acids D-lactate or D-phenyllactate into the enniatin and beauvericin backbones[5]. By swapping the C_3-domain of ESYN, BaSYN and BeSYN, we could further investigate the ring size determining factors of the synthetases. This enabled us to reprogram the synthetases to generate the novel compounds octa-enniatin and octa-beauvericin.

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D4-2: Unnatural amino acids as bioorthogonal tags

Jan-Stefan Völler[1], Vladimir Kubyshkin[1], Patrick Durkin[1], Hernan Biava[1], Benjamin Noichl[1], Peter Hildebrandt[1], Christian Hackenberger[2] Thomas Braun[3] Ned Budisa[1]

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Methodologies and approaches for the evolution of tRNA:aminoacyl-ligase orthogonal pairs (o-pair) for the ribosomal site-specific incorporation of non-canonical amino acids (ncAA) into proteins are now well established in the UniCat cluster.

This general method has been successfully applied to study and parametrize a variety of biological systems and processes. For example, we have used ncAAs as sensitive spectroscopic probes to map the local protein electrostatics[1] for a better understanding of natural catalytic processes and improvement of biocatalyst engineering.[2] Next, we have generated a structurally defined framework for the presentation of multivalent ligands by the combination of ncAAs incorporation and bioorthogonal reactions.[3] In order to further ensure the incorporation efficiency, we have established an expression system with intracellular ncAA synthesis and subsequent translation into target proteins.[4] Undoubtedly, metabolic engineering will further diversify the chemical arsenal for the large-scale production of proteins or peptide-based drugs with useful markers.[5]

Currently, we are developing various innovative catalytic methods for the synthesis of fluorine and carborane containing ncAAs for orthogonal translation (Braun and Budisa) as well other unique functionalities such as photo-switches, novel spectroscopic probes (with P. Hegemann, see section E4-1), redox activity, introduction of unnatural metal cofactors, moieties capable of novel orthogonal chemical reactivity and metal ion binding or novel steric properties. [6]

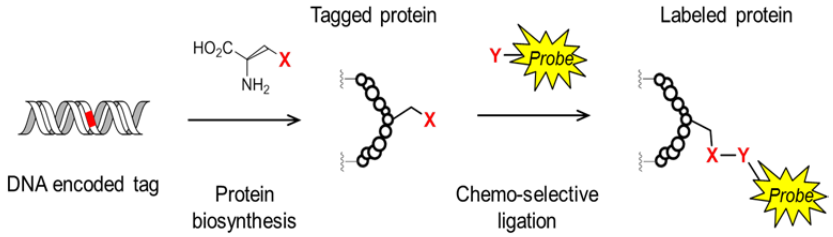

Illustration of a systematic and modular way to engineer proteins as structured scaffolds. Unnatural protein translation enables for the ribosomal incorporation of a specific number of unnatural functional groups (bioorthogonal tags) into a protein, which can be chemoselectively conjugated (functionalized) after bio-expression.

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E2-1: C_1 compound activation and turnover at the Ni,Fe active site of a CO dehydrogenase

Domnik, L.[1], Ciaccafava, A.[2], Jeoung, J.H.[1], Fesseler, J. [1], Tombolelli, D.[3], Schrapers, P.[4], Haumann, M.[4], Dau, H.[4], Mroginski, A.M. [3], Zebger, I. [2], Hildebrandt, P.[3], Dobbek, H.[1]

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Bacteria can use different pathways to grow on CO/CO_2 among which the reductive acetyl-CoA pathway is likely the oldest and of primordial origin. A central catalyst in this pathway is the Ni,Fe-containing CO dehydrogenase (CODH) that reversibly interconverts CO_2 and CO at a [NiFe4S4S] cluster in their active site.

Recently, we could show that CODH activates CO_2 for reduction to CO by binding it between Ni and Fe. CO_2 is two-electrons reduced in the trapped state and is likely stabilized by strong π-backbonding interactions featuring a short Ni-C bond, reminiscent of a Ni-carbene complex. Other C1-compounds are also activated at the Ni,Fe-dyad: cyanide, an isoelectronic surrogate of CO and competitive inhibitor binds at Ni, completing its square-planar coordination.

A combination of vibrational spectroscopy and DFT calculations revealed that CN-binding occurs concomitant with removal of a hydroxy-ligand from an Fe of the [NiFe4S4S] cluster that upon dissociation is protonated by a neighboring lysine residue. A cyanide bound state can also be generated from cyanate, which binds like CO_2 between Ni and Fe and undergoes reduction to CN^-.

Our results show how inhibited states and alternative substrates provide novel insights into the reaction mechanism of CODHs.

E2-2: The mechanism of formate oxidation catalyzed by formate dehydrogenase from *rhodobacter capsulatus*

Duffus, B.R.[1], Hartmann, T.[1], Mitrova, B. [1], Wahlefeld, S.[2], Schrapers, P.[3], Belger, D.[4], Haumann, M.[3], Hildebrandt, P.[2], Zebger, I.[2], Mroginski, A.M. [4], Wollenberger, U. [1], Teutloff, C.[3], Leimkühler, S.[1]

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Biological carbon dioxide (CO_2) reduction is an important step by which organisms obtain energy and carry out metabolic processes. The photosynthetic bacterium *Rhodobacter capsulatus* encodes a Mo-dependent and NAD^+-requiring formate dehydrogenase (FDH) that is proposed to catalyze formate oxidation and CO_2 reduction in the cytoplasm at a bound bis-molybdopterin guanine dinucleotide (bis-MGD) cofactor. Additional active site features include an essential sulfur ligand and a participatory Cys386 residue.

The inhibiting anion nitrate displays competitive inhibition, which supports direct binding to the Mo atom. To provide mechanistic insight regarding the mechanism of substrate conversion and inhibition, careful spectroscopic studies have been performed on the enzyme, including EPR, IR, resonance Raman and XAS spectroscopy in combination with DFT calculations.

Collectively, our results support our mechanistic model of FDH, in that the Cys residue becomes displaced upon reduction of Mo(VI) to Mo(IV), and in that a C_1-intermediate binds directly to a diamagnetic Mo(IV) oxidation state.

E2-3: Expression and characterization of active-site variants of *Oligotropha carboxidovorans* CO dehydrogenase

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Carbon monoxide dehydrogenases (CODH) catalyze the oxidation of CO with H_2O to yield CO_2, two protons and two electronsTHe molybdenum and copper containing CODH from *Oligotropha carboxidovorans* catalyzes the oxidation of carbon monoxide to carbon dioxide, providing the organism both a carbon source and energy for growth. The heterotrimeric CODH $(\alpha\beta\gamma)_2$ is composed of a large molybdopterin cytosine dinucleotide cofactor-containing (MCD) subunit (CoxL), a small iron-sulfur-containing subunit (CoxS) and a midium flavin-containing subunit (CoxM).

The characteristic of this enzyme is its unique binuclear metal center containing a molybdenum atom and a copper atom bridged by a μ-sulfido ligand ($CuSMoO_2$). The posttranslational assembly of the complex binuclear center involves a number of gene products encoded by the megaplasmid-localized *coxBCMSLDEFGHIK* gene cluster. While several studies on the Mo- and Cu-dependent CODH where carried out to date, the posttranslational assembly of the binuclear metal center ($CuSMoO_2$) in addition to details on the catalytic mechanism remain to be clarified.

To obtain more mechanistic details, the production of site-directed active site variants in CODH is of great importance. Here, we present for the first time a heterologous expression system in *E. coli* yielding in correctly assembled and active CODH. With this system we were able to identify the chaperone involved in MCD cofactor insertion into CODH. Furthermore, we expressed and purified active site variants (E763Q, F390V, F390Y, F390P and ΔC388) of CODH to study the effects of these amino acid exchanges on enzyme assembly and the catalytic mechanism. First spectroscopic data on the enzyme are presented.

E3-3: Structural insights into the light-driven auto-assembly process of the water-oxidizing Mn_4CaO_5-cluster in photosystem II

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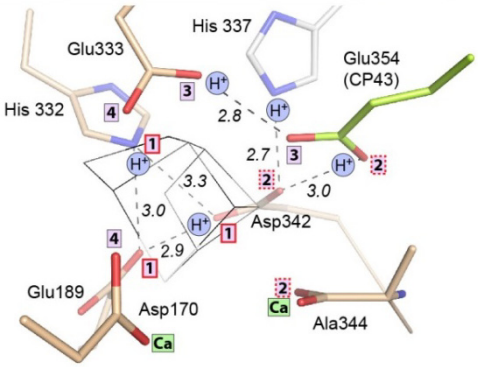
In plants, algae and cyanobacteria, Photosystem II (PSII) catalyzes the light-driven oxidation of water at a protein-bound Mn_4CaO_5-cluster, the water-oxidizing complex (WOC). In the intact organism, the light-induced assembly and disassembly of the WOC proceed parallel to the physiologically important PSII repair cycle. How WOC depletion affects the structure of PSII is still unclear, but essential for understanding the assembly/disassembly process. We studied dimeric PSII core complex (dPSIIcc) crystals, in which the Mn_4CaO_5-cluster was fully depleted, and obtained the crystal structure of 2.55 Å resolution [1].



Apo-WOC at 2.55 Å resolution: Arrangement of the amino acid side chains around the WOC without the Mn_4CaO_5-cluster. Numbers indicate distances (Å) between O/N atoms, which are likely connected by H-bonds.

Surprisingly, the removal of the Mn_4CaO_5-cluster leaves the positions of all coordinating amino acid residues and most nearby water molecules largely unaffected, resulting in a nearly perfectly pre-organized ligand shell for incorporation of the Mn ions during light-driven metal-cluster assembly (photo-activation). This pocket structure likely serves as basis for kinetically competent and error-free formation of the WOC under illumination. First experiments initiating (i) partial disassembly and (ii) partial re-assembly after complete depletion of the Mn_4CaO_5-cluster provided preliminary insight into a distinct metal-cluster intermediate formed during both assembly and disassembly, which may comprise two Mn ions bound at the Mn1 and Mn2 site and interconnected by two bridging oxides (Mn1-$(\mu\text{-}O)_2$-Mn2).

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E3-4: Biocatalytic activation of oxygen species

Neumann, B.[1], Jetzschmann, K.J.[1], Yarman, A.[1], Peng, L.[1], Kielb, P.[2], Götz, R.[2], Ly, K.H.[2], Utesch, T.[2], Hildebrandt, P.[2], Schwalbe, M.[3], Fischer, A.[4], Dobbek, H.[5], Weidinger, I. M.[2,6], Mroginski, A.M.[2], Scheller, F. W.[1], Wollenberger, U.[1]

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Activation of oxygen by both inorganic but also biological catalysts is a challanging task for alternative energy conversion, bioanalysis and selective functionalization of unactivated C–H bonds in organic compounds. The catalytic reduction of dioxygen or hydrogen peroxide to water by immobilized catalysts on an electrode is a key element in fuel cells, and biosensor technology. Peroxidases, oxygenases and peroxygenases are able to catalyse these reactions, however with the inherent instability of biological catalysts.

In this project we demonstrate that biomimetic and bioengineered catalysts are attractive targets, as they allow to combine appropriate catalytic efficiency with robustness under reaction conditions. Biomimetic catalysts for oxygen and peroxide activation on the basis of heme peptides and synthetic porphyrin structures were developed in synergetic combination with electrode surface design.

As a new level of surface structuring molecularly imprinted polymers (MIPs) have been introduced in order to allow reproducible regeneration of the enzyme/electrode architecture and to enhance the selectivity by suppressing interfering side reactions. The structure and functionality of these surface architectures were characterized by means of electrochemical and spectroelectrochemical methods.

The presented highlights are: (1) surface tuned electron transfer and electrocatalytic peroxide activation by a hexameric tyrosine-coordinated heme protein HTHP [1, 2], (2) peroxide activation by MP-11 in ATO [3] and electropolymerized TThP, (3) proton coupled electron transfer and oxygen activation with a surface immobilized Hangman porphyrin compound [4,5], (4) molecularly imprinted polymers for recognition of subunits, and stabilization of Cytochrome P450s and (5) induced selectivity by product imprinting of electropolymers in combination with enzyme- catalyzed reactions [6].

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E3-1: Biocatalytic H_2/H^+ cycling in the presence of O_2

R. Bittl, A. Fischer, S. Frielingsdorf, B. Friedrich, J. Fritsch, T. Goris, R. King, L. Lauterbach, F. Lendzian, J. Löwenstein, N. Heidary, P. Hildebrandt, M. Horch, M. Kaupp, J. Kalms, D. Millo, M. A. Mroginski, F. Neddermeyer, V. Pelmenschikov, Y. Rippers, M. Saggu, P. Scheerer, A. Schmidt, J. Schoknecht, E. Siebert, C. Teutloff, T. Utesch, I. Zebger, O. Lenz, & collaborators

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Hydrogenases are nature's most efficient biocatalysts for the reversible catalytic splitting of molecular hydrogen into two protons and electrons [1]. From an application point of view, the so-called "O_2-tolerant" [NiFe] hydrogenases, which are capable of H_2/H^+ cycling even under aerobic conditions, are of particular interest [2,3].

In a highly collaborative approach, a team of UniCat researchers employed a great variety of experimental and theoretical methods to provide detailed – and partially unexpected – insights into structure and function of several O_2-tolerant [NiFe] hydrogenases present in the model Knallgas bacterium *Ralstonia eutropha*.

Some of the most important findings are summarized below:

(1) The first crystal structure of an O_2-tolerant [NiFe] hydrogenase uncovered an unprecedented [4Fe-3S] cluster [4].

(2) The unique [4Fe-3S] cluster undergoes redox-dependent structural rearrangements, which are crucial for the O_2 tolerance of the corresponding hydrogenase [5, 6].

(3) O_2 tolerance of certain hydrogenases is based on the catalytic reduction of O_2 to harmless water [7].

(4) An integral experimental/theoretical approach provided detailed insights into the adsorption process of hydrogenase on biocompatible gold electrodes, which has biotechnological implications [8].

(5) Resonance Raman spectroscopy has been established as a tool to reveal novel insights into the hydrogenase active site geometry [9].

(5) The re-interpretion of infrared vibrational spectra based on *in vivo*, *in vitro,* and *in silico* studies inspired a new model for O_2 tolerance based on the reversible sulfoxygenation of the catalytic center of the NAD^+-reducing [NiFe] hydrogenase [10,11].

(6) The *in vivo* production of the NAD^+-reducing [NiFe] hydrogenase has been successfully modelled using an on-line optimal experimental design [12].

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E4-1: Introduction of analytically valuable unnatural amino acids to monitor and control protein functions

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The incorporation of unnatural amino acids is a promising method capable of delivering new chemical functions and specific spectroscopic probes in protein structures. There is a particular need to control protein functions with light that can direct and respond to biological processes on demand. In all of these experiments, the requirements for minimal disruption of the biological context inevitably lead to the use of an expanded genetic code in the design of such systems.

Traditionally, we carry out site and residue-specific incorporation of different unnatural amino acids and visualize them in various spectroscopic settings. For example, we have found by chemical modifications of the essential Trp that electron transfer processes of a flavoprotein photocycle can be selectively imanipulated.[1] Next, we have determined the subtle modifications of the proline side chains (the side chain steric, inductive effects and pKa) to allow the quantification of the contributions of the proline residues to protein expression capacity[2] and structural integrity.[3]

Recently, we have developed orthogonal pairs for the site-specific incorporation of FTIR[4] and NMR-active markers (see section D4-2). We were particularly successful in the development of a system for the incorporation of blue amino acids azulenylalanine to map vibrational energy transfer in proteins (Baumann et al., under revision). We have also made advances in the chemical preparation and bio-expression of photo-caged amino acids (ONB-DOPA)[5], which are substrates for suitably constructed orthogonal pairs (Hauf, Möglich et al., under revision)

In this context, an expanded genetic code provides three general strategies [6] for the engineering of light-sensitive protein behavior: (1) direct introduction of the fluorophore or bioorthogonal marker which can be post-translationally modified, (2) uncaging of masked substrates (i.e. photolabile groups), and (3) the incorporation of a reversible photoswitching groups (which is the focus of current and future research in the UniCat cluster).

These technologies together will enable spatiotemporal manipulation and interrogation of individual proteins, biocatalytic cascades and whole cells.

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E4-2: Enzymatic and vectorial catalysis as the basis for optogenetics in neuroscience

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In Biology, many processes as energy consumption, as well as synthesis, assembly, and targeting of macromolecules, transport of ions, replication and stress responses etc. are catalyzed by more or less complex catalysts.

In the past 10 years our group studied photocatalysed ion transport across membranes mediated by light-gated ion channels or light driven ion pumps from microalgae. We have studied the principles photocatalysed vectorial transport (vectorial catalysis) by employment of biochemical, electrical, spectroscopic and structural techniques or incorporation of synthetic artificial chromophores in collaboration with several UniCat members (P.Hildebrandt, A.Zouni, P. Scheerer, R. Bittl, N. Budisa etc).

We engineered many different transporters respective absorption, kinetics, ion selectivity and converted active into passive transporters that are in total widely used as instruments for the analysis of neuronal networks in the neurosciences (for example in Neurocure) founding the basis for the new field of Optogenetics. We also began to study natural and engineered light-gated enzymes as Histidin-Kanase-Rhodopsins (HKRs), light-activated phosphodiesterases (LAPDs, designed by Andreas Möglich) and photo-activated cyclases with BLUF or rhodopsin-type photosensory domains.

BasCat – the UniCat BASF JointLab: towards a new rational design concept for catalysts

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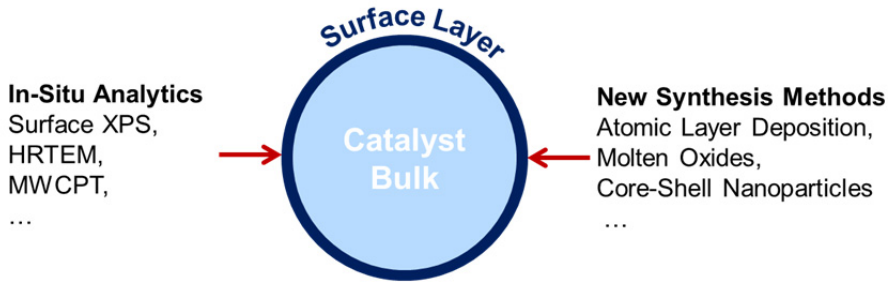
In 2011 the Cluster of Excellence "Unifying Concepts in Catalysis" (UniCat) and the chemical company BASF SE founded the new joint lab BasCat, an academic institution including more than 20 scientists (3 Directors, 7 Postdocs, 9 PhDs, scholars and students) at the Technische Universität Berlin. In 2016, The cooperation contract between TU Berlin and BASF was extended for additional five years till end of 2021.

Heterogeneous catalysis is crucial for meeting the challenges of our future. The partners of BasCat are dedicated to improve our fundamental understanding of heterogeneous catalysis, to transfer this understanding to a new rational design concept for industrially relevant catalysts, and to bring these catalysts to application in industry. BasCat pursues multidisciplinary approaches to generate the fundamental knowledge needed for developing alternative processes to activate less reactive molecules. The current research program focuses on oxidation catalysis, but also includes synthesis gas reactions. One example is the oxidative coupling of methane which has been investigated within UniCat since 2007, another example is the conversion of propane and butane into oxygenates (acrylic acid, maleic anhydride) in a one-step reaction.

Key for establishing novel processes are long term stable, highly selective and sufficiently active catalysts. All previously proposed empirical and solid state (bulk structure-function relationships) concepts in oxidation catalysis have not had the predictive power to generate new catalysts. This is related to the fact that under reaction conditions catalyst surfaces usually differ from the bulk, e.g. in composition and oxidation state, due to self adapting processes. For a rational catalyst design concept and a successful knowledge-based prediction of catalyst performance, new development of methods for dedicated analysis and synthesis of catalyst surface layers is essential.



In-situ analytics and dedicated synthesis of self adapting catalyst surface layer

The scientists at BasCat are in a strong position for achieving this goal, benefitting from the combination of academic base research, e.g at the forefront of In-situ analytics within the FHI, and deep insights into industrial research via BASF and hte.

Berlin International Graduate School of Natural Sciences and Engineering

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The BIG-NSE was founded in May 2007, as PhD school of the Cluster of Excellence UniCat (Unifying concepts in Catalysis) in order to attract excellent students from all over the world to write their PhD in one of the approx. 50 labs of the member institutions of the Cluster.

Main aims of the School, besides attracting talented young people to Berlin, were as well to

i) help the students write their PhD under the best possible conditions, meaning, among others, help them:
   - perform all administrative tasks (visa prolongation, enrollment, health insurances etc.) in a short time,
   - find an accommodation prior to/on arrival,
   - integrate (learn German, find friends, etc.) in their new environment as quickly as possible,
   - find a suitable research group, topic etc. among the numerous offers of the Cluster, and write a work plan of their PhD.
ii) support them in all possible matters ("mentoring") during the PhD and offer them possibilities two acquire new soft skills in addition to an excellent scientific education
iii) help them finish their PhD under a reasonable amount of time and quickly find a good job once they are finished.

So far, the BIG-NSE has had 123 PhD students, 76 of them being already finished. Only approximately half of the BIG-NSE members have been financed by a BIG-NSE/UniCat/DFG scholarship, though: the other half was financed by external funding sources (national scholarships, in particular form the Chinese Scholarship Council – CSC -, but also DAAD or industry scholarships). Every year in October, a new batch of approx. 10 new PhD students starts the BIG-NSE program with the 3.5 months-long "Initial Phase" which will be described in part C. below. After the IP, it then usually takes 4 years in average to finish the thesis and defend it.

67% of all BIG-NSE Ph.D. students have/have had an international origin (current students: 76%). 49% have/have had a European origin (current students: 36%). 41% of all BIG-NSE Ph.D. students are/have been female (current students: 40%). More than half (52%) of the BIG-NSE scholarships were attributed to women. 91% of our alumni obtained their "Ph.D." with either an "excellent" (36%) or "very good" (56%) grade. 49% of our alumni had to change their country to study at BIG-NSE. 48% changed their country of residence after the Ph.D. as well. 33% of the German students went abroad after their Ph.D.. 52% of the international students stayed in Germany after their Ph.D., 39% in Berlin. 29% went to another country to pursue their career, only 19% went back home (most of them, the CSC financed ones, being forced to do so). 49% of the BIG-NSE students had supervisors/collaborators from at least two different UniCat institutions, and 94% had more than one supervisor.

More than 420 publications have been published (in peer-reviewed journals, + patents and book chapters) by 83 finished or almost finished BIG-NSE students; Average: 5 publications per student. 67% (281) of these publications are first-author ones. 69 of these publications (16%) have more than one BIG-NSE author, which underlines the high level

of collaboration between our students. An even higher percentage of these papers (45%) are the result of collaboration between different UniCat groups.

62% of the alumni took a PostDoc position immediately after their PhD. Only 15% of them stayed at the same university (11% in the same group) for their PostDoc, the other 47% changed the university, 36% even performed their PostDoc abroad. 20% of them moved to a position as group leader a couple of years after having started their PostDoc, 5% then took a job in the industry. 28% of our alumni took a job in the industry (20% in a big company, 6% in a small or middle-size one, 2% tried a startup) immediately after their PhD. 5% took a sales job in the scientific publication branch (Wiley, Research Gate, De Gruyters). 1% now works in the patenting area. Finally, 2% are busy in the undergraduate education area and 2% stay home to take care of their children.

BIG-NSE - Berlin International Graduate School for Natural Sciences and Engineering

Fundamental studies of NiFe hydrogenases by IR spectroelectrochemistry, and their applications in biocatalytic hydrogenation catalysis

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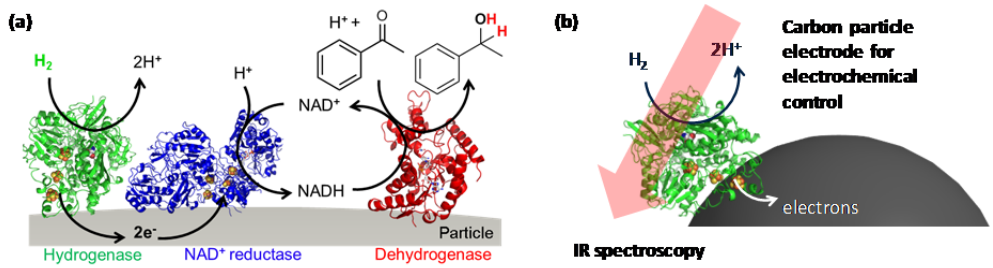
This collaborative work concerns mechanistic study and applications of NiFe hydrogenases. These enzymes are found in a number of microorganisms, and catalyse the oxidation or evolution of H_2 at a NiFe active site where the Fe is coordinated by CO and CN^- ligands.

Together with the group of Oliver Lenz, we have developed a system of catalytic beads based on carbon black particles modified with hydrogenase and an NAD^+-reducing moiety for catalysis of H_2-driven reduction of the biological hydride transfer cofactor NAD^+.[1,2] Electrons released from H_2 oxidation by the hydrogenase pass through the conductive carbon particle and are transferred to the NAD^+-reductase for reduction of NAD^+ to NADH. When a dehydrogenase enzyme is co-immobilised, Figure (a), NADH is continuously regenerated under a H_2 atmosphere to supply NADH for a selective biocatalytic C=O bond reduction. This system offers many new opportunities for heterogeneous biocatalytic hydrogenations.[3.4]

We have also used infrared (IR) spectroscopy to study fundamental aspects of the mechanism of NiFe hydrogenases, Figure (b). In collaboration with Ingo Zebger, we applied a suite of electrochemical and IR spectroscopic approaches to study the regulatory hydrogenase (RH) from *Ralstonia eutropha*.[5] These experiments showed the RH to be active in H^+ reduction as well as H_2 oxidation and to have a similar set of catalytic states to more standard NiFe hydrogenases.

We continue to enjoy productive collaborations with TU Berlin on fundamental and applied aspects of hydrogenase chemistry.



(a) Hydrogenases can be applied as part of an enzyme cascade on carbon particles for biocatalytic hydrogenation reactions. (b) IR spectroscopy of NiFe hydrogenase immobilised on a carbon particulate electrode allows characterisation of hydrogenase active site chemistry during catalytic turnover;

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Characterization and reactivity studies on a terminal copper-nitrene species

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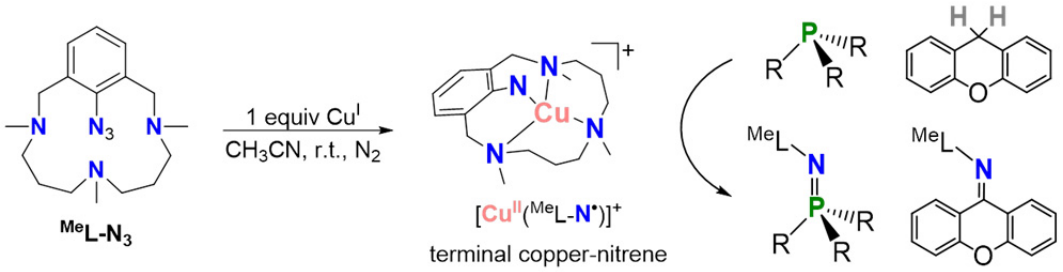
High-valent copper-nitrene species have been postulated as key intermediates in several copper-catalyzed reactions such as aziridination and amination reactions.[1] The high reactivity of these intermediates has eluded their characterization for decades, thereby making the mechanism ambiguous. However, seminal works have evidenced their formation. For instance, Warren et al. could crystallize a dicopper(II)-nitrene complex as a precursor of a terminal copper(III)-nitrene species.[2] Very recently, the Lewis acid adduct of a copper-nitrene intermediate has been trapped at -90°C and shown to be active in various oxidation reactions.[3,4]

Herein, we describe for the first time the synthesis and spectroscopic characterization of a room temperature stable terminal copper(II)-nitrene radical species in the absence of any Lewis acid (see Scheme).[5] The azide derivative of a triazamacrocyclic ligand has been employed as an ancillary ligand in the study, which has previously been utilized in the stabilization of aryl-Cu^{III} intermediates. This copper-nitrene species is able to perform nitrene-transfer to phosphines and H-atom abstraction from weak C-H bonds leading to the formation of oxidized products in modest yields.



Scheme. Generation of a terminal copper-nitrene species and its N-atom transfer ability towards phosphines and C-H bonds.

[1] R.T. Gephart, T. H. Warren, *Organometallics* **2012**, *31*, 7728.
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$BArF_3$-catalyzed imine hydroboration with pinacolborane not requiring the assistance of an additional lewis base

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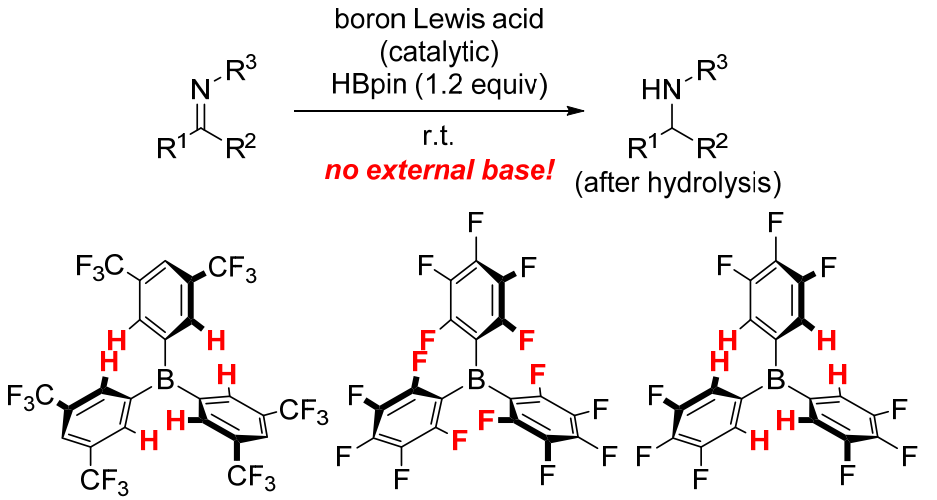
Catalytic imine hydroboration is a straightforward way of preparing amines.[1] However, catalytic protocols typically rely on transition metals as catalysts, and imine hydroboration using catalysts based upon the main-group elements is an underdeveloped field which is recently attracting attention.[2]

We have found that the rarely used boron Lewis acid tris[3,5-bis(trifluoromethyl) phenyl]borane ($BArF_3$) is an excellent catalyst for metal-free hydroboration of imines. In the presence of 1 mol% of $BArF_3$, several ketimines and aldimines undergo hydroboration with pinacolborane (HBpin) at room temperature. $BArF_3$ is more reactive than other Lewis-acidic boranes, including the more commonly used tris(pentafluorophenyl)borane [$B(C_6F_5)_3$]. Mechanistic control experiments indicate conventional Lewis-acid catalysis involving imine activation and hydride transfer from HBpin.[3]



Borane Catalyzed Imine Hydroboration with Pinacolborane

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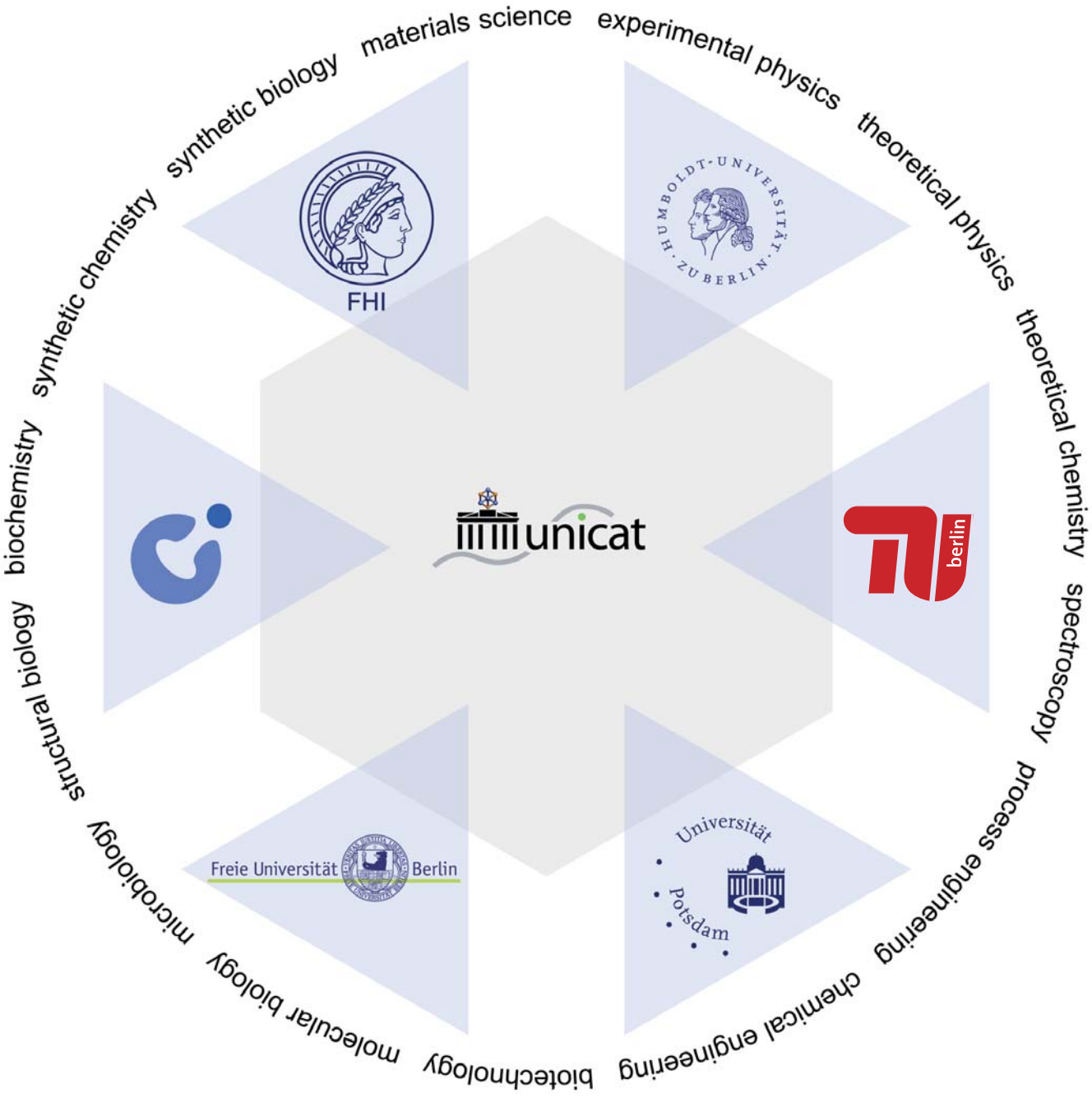

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