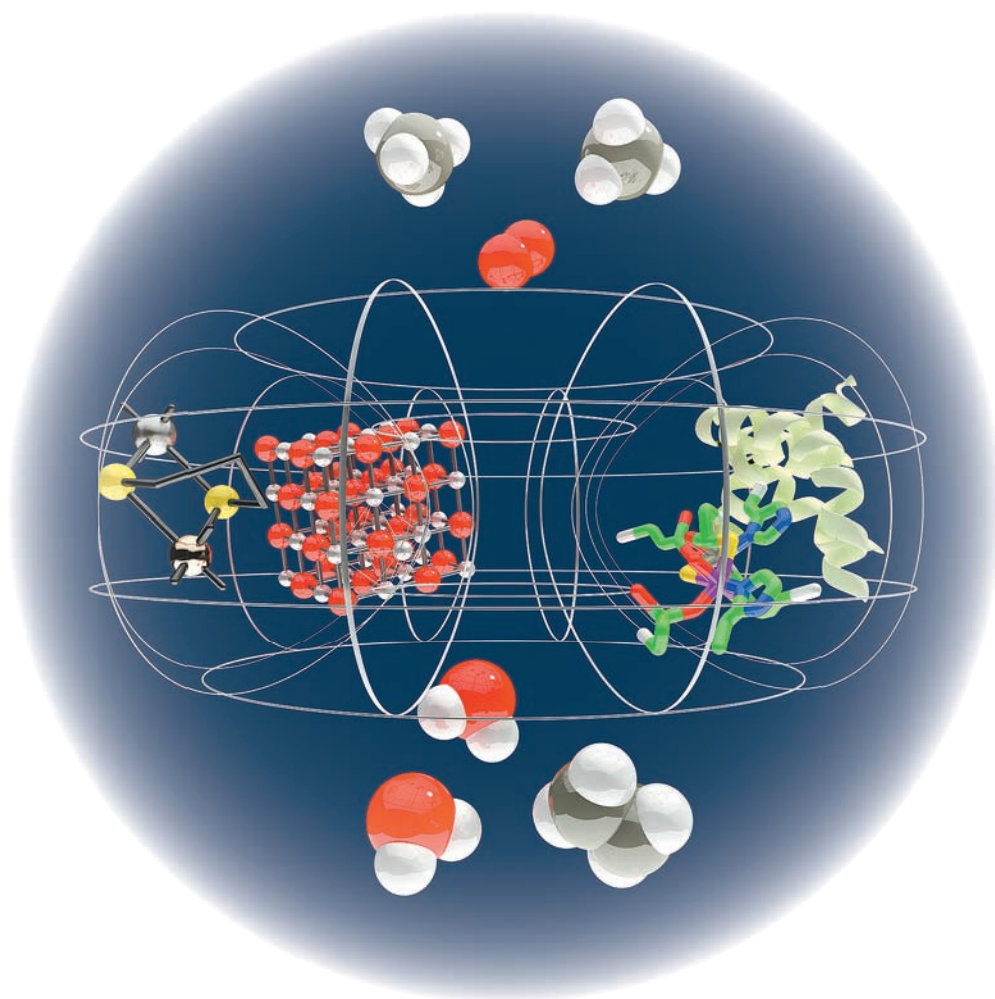


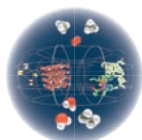
Cluster of Excellence “Unifying Concepts in Catalysis”

At a Glance





www.unicat-berlin.de



Cover picture

The cover picture shows the oxidative coupling of methane with dioxygen leading to ethylene and water, adapted from ChemCatChem, special issue 07/2010.

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At a Glance



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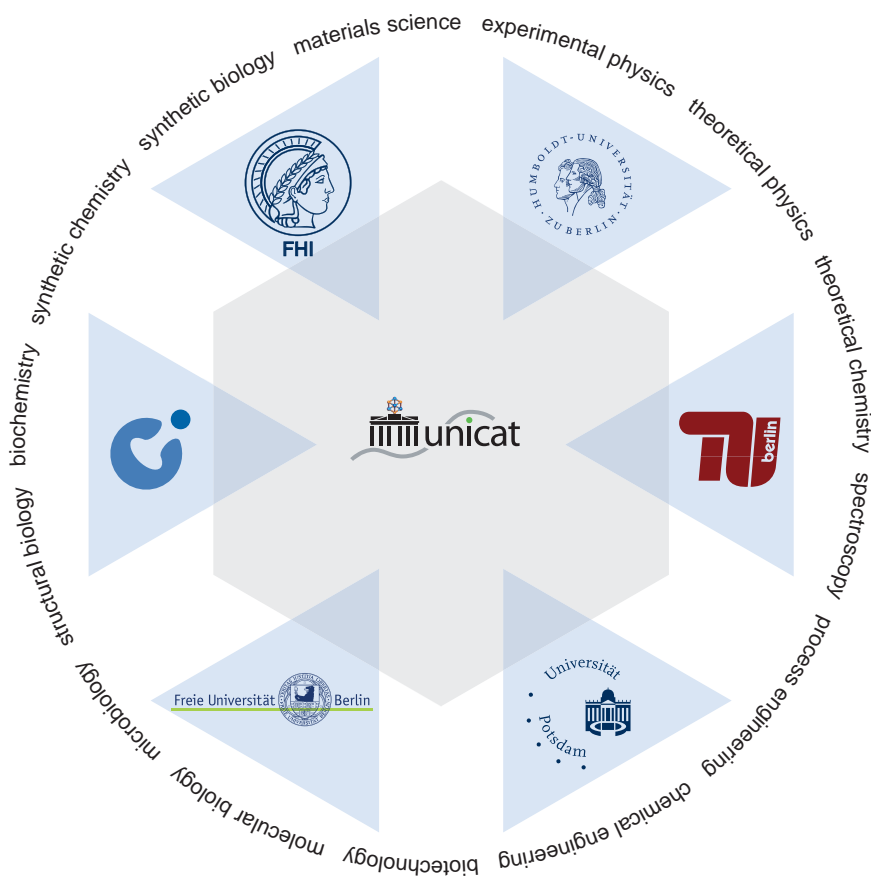
The UniCat Network – Mission and Members



“Unifying Concepts in Catalysis” (UniCat) is an interdisciplinary research network within the framework of the Excellence Initiative of the German Federal and State Governments. UniCat’s main focus is on catalysis. Four universities and two Max Planck Institutes in Berlin and Potsdam are involved in UniCat:

- Technische Universität Berlin as host university
- Freie Universität Berlin
- Humboldt-Universität zu Berlin
- Universität Potsdam
- Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin
- Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Potsdam

Approximately 50 research groups collaborate across disciplines on fields of major interest to future scientific developments in raw material change and energy turnaround. The areas studied include the chemical conversion of methane to ethene, the chemical and enzymatic activation of carbon dioxide, the catalytic production of hydrogen from water using sunlight as the energy source, and the synthesis of drugs with the help of artificial enzymes.



Mission

UniCat unifies concepts in catalysis by bridging the gaps between homogeneous, heterogeneous and biological catalysis, ranging from elementary gas-phase reactions to complex processes in highly organised biological systems, in fundamental as well as in applied catalysis research. UniCat's research focuses on analysing catalytic mechanisms, designing novel catalytic materials and strategies, and developing new catalytic processes on the laboratory and mini-plant scale.

UniCat accelerates the transfer of basic research and application-orientated research into large-scale processes in industry. UniCat promotes the cross-disciplinary education of young scientists through its Graduate School BIG-NSE. By establishing a common language between PhD students of various disciplines, the different parts in UniCat become tightly interconnected.

Concept, Research Programme, and Objectives

Scientific Concept

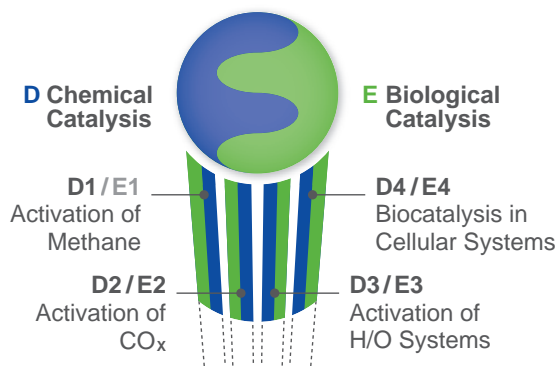
A unique research concept has been implemented to overcome the artificial fragmentation of catalysis research in different disciplines, and in response to the increasing importance of interactions between chemical and biological catalysis. The ultimate aim is to achieve a comprehensive view of fundamental catalytic concepts, identifying the similarities and differences of related processes in chemistry and biology.

The targets range from the activation of small molecules in single and coupled catalytic processes to the elucidation and manipulation of biocatalytic processes in cellular systems. Each target is studied from both sides, i.e. using chemical and biological catalysis. This research concept is unique, both nationally and internationally.

“Unifying concepts in catalysis” means that we identify common reaction mechanisms in chemical and biological catalysis and bundle competences and methods from different disciplines within an integrated approach. In this context, UniCat aims to detect key parameters that control the mechanisms and dynamics of specific catalytic processes at different levels of complexity of the systems and to identify the similarities and differences in the concepts ruling heterogeneous, homogeneous, and biological catalysis. In addition, a more general understanding of catalysis is promoted in order to pave the way towards a knowledge-based prediction of catalyst performance and potential new applications.

The result of the strengthening of the cluster team through strategic appointments, the successful development of a methodological

toolbox and the increased interactions between chemical (Area D) and biological (Area E) catalysis is reflected in UniCat's research structure focussed on similar targets (see below).



Organisation of the research structure within UniCat.

The projects in both areas are intertwined to form four research bands devoted to the same or similar target processes in chemical and biological catalysis.

Three Research Bands (D1/E1, D2/E2, and D3/E3) are dedicated to elucidate the activation mechanisms of small molecules (methane, carbon oxides, dihydrogen, dioxygen, water, and hydrogen peroxide), processes of utmost importance in nature and technology. To gain insight into the molecular coupling mechanisms as a prerequisite for designing novel tailor-made systems, catalytic hybrid systems are developed, aiming at the yet unknown combination of chemical and biological catalysis within one system.

These challenges constitute a bridge to the fourth Research Band D4/E4 that is dedicated to multi-component enzyme complexes for producing peptide antibiotics and light-gated controlling of physiological processes. This may pave the way towards medical applications; for example optogenetics harbouring the potential to control cell function with light in the field of neuroscience.

Protein modification through the expansion of the genetic code to non-natural amino acids, prepared by innovative synthetic routes, is essential for mechanistic and structural analyses and for the knowledge-based design of novel enzyme complexes with modified or new functions.

Central to the success of all projects is the availability of a wealth of tailored experimental and theoretical methods that are suitable for multi-scale analysis and *in-situ* monitoring of (bio)catalytic reactions in highly complex environments.

Research Bands

1 Activation of Methane

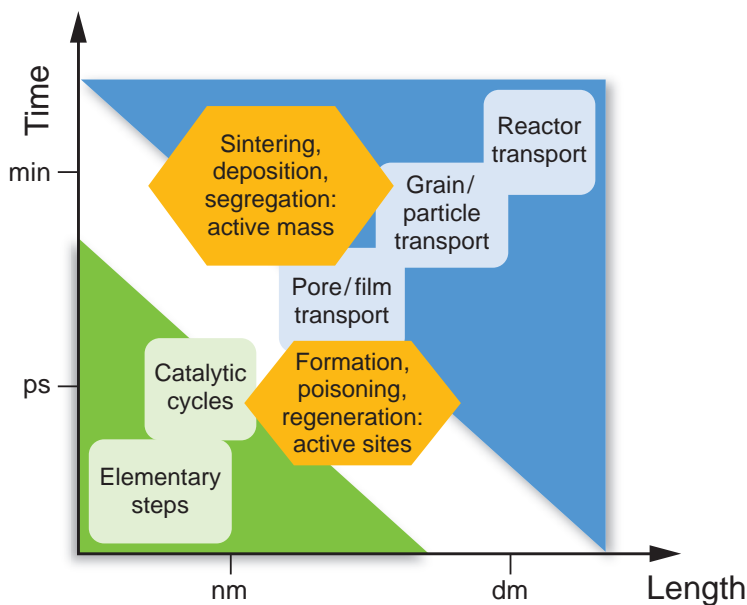
The proven reserves of natural gas have enormous potential as an alternative to the decreasing crude oil reserves. The main component of natural gas is methane (CH_4), the most stable hydrocarbon. The conversion of methane into value added products, particularly its direct conversion, is still a major challenge.

To understand how methane is activated, we need to describe chemical and physical processes extending over a wide range of space and time. These processes span from the identification of elementary steps and catalytic cycles through theoretical and experimental studies on model systems to the coupling of these molecular processes with transport of energy and molecules in meso- and macroscopic dimensions. In addition, we elucidate how catalyst precursors are chemically transformed into active phases, while simultaneously being deactivated by compound formation, poisoning and reactant-induced restructuring.

D1 Oxidative Coupling of Methane

When methane (CH_4) reacts with oxygen (O_2) oxygen must be activated first. This step is quite complex mainly because there is a high risk the methane will burn completely to carbon dioxide (CO_2). The

oxidative coupling of methane (OCM) is a highly promising reaction for its direct conversion to ethylene. UniCat pursues a multi-scale approach that combines concepts and methodologies of chemical synthesis, physical chemistry and surface science with chemical engineering.



Multi-scale approach for bridging the gaps in time and length scale of OCM towards a unified model.

In our first research project we analyse homogeneous gas phase processes by combining experiments with theoretical knowledge. Investigated processes extend across all relevant dimensions of transport, to achieve a comprehensive kinetic description based upon observables or theoretically verified input data.

We validated the existing family of reaction models and combined them with our second research project, in which we identify the relevant surface reactions, determine the concomitantly released heat, and detect the species that are released from the catalyst surface to activate the gas phase reaction.

Radical detection in harsh environments by means of laserinduced fluorescence using a single bidirectional optical fiber, H. Schwarz, R. Schlögl, R. Horn, *Applied Physics B* 2012, 109, 19–26.

Research Achievements and Research Highlights

UniCat researchers demonstrated that the established Lunsford mechanism for the oxidative coupling of methane (CH_4) needs to be revised and proposed a new mechanism.

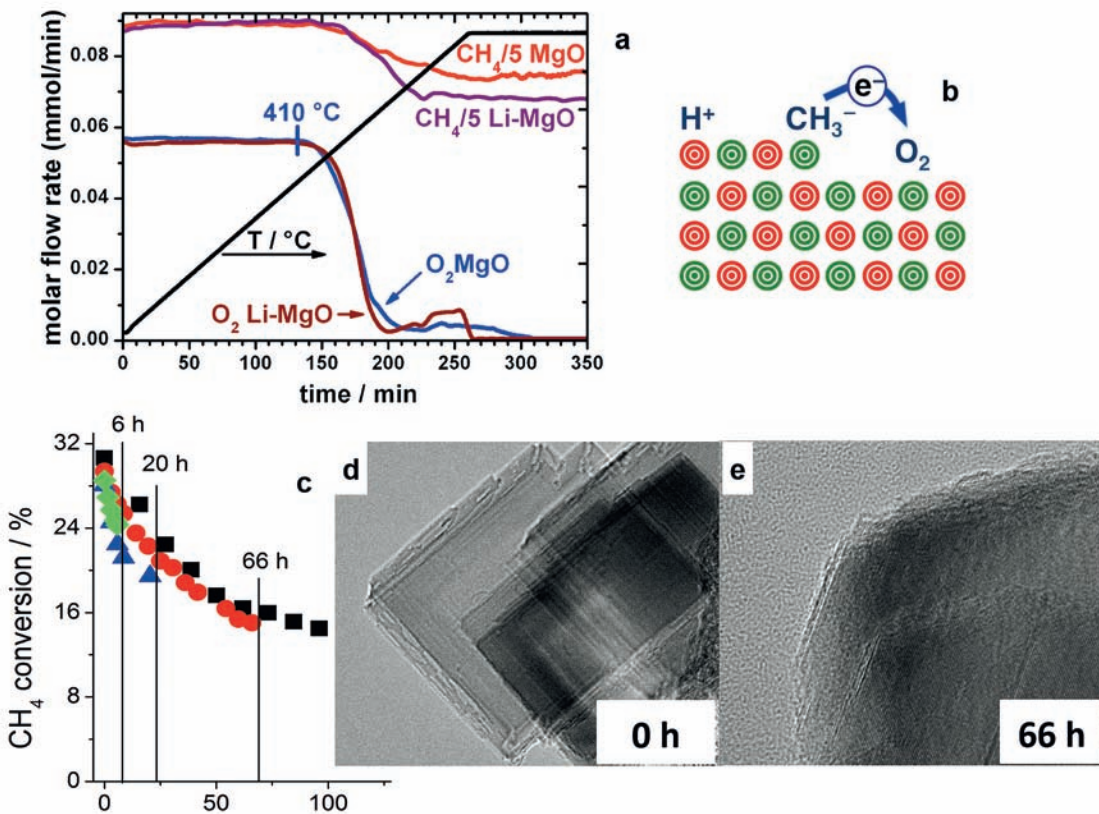
Temperature-dependent morphology, magnetic and optical properties of Li-doped MgO, P. Myrach, N. Nilius, S. V. Levchenko, A. Gonchar, T. Risse, K.P. Dinse, L.A. Boatner, W. Frandsen, R. Horn, H.J. Freund, R. Schlögl, M. Scheffler, *ChemCat-Chem* 2010, 2, 854–862.

The calculated energy barriers for methane activation by hydrogen abstraction at oxygen radical sites of lithium-doped magnesium oxide (MgO) are unrealistically low: Density functional calculations yield energy barriers that are much smaller than the barriers inferred from different experimental studies. This raises further doubts that the Li^+O^- site is the active site as postulated by Lunsford.

a) Temperature-programmed reaction experiments show that the same active sites are responsible for methane activation on both lithium-doped MgO and pure MgO catalysts. Measurements with differently prepared pure MgO catalysts hint to morphological defects as the origin of catalytic activity.

b) Methane binds heterolytically on $\text{Mg}^{2+}\text{O}_2^-$ sites at steps and corners, and methyl radicals are released into the gas phase when

Oxidative coupling of methane: research achievements.



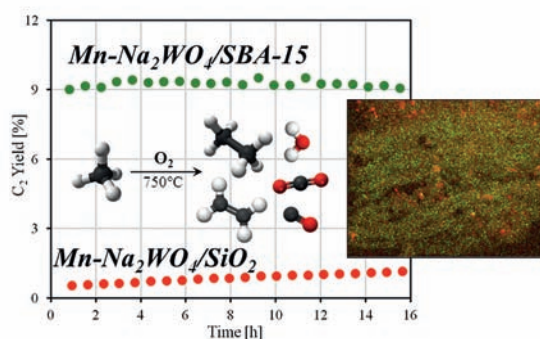
O_2 is present on the surface. The role of the catalyst surface is to bind CH_4 and O_2 , which exchange redox equivalent directly among themselves, but not with the catalyst.

- c) The activity proved to be very different in the initial phase of the OCM reaction and in the steady state.
- d, e) This was accompanied by substantial morphological changes and restructuring of the terminations as revealed by transmission electron microscopy.

Many catalysts deactivate due to the harsh reaction conditions

Although a large number of catalysts have been studied, a breakthrough leading to industrial application has not yet been achieved, especially because many catalysts deactivate due to the harsh reaction conditions.

However, silica (SiO_2) supported $Mn_xO_y-Na_2WO_4$ is a suitable catalyst for the oxidative coupling of methane. $Mn_xO_y-Na_2WO_4/SiO_2$ is very active, selective, and stable. UniCat has tested a variety of different silica materials as supports and developed a fluidized bed process for the large scale preparation of this catalyst allowing its application in UniCat's OCM mini-plant at the Technische Universität Berlin.



Sites for Methane Activation on Lithium-Doped Magnesium Oxide Surfaces, 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.

Enhanced catalytic performance of $Mn_xO_y-Na_2WO_4/SiO_2$ for the oxidative coupling of methane using an ordered mesoporous silica support, M. Yildiz, Y. Aksu, U. Simon, K. Kailasam, O. Görke, F. Rosowski, R. Schömäcker, A. Thomas, and S. Arndt, *Chem. Commun.* 2014, 50, 14440-14442.

Methane conversion: C_2 selectivity as a function of time on stream for two different $Mn_xO_y-Na_2WO_4/SiO_2$ catalysts.

For the first time since oxidative coupling of methane has been investigated, one catalyst exists, which can be reproducibly prepared with either good, medium or low stable catalytic performances. This offers the opportunity for comprehensive studies on the structure–activity relationship of this catalyst.

The catalytic performance of the $\text{Mn}_x\text{O}_y\text{-Na}_2\text{WO}_4/\text{SiO}_2$ catalyst is greatly enhanced by the application of SBA-15 (one of the most common mesoporous silica nanoparticles) as the silica precursor, approaching a level which might allow an industrial application.

*UniCat's mini-plant
for the oxidative coupling
of methane.*



E1 Biological Activation of C-H Bonds

Microorganisms can oxidatively degrade methane with high efficiency. The enzymes at the heart of this process are called methane monooxygenases (MMOs) and are studied by our cooperation partner at the Northwestern University (NWU) in Evanston, Illinois (USA) in the research group of Amy C. Rosenzweig.

UniCat and NWU collaborate in the synthesis of bioinspired models for the hydroxylation of methane.

2 Activation of Carbon Oxides

The chemical and biological transformations of carbon dioxide (CO₂) and carbon monoxide (CO) are key processes in industry and nature. Carbon oxides are the central players in the global biogeochemical cycle of carbon. However, within the past century the civilization-based production of carbon dioxide has disturbed the original balance leading to an exponential increase of carbon dioxide in the atmosphere, a parameter that is known as the prime contributor to global warming.

Thus, strategies to reduce the emission of carbon dioxide as well as of poisonous carbon monoxide are needed. Mastering this challenge requires not only lowering the combustion of fossil fuels but also developing new strategies to catalyse the transformation of carbon oxides into value-added products.

D2 Dry Reforming of Methane

Due to the low selectivity of methane (CH₄) activation, oxidative coupling of methane (OCM) is associated with a considerable production of CO₂, which in turn requires costly separation of the products in industrial applications.

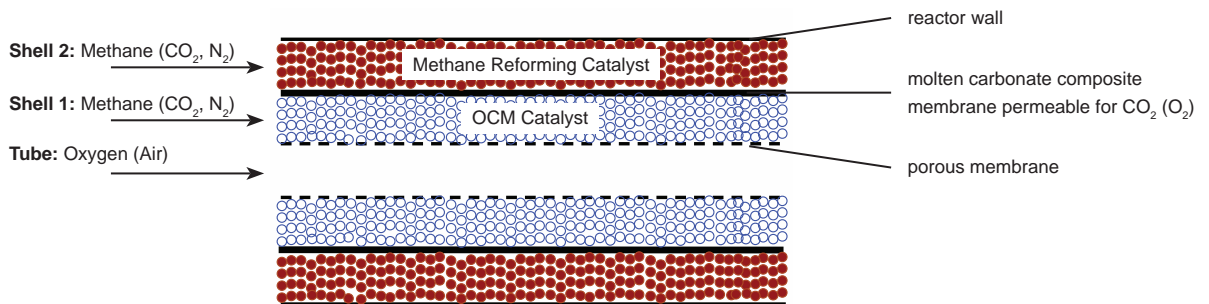
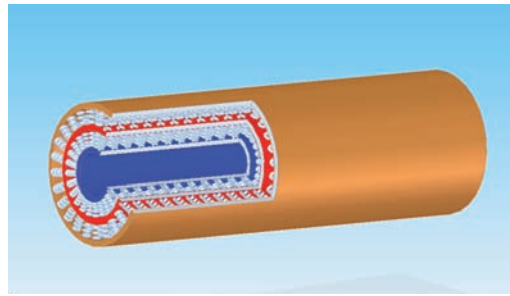
Thus, concomitant to the improvement of the OCM process, the studies in this research band aim at conversion routes of CO₂ that may be combined with the OCM process, i.e. the dry reforming of methane (DRM):



Research Achievements and Research Highlights

UniCat has introduced the concept of a novel dual-membrane reactor, which integrates a reactor for the oxidative coupling of methane (OCM) with a reactor for CO₂ methane reforming (dry reforming). The OCM reactions occur in a conventional porous packed bed membrane reactor structure and a portion of the undesired produced CO₂ and generated heat are transferred through a molten-carbonate perm-selective membrane and consumed in the adjacent dry methane reforming catalytic bed.

Dual-membrane reactor for methane oxidative coupling and dry methane reforming: Reactor integration and process intensification, H. R. Godini, S. Xiao, M. Kim, O. Görke, S. Song, G. Wozny, *Chem. Eng. Process. Process Intens.* 2013, 74, 153–164.



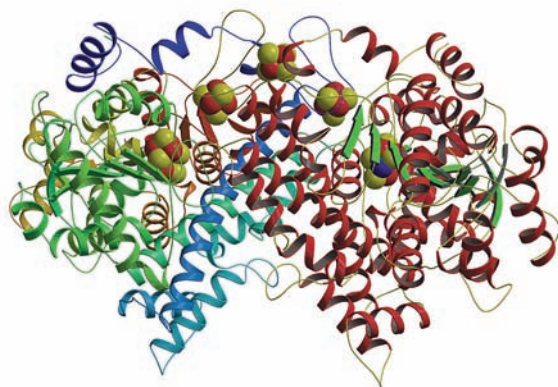
Inside the catalytic bed of an individual OCM membrane reactor, the local operating temperature can easily reach above 900 °C, which intensifies the combustion reactions. However, our integrated reactor has a very promising thermal performance by controlling the temperature peak to be below 50 °C in reference to the average operating temperature in the OCM section.

The dual-membrane reactor alone can use a significant amount of the carbon dioxide generated in the OCM catalytic bed. In combination with an adsorption unit downstream of the integrated process, 90% of the produced CO₂ can be recovered and further converted to valuable syngas products. The experimental data, obtained from a mini-plant scale experimental facility, were exploited to verify the performance of the OCM reactor and the CO₂ separation section.

The conceptual representation of the novel dual-membrane reactor to combine the OCM and methane reforming reactors (top: axial cross sectional representation; bottom: three dimensional cut).

E2 Understanding the molecular mechanisms of enzymatic conversions of carbon oxides

The main objective of the biological part of the second Research Band is to understand how enzymes convert carbon oxides by analysing the catalytic cycles of selected enzymes using different co-factors. Thus, by elucidating the respective catalytic mechanisms we provide insight on how similar reactions are catalysed by fundamentally different active sites.



Presentation of a carbon monoxide dehydrogenase dimer (CODH II).

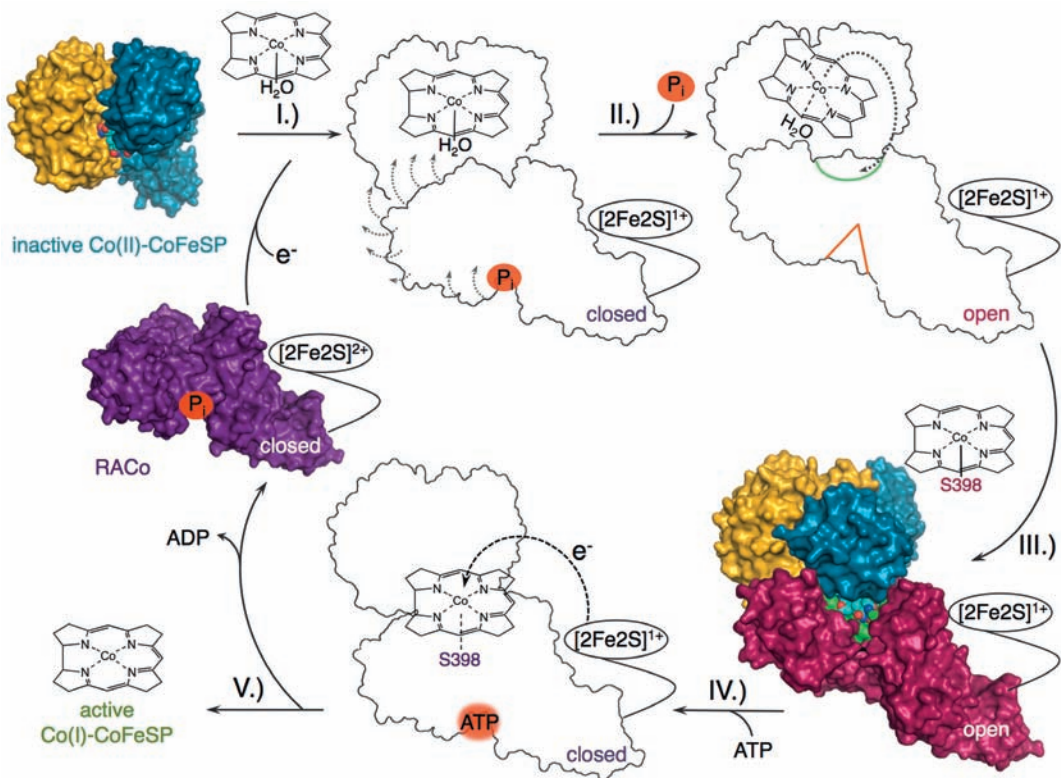
Among them, the [NiFe]-containing carbon monoxide dehydrogenase (CODH) catalyses the reversible reduction of CO_2 to CO and constitutes an excellent reference system for the studies in this Research Band, as high-resolution three-dimensional structures of different catalytic states are available that are an excellent basis for EPR, IR and Mößbauer spectroscopic and theoretical studies.

Research Achievements and Research Highlights

Adenosine triphosphate (ATP) is a nucleoside triphosphate used in cells as a coenzyme. ATP can induce an electron transfer by redox-selective partner recognition.

Thermodynamically unfavourable electron transfers are enabled by coupling to an energy-supplying reaction. How the energy is transduced from the exergonic to the endergonic process is largely unknown.

Here, UniCat provides the structural basis for an energy transduction process in the reductive activation of B_{12} -dependent methyl-



Proposed mechanism of the ATP-induced reactivation of CoFeSP by its activator. Proteins are shown as surfaces. Intermediary states not captured in crystal structures are presented as contour plots.

ATP-induced electron transfer by redox-selective partner recognition, S. E. Hennig, S. Goetzl, J. H. Jeoung, M. Bommer, F. Lendzian, P. Hildebrandt, H. Dobbek, *Nature Communications* 2014, 5, Article no 4626.

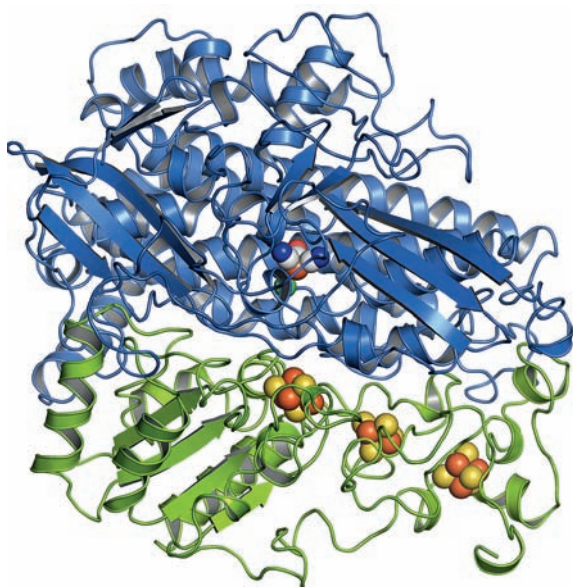
transferases, which ultimately link the coupling of carbon monoxide (CO) and activated methane to acetate. The transfer of one electron from an activating enzyme to the cobalamin cofactor is energetically uphill and relies on coupling to an ATPase reaction.

Our results demonstrate that the key to coupling is, besides the oxidation state-dependent complex formation, the conformational gating of the electron transfer. Complex formation induces a substitution of the ligand at the electron-accepting cobalt (Co) ion. Addition of ATP initiates electron transfer by provoking conformational changes that destabilise the complex. UniCat shows how remodeling of the electron-accepting Co^{2+} promotes ATP-dependent electron transfer; an efficient strategy not seen in other electron-transferring ATPases.

3 Activation of H/O-Systems

Research on the activation of molecular hydrogen (H_2), oxygen (O_2) and water (H_2O), a topic originally centred in biocatalysis (Research Field E3), has received a steadily growing “chemical” counterpart (Research Field D3). Initially, restricted to the synthesis of biomimetic models this field has recently been extended to the synthesis of (bioinspired) functional catalysts.

Hydrogenase and photosystems are investigated in Research Field E3, where we want to unravel their catalytic mechanisms. But we also want to take a step forward to probing and controlling the catalytic processes within complex environments, ranging from hybrid systems up to the whole cell level. Special emphasis is put on the coupling of H_2 and O_2 activation.



*Crystal structure
of an oxygen-tolerant
hydrogenase.*

D3 Chemical activation of dihydrogen, dioxygen, water, and hydrogen peroxide

The chemical part of this Research Band covers the activation of hydrogen and water. Molecular hydrogen is one of the most environmentally friendly sources. Upon combustion with oxygen a large amount of energy is released, where water is the only waste product.

Our research interests range from biomimetic cofactor models via bioinspired complexes up to functional catalysts. A trinuclear nickel (Ni) compound able to catalytically activate dihydrogen serves as a promising starting point for further syntheses including Ni hydride bonds as essential building blocks and are extended to hetero-trinuclear nickel iron [Ni₂Fe] complexes. The same targets can be geared using “frustrated Lewis pairs” (FLPs) which may heterolytically split dihydrogen and catalyse hydrogenation at atmospheric pressure and ambient temperature without involving precious metals.

Chemical catalysts for small molecule reactions are also accessible following a bioinspired strategy to synthesise molecular iron-based and (hetero)-bimetallic iron, nickel, and/or molybdenum-containing complexes as well as metal-free graphitic carbon nitride (C₃N₄) based materials.

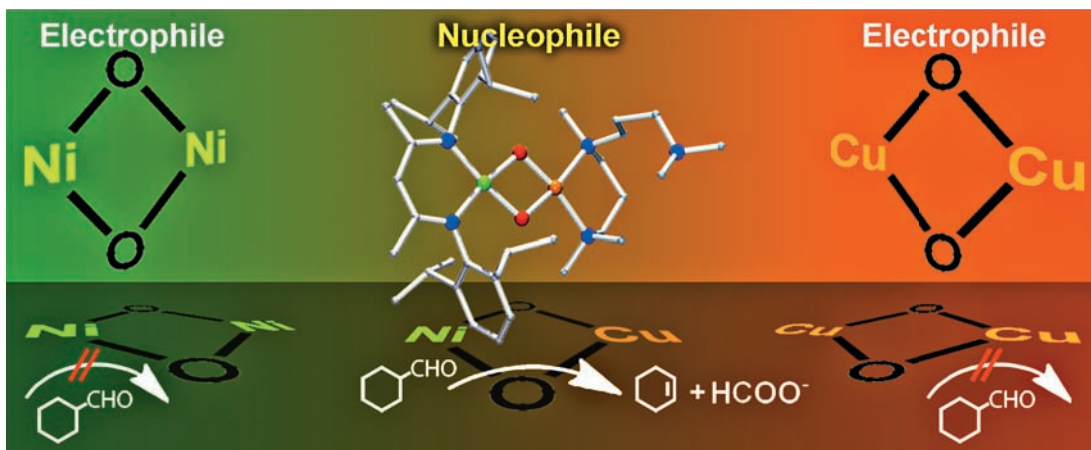
Complementary bioinspired functional metal oxides, which are suitable for catalytic water oxidation are synthesised. Molecular single-source precursors enable the low temperature synthesis of metastable metal oxides in different morphologies and environments which are inaccessible by “classical” high-temperature solid state synthesis.

Research Achievements and Research Highlights

Heterobimetallic dioxygen complexes are interesting because they are models for the structures and reactivities of metalloenzymes containing two different metal ions at their active sites. Moreover, such investigations may lead to the discovery of novel species exhibiting alternative reactivity patterns compared to their homobimetallic counterparts.

This has been demonstrated very recently within UniCat by the low temperature trapping of a novel heterobimetallic nickel(III)copper(III) bis(μ-oxo) intermediate, where the oxo groups were found to act as nucleophiles, in sharp contrast to the electrophilic oxo groups of the well-characterised homometallic [Ni₂(μ-O)₂]²⁺ and [Cu₂(μ-O)₂]²⁺ analogues. In fact, the trapped Ni^{III}(μ-O)₂Cu^{III} complex represents the only example of a high-valent bis(μ-oxo)dimetal core involving nucleophilic oxo groups that can perform deformylation of aldehydes. Based on this report UniCat strongly suggests that mixed-metal bis(μ-oxo) cores are viable intermediates in the deformylation of fatty aldehydes by cyanobacterial aldehyde decarboxylase, for which a similar cofactor has been suggested, but not yet isolated.

A High-Valent
Heterobimetallic
[Cu^{III}(μ-O)Ni^{III}]²⁺
Core with Nucleophilic
Oxo Groups, S. Kundu,
F. F. Pfaff, E. Miceli,
I. Zaharieva, C. Herwig,
S. Yao, E. R. Farquhar,
U. Kuhlmann, E. Bill,
P. Hildebrandt, H. Dau,
M. Driess, C. Limberg,
K. Ray, *Angewandte
Chemie International
Edition* 2013, 52,
5622–5626.

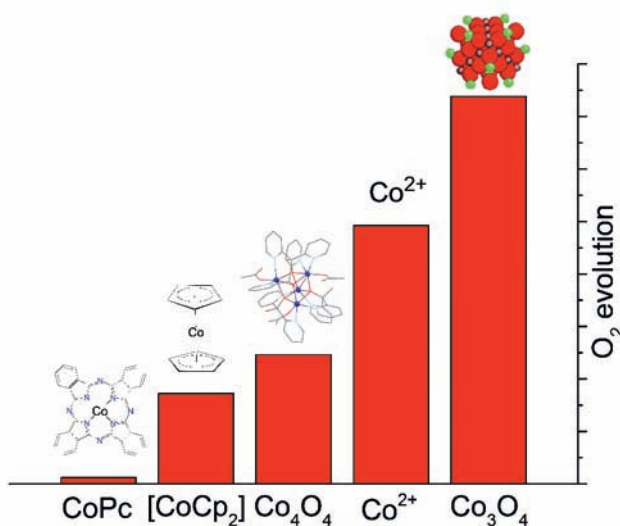


Unique properties
of a heterobimetallic
bis(μ -oxo) core

Electro- and Photochemical Water Oxidation

Splitting of water to hydrogen and oxygen on colloidal catalysts is a promising method for future energy and chemistry cycles. The currently used high-performance oxides containing expensive elements (ruthenium, iridium) are progressively being replaced by more sustainable ones, such as cobalt(II,III) oxide (Co_3O_4).

Precise control over size of the cobalt oxide nanoparticles, their colloidal stability, and the ligand-free surface affect the performance



Effect of the composition
of the molecular
cobalt (Co) catalyst on
oxygen (O_2) evolution.

Electro- and Photochemical Water Oxidation on Ligand-free Co_3O_4 Nanoparticles with Tunable Sizes, M. Grzelczak, J. Zhang, J. Pfrommer, J. Hartmann, M. Driess, M. Antonietti, X. Wang, *ACS Catalysis Scientific Reports* 2013, 3, 383–388.

of the photocatalytic oxygen evolution. Correlating photo- and electrochemical results, reveal that the accessibility of the active species on the particles' surface is a crucial parameter in water oxidation.

E3 Biological activation of dihydrogen, dioxygen, water, and hydrogen peroxide

In nature, photosystem I (PSI) is coupled to photosystem II (PSII) where water is oxidised to molecular oxygen. Against the background of the progress in elucidating the structure of the water-oxidising complex, the analysis of the enzymatic process focuses on the electronic structures of the manganese (Mn) cluster during the catalytic cycle as well as on assembly strategies.

The reversed process, i.e. the reductive activation of dioxygen, as well as the reduction of hydrogen peroxide (H_2O_2) is centered in another research project, which involves the study of natural oxygenases and peroxidases and aims to design artificial catalysts based on "minimum" cofactor-protein complexes.

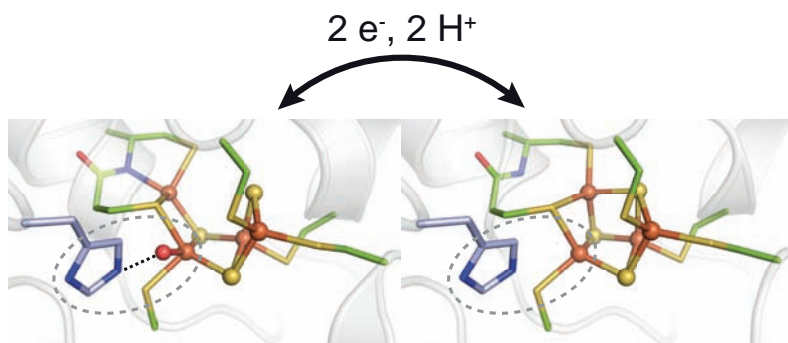
A substantial unit of the biological part within this Research Band is dedicated to oxygen-tolerant hydrogenases, covering systems with different levels of complexity in analogy to the studies on OCM (Research Field D1).

Hydrogenase research combines the analysis of the catalytic processes on a molecular level in the isolated enzyme via hybrid devices and whole cells up to the optimisation of the fermentation processes, eventually leading to the development of large-scale reactors for technological exploitation of the light-driven hydrogen formation.

Research Achievements and Research Highlights

Reversible iron sulfur [4Fe-3S] cluster morphing in an oxygen-tolerant [NiFe] hydrogenase is monitored by crystallography, spectroscopy and computation. Hydrogenases catalyse the reversible oxidation of H_2 into protons and electrons and are usually readily inactivated by O_2 .

However, a subgroup of the [NiFe] hydrogenases, including the membrane-bound [NiFe] hydrogenase from *Ralstonia eutropha*, has evolved remarkable tolerance toward O_2 that enables their host organisms to utilise H_2 as an energy source at high partial pressure of O_2 .



Morphing of the [4Fe-3S] cluster during a two electron redox-transition.

Certain oxygen-tolerant hydrogenases contain a unique [4Fe-3S] cluster near the catalytic site, however, the role of this cofactor has not yet been fully understood.

This feature is crucially based on a unique six cysteine-coordinated [4Fe-3S] cluster located close to the catalytic centre, whose properties were investigated using a multidisciplinary approach. The [4Fe-3S] cluster undergoes redox-dependent reversible transformations, namely iron swapping between a sulfide and a peptide amide nitrogen.

Moreover, the investigations unravelled the redox-dependent and reversible occurrence of an oxygen ligand located at a different iron. This ligand is hydrogen bonded to a conserved histidine that is essential for H₂ oxidation at high O₂ partial pressure. We propose that these transformations, reminiscent of those of the P-cluster of nitrogenase, enable the consecutive transfer of two electrons within a physiological potential range.

Together, these data obtained by crystallographic, spectroscopic, and computational studies provide evidence for redox-dependent transformations of this cluster, potentially explaining how specialised hydrogenases can safely reduce inhibitory oxygen (O₂).

Reversible [4Fe-3S] cluster morphing in an O₂-tolerant [NiFe] hydrogenase, S. Frielingsdorf, J. Fritsch, A. Schmidt, M. Hammer, J. Löwenstein, E. Siebert, V. Pelmeshnikov, T. Jaenicke, J. Kalms, Y. Rippers, F. Lenzian, I. Zebger, C. Teutloff, M. Kaupp, R. Bittl, P. Hildebrandt, B. Friedrich, O. Lenz, P. Scheerer, *Nature Chemical Biology* 2014, 10, 378–385.

4 Biocatalytic Processes in Cellular Systems

The fourth Research Band (D4/E4) is dedicated to the non-invasive analysis of complex and coupled catalytic networks in cellular systems. After key components had been identified and characterised, their mechanistic interactions have been analysed using newly developed chemical and biological tools, and our studies eventually aim to alter and optimise the function of the overall system, i.e. synthetic biology and optogenetics.

D4 Synthetic tools for elucidating and manipulating biocatalytic processes

Innovative methods in homogeneous catalysis to synthesise biocompatible building blocks, developed in Research Field D4, are essential to analyse catalytic mechanisms and communication between the coupled modules, as well as to manipulate the overall processes.

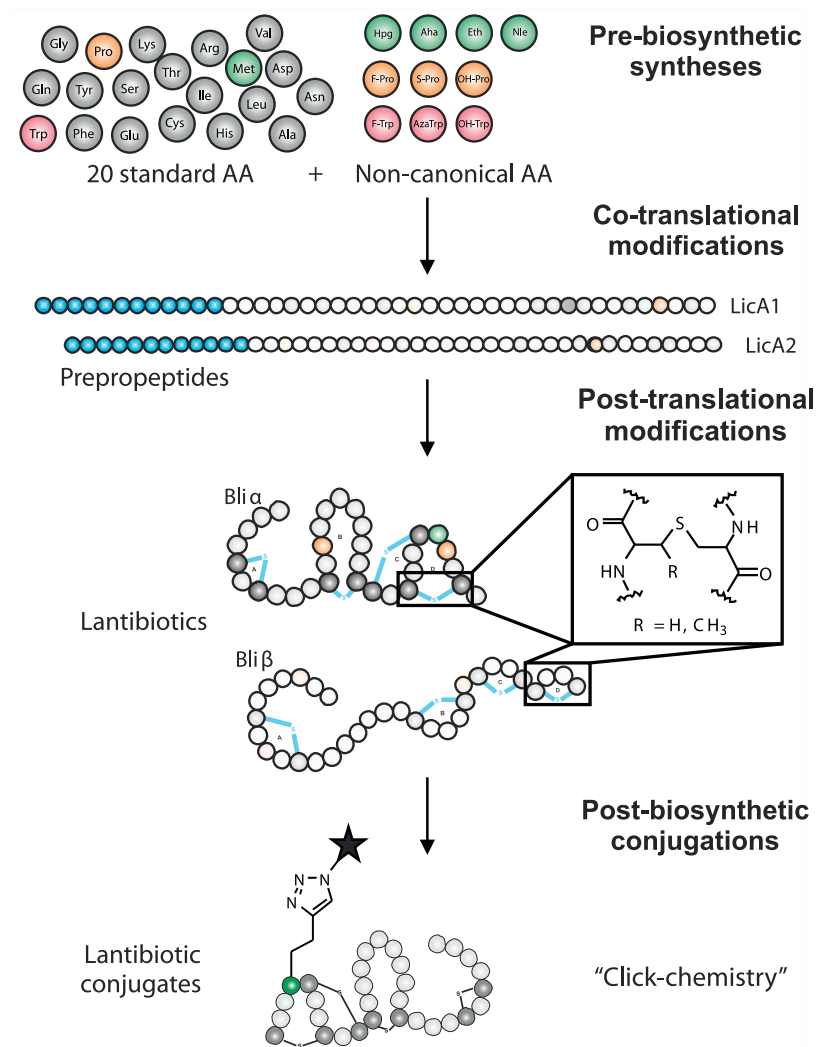
Understanding the molecular function of sensor and catalyst, and the coupling of both entities is a prerequisite to construct novel light-gated enzyme complexes. Thus, it requires molecular structure information in a wide dynamic range from tailored spectroscopic techniques combined with protein labelling techniques (Research Field E4). These approaches include the synthesis of isotopically labelled cofactors and spectroscopic probes introduced into the proteins via genetic engineering and post-translational modifications.

Further expansion of the structural diversity of the peptide products may be achieved by incorporating bio-orthogonal (non-biological functionality) reactive groups for post-translational chemical modifications. Here, the central challenge is to develop synthetic routes for novel catalytic transformations in aqueous environments, including biocompatible olefin metathesis for biological systems to provide access to C=C bond formation under physiological conditions.

Research Achievements and Research Highlights

Lantibiotics are a class of peptide antibiotics that contain the characteristic polycyclic thioether amino acids lanthionine or methyllanthionine, as well as the unsaturated amino acids dehydroalanine and 2-aminoisobutyric acid.

Ribosomally synthesised peptide antibiotics constitute an important group of secondary metabolites synthesised by bacteria and fungi. Among these are lantibiotics, lanthionine (Lan)-containing



Expansion of the synthetic possibilities for the design of ribosomal peptide antibiotics by an expanded amino acid repertoire.

Congeneric Lantibiotics from Ribosomal In Vivo Peptide Synthesis with Noncanonical Amino Acids, F. Oldach, R. Al Toma, A. Kuthning, T. Caetano, S. Mendo, N. Budisa, R. Süssmuth, *Angewandte Chemie International Edition* 2012, 51, 415–418.

bioactive polycyclic peptide antibiotics produced by various Gram-positive bacteria. Lantibiotics exhibit antimicrobial activity against a variety of pathogenic bacteria, including *Staphylococcus*.

Subsequent to ribosomal peptide synthesis (RPS) peptides are posttranslationally modified. In the case of lantibiotics the amino acids serine/cysteine (Ser/Cys) and threonine/cysteine (Thr/Cys) form the thioether-containing amino acids lanthionine and methyl-lanthionine, respectively.

Attempts to broaden the structural diversity of such peptides are limited by the restriction of ribosomal peptide synthesis to the set of 20 canonical amino acids (cAAs). While the viability of total synthesis approaches to such peptides, albeit arduous, is limited, only semi-synthetic modifications with easily accessible functional groups have been exploited, and site-directed mutagenesis approaches have also met with restricted success.

Expressed protein ligation allows the generation of semisynthetic proteins with an almost unlimited number of noncanonical amino acids (ncAAs).

E4 Biocatalytic processes in cellular systems

One project is geared to a knowledge-based control and manipulation of the synthesis of antibiotic peptides, complemented by the ribosomal synthesis of antibiotic and lantibiotic peptides. Hence, the two fundamental peptide assembly lines are exploited for engineering new structural and functional diversity.

For both compound classes appropriate biosynthetic systems that can be expressed in *Escherichia coli* are available and can now be engineered by genetic methods. Such manipulations serve for both analysing structure-function relationships of the target enzymes and for generating new peptide structures either by mutations on the DNA level (site-directed mutagenesis, module swapping, synthetic DNA) or by the re-interpretation of the genetic code by codon re-assignment.

In another project, photoreceptors are coupled with catalytic modules that are retrieved from natural sources or assembled from enzymatic and photoresponsive modules. The generated light-gated enzymes are studied in detail in close collaboration with researchers from Research Field D4. UniCat primarily focuses on the photo-activated cyclases (PAC) by exchanging the catalytic module from an adenylate to a guanylate cyclase.

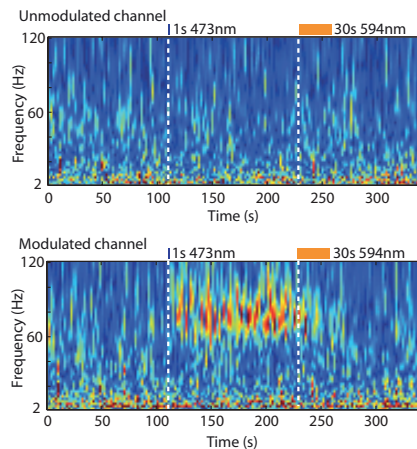
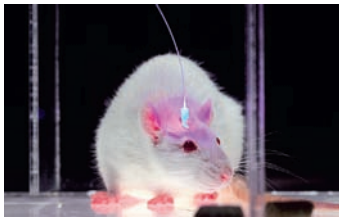
Research Achievements and Research Highlights

Sensory photoreceptors elicit vital physiological adaptations in response to incident light. As light-regulated actuators, photoreceptors underpin optogenetics, which denotes the noninvasive, reversible, and spatiotemporally precise perturbation of living cells and organisms by light.

Severe behavioural deficits in psychiatric diseases such as autism and schizophrenia have been hypothesised to arise from elevations in the cellular balance of excitation and inhibition (E/I balance) within neural microcircuitry. This hypothesis could unify diverse streams of pathophysiological and genetic evidence, but has not been susceptible to direct testing.

Several novel optogenetic tools are designed and tested to causally investigate the cellular E/I balance hypothesis in freely moving mammals, and explore the associated circuit physiology. Elevation, but not reduction, of cellular E/I balance within the medial prefrontal cortex of mice was found to elicit a profound impairment in cellular information processing, associated with specific behavioural impairments and increased high-frequency power in the 30–80 Hz range, which have been observed in clinical conditions in humans.

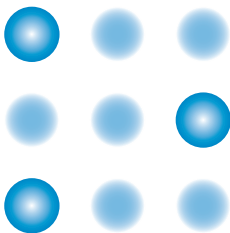
Neocortical excitation/inhibition balance in information processing and social dysfunction, O. Yizhar, L. E. Fenno, M. Prigge, F. Schneider, T. J. Davidson, D. J. O'Shea, V. S. Sohal, I. Goshen, J. Finkelstein, J. T. Paz, K. Stehfest, R. Fudim, C. Ramakrishnan, J. R. Huguenard, P. Hegemann & K. Deisseroth, *Nature*, 2011, 477, 171–178.



Illuminated mouse and local-field-potential wavelet spectrogram.

Sustainable Impact on University Research and Teaching

Gerhard Ertl Center



GERHARD ERTL CENTER

In 2012, the Gerhard Ertl Center was officially opened by the Berlin State Secretary for Science, Dr. Knut Nevermann. The Gerhard Ertl Center serves as a think tank, a host institution for outstanding guest scientists, a location for strategy meetings, the home to the Cluster of Excellence UniCat, its Graduate School BIG-NSE, and research projects in the field of catalysis.

Night view on the illuminated Gerhard Ertl Center located at Marchstr 6 at the TU Berlin.





*Nobel Laureate
Gerhard Ertl in front of
his signature in the
Gerhard Ertl Center*

Focal point: “Gerhard Ertl Center”

The Gerhard Ertl Center is dedicated to bundling all major future activities in catalysis research in the Berlin area and the interdisciplinary promotion of young scientists. Furthermore, it is the physical home of UniCat and BIG-NSE to enhance the corporate identity, to provide a place for formal and informal discussions, hosting workshops (“Frontiers in Catalysis” etc.), and to exploit synergies in merging the administrations of UniCat and BIG-NSE. The Gerhard Ertl Center is supported by the participating institutions.

BasCat – UniCat-BASF Joint Lab



In 2012, the Cluster of Excellence “Unifying Concepts in Catalysis” (UniCat) and the chemical company BASF SE founded the new joint lab BasCat at the TU Berlin (www.bascat.tu-berlin.de). BASF and TU Berlin are putting substantial resources into setting up BasCat: the total volume amounts to about €14 million.

In 2014, the joint laboratory BasCat moved into a new science building. The roughly 1,000 square meters of laboratory and office space are fully equipped for chemical synthesis, *in-situ* spectroscopy, and catalyst tests. 17 scientists will be researching the fundamentals of heterogeneous catalysis for material change, and promoting the search for alternatives to petroleum.



BasCat's new home.

BasCat is dedicated to the development of new catalytic processes for raw material change. It aims at fundamental research in heterogeneous catalysis on the activation of small molecules. The research



Prof. Dr. Matthias Driess (TU Berlin) and Dr. Frank Rosowski (BASF), Scientific Directors of BasCat.

programme promotes the search for alternatives to petroleum, e.g. by using natural gas. The long-term goal is to ensure the future availability of raw materials for the production of chemicals.

BasCat pursues multidisciplinary approaches to generate the fundamental knowledge needed for developing alternative processes to activate less reactive molecules. The current research programme focuses on catalytic oxidation reactions. One example is the oxidative coupling of methane, which has been investigated within UniCat since 2007.

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. Our vision is to develop a rational design concept for catalysts and to accomplish a knowledge-based prediction of catalyst performance through scaling from atomistic to industrial level. This requires new development of methods for catalyst synthesis and characterisation, *in-situ* spectroscopy, and modelling.

BIG-NSE – Berlin International Graduate School of Natural Sciences and Engineering

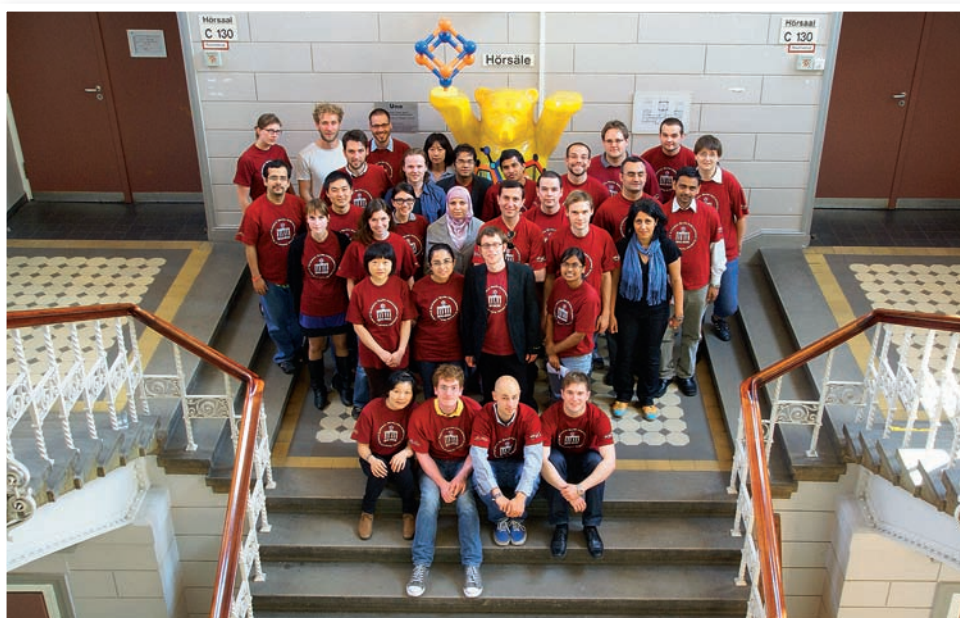


The BIG-NSE (www.big-nse.tu-berlin.de) is UniCat's graduate school. It was founded in 2007 with the perspective of establishing a durable PhD School for the recruitment and training of highly-qualified young researchers. The BIG-NSE offers a modern and innovative structured curriculum for obtaining the doctoral degree within three years and it is specifically designed for the integration of international students in the research network of UniCat. The central challenge, however, was to set up a concept that reflects the broad topical and methodological scope of UniCat and supports BIG-NSE members to become PhD students of UniCat rather than of individual research groups.



The BIG-NSE concept

To attract the most talented students for BIG-NSE world-wide, substantial efforts are made for a careful recruitment process. BIG-NSE scholarships are offered only once a year, starting with an interna-



*BIG-NSE students
embedding UniCat's
mascot Uno.*

tional advertisement in January. Typically, hundreds of students apply each year, using the internet portal, and the number of applicants has been steadily increasing since 2008. As a first step, candidates are screened on the basis of formal criteria and the application documents to select about 20–30 of the most promising candidates, who are invited for an interview in the Spring. Between 5 and 10 of the interviewing students are accepted and receive a 3-year fellowship that begins in October.

The successful candidates and further new associated members (i.e. about 5–10 PhD students funded by other sources) join the BIG-NSE for a three-month “initial phase”, which provides an overview of the research in UniCat and the various fields involved, and prepares the students for the subsequent “lab phase”.

Basic lectures

First, the students attend a series of basic lectures (approx. 60h) on the various aspects of catalysis. Thus, we generate a sound and interdisciplinary knowledge base and establish a “common language”, considering the different scientific backgrounds of the students and the variety of disciplines joined in UniCat.

Introduction into the research of UniCat

The second part of the initial phase is an introduction into the research of UniCat, including lectures and lab excursions to acquaint the new members with the participating research groups and the methodological repertoire. This part of the initial phase is of particular importance since, unlike most other PhD programmes, the BIG-NSE scholarship holders are not requested to decide on a supervisor and the topic of their PhD project *a priori*. Instead, the initial phase serves as an orientation for the students to help them define and allocate their PhD projects in the consortium in close interaction with the respective research group leaders.

Furthermore, the initial phase also promotes the students' capability to initiate collaborations and exploit the wealth of methodological approaches established in UniCat. An essential criterion for the approval of a PhD project is the supervision by two UniCat project leaders from different fields to strengthen the interdisciplinary quality of the research.

Preparation of work plans

The final part of the initial phase is dedicated to the preparation of the "PhD work plans", which are presented to UniCat within a BIG-NSE workshop. Various meetings and workshops, partly involving external guests, are organised by the BIG-NSE students and further promote the scientific education.

Besides the scientific programme, the BIG-NSE offers courses in soft-skills, intercultural competences, and languages during the initial phase, and a variety of extracurricular activities such as social evenings, sports, or visits to cultural events, which are of particular importance for promoting a corporate identity.

*BIG-NSE student
in his lab.*



Achievements in Recruiting, Promoting Scientists, and Gender Equality

Recruiting

The integration of new scientists, especially the installation of new junior research groups in UniCat is a very important instrument to strengthen research priorities.

Scientists integrated into UniCat 2012–2014

Elke Dittmann (UP)	Microbiology
Sabine Enders (TU)	Thermodynamics
André Fielecke (TU)	Gas Phase Spectroscopy
Oliver Görke (TU)	Materials Science
Andreas Möglich (HU)	Biophysics
Vera Meyer (TU)	Molecular Microbiology
Maria Mroginski (TU)	Biomolecular Modelling
Matthias Schwalbe (HU)	Inorganic Chemistry
Patrick Scheerer (Charité)	Structural Biology
Inez Weidinger (TU)	Surface Spectroscopy

Promoting Researchers at the early Stages of their Careers

The excellent working conditions at UniCat provide an outstanding environment for young researchers such as postdoctoral fellows, independent junior research group (JRG) leaders, and junior professors.

The JRG leaders receive the same faculty status as junior professors, allowing them to supervise PhD students independently. Junior researchers, as well as postdoctoral fellows at UniCat, are involved in the teaching programmes (MSc, PhD) to acquire qualifications required for a career in academia.

Junior Researchers who have received a call for a professorship

Constantin Czekelius, U Düsseldorf
Anja Drews, U Oxford; HTW Berlin
Anna Fischer, U Freiburg
Claudio Greco, U Mailand
Raimund Horn, TU Hamburg
Thomas Renger, U Linz
Jens-Uwe Repke, TU Freiberg
Karsten Reuter, TU München
Thomas Risse, FU Berlin
Marek Sierka, U Jena

Appointments of UniCat Professors

■ Marion Ansorge-Schumacher, U Dresden
■ Andrea Hartwig, KIT – Karlsruhe Institute of Technology
■ Gerard Meijer, U Nijmegen

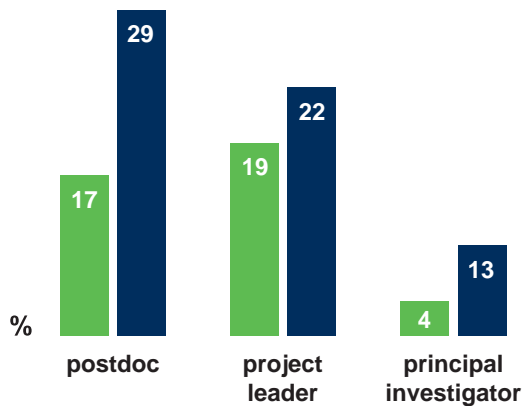
Current and former junior researchers.



Promoting Gender Equality

Due to the increased awareness and efforts in the recent years, the rate of female professors in Germany has almost doubled between 1999 and 2009, but still remains low at 18%. In 2009, the rate of newly appointed female professors was only 29%. Therefore, lack of gender equality remains one of the biggest weaknesses of German universities and research institutions.

The TU Berlin and the other participating universities are firmly committed to further implement standards of the DFG (Deutsche Forschungs Gemeinschaft – German Research Foundation) research-oriented standards on gender equality at all levels of the university organisation. The central objectives of the TU Berlin refer to an increase in the number of female professors, an increase in the percentage of female students, specifically in science and engineering, and an improvement of the work-life balance.



Increase of female scientists in UniCat from 2008 (green) to 2014 (blue)

UniCat has undertaken specific measures to increase the number of female students and scientists in the cluster and to strengthen their active role at all levels of the cluster's hierarchy.

Promoting the role of women at all levels of UniCat

Seminars

to convey strategies, *inter alia*, to overcome restrictive (male-coined) behavioural patterns that impair successful planning of professional career

Networks

dedicated to mutual support and exchange of experience in daily (scientific) work, which may also be extended to a “career lounge”

Individual mentoring and coaching

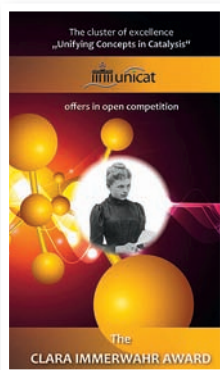
to promote professionalisation of female scientists

Continuous monitoring of women’s integration in UniCat and analysing the specific needs of female UniCat members as a prerequisite to develop further tailored. For example, UniCat members with children will receive support for organising child care or working from home as necessary.

Annual Clara Immerwahr Award for young outstanding female scientists

In 2011, UniCat launched the Clara Immerwahr Award to promote outstanding young female scientists. It is conferred annually to a young female scientist from Germany or abroad at an early stage of her career (postdoctoral fellow, junior researcher) for outstanding results in Catalysis Research. It is associated with a financial support of 15 000 Euro for a research stay at UniCat and thought to establish close collaborative links with UniCat research groups.

The call for applications starts in September each year. The winner is honoured during a public ceremony in February: www.unicat.tu-berlin.de/clara-immerwahr-award



Poster of the ongoing call of the Clara Immerwahr Award.

Dr. Teresa Santos-Silva from Nova University of Lisbon, Clara Immerwahr Awardee 2014 (left), together with laudator Prof. Dr. Silke Leimkühler.



UniCat at a Glance

UniCat

Technische Universität Berlin
Gerhard Ertl Center, Sekr. BEL 4
Straße des 17. Juni 135
10623 Berlin, Germany
Phone: +49(0)30 314-28590; Fax: -94

Chair

Prof. Dr. Matthias Driess
Phone: +49(0)30 314-297 31
E-mail: matthias.driess@tu-berlin.de

Vice Chair

Prof. Dr. Peter Hildebrandt
Phone: +49(0)30 314-214 19
E-mail: hildebrandt@chem.tu-berlin.de

Participating Institutions

- Technische Universität Berlin as host university
- Freie Universität Berlin
- Humboldt-Universität zu Berlin
- Universität Potsdam
- Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin
- Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Potsdam
- Charité – Universitätsmedizin Berlin (close cooperation)

People

- 250 members, thereof about 180 scientific coworkers
- 50 professors and research group leaders, thereof 10 junior professors or scientists
- More than 1 100 scientific publications since 2008:
www.unicat.tu-berlin.de/publications

Budget

UniCat is supported by the German Research Association (DFG) with funds of up to 5.5 million euro annually from the Excellence Initiative of the German Federal and State Governments (*Exzellenzinitiative*). The participating institutions co-fund the programme in approximately the same amount.

Scientific Advisory Board

The members of UniCat's Scientific Advisory Board are high-ranking German and international scientists from academia and industry. The board meets once per year to evaluate the status, structure and focus of the cluster and to give scientific and strategic advice. The report of the Scientific Advisory Board is presented at UniCat's General Assembly.

Important cooperation partners from academia

Northwestern University, Evanston, Illinois [USA]; Universitat Rovira i Virgili Tarragona [Spain]; Argonne National Lab [USA]; Swedish Consortium for Artificial Photosynthesis [Sweden]; Leibniz Institute for Catalysis [Germany]; Max-Planck Institute of Chemical Energy Conversion [Germany]

Einstein Visiting Fellows at UniCat:

- 2011–2014: Prof. Dr. John F. Hartwig, University of California, Berkeley
- Since 2014: Prof. Dr. Dieter Vogt, University of Edinburgh

Research transfer

UniCat is successfully linked to various industrial companies providing the basis for the transfer of results to industrial applications. The most intensive collaboration has been established with BASF SE, originally in the field of oxidative coupling of methane (OCM). Other important industrial cooperation partners include Bayer, Clariant, Endress+Hauser, Evonik, IonGate Biosciences, PolyanGmbH, Sanofi-Aventis AG, Siemens, Uhde. DexLeChem is an UniCat spin-off focusing on reusing homogeneous chiral catalysts.



UniCat's mascot
Buddy Bear Uno.

Four Universities and two Max Planck Institutes are involved in UniCat



UniCat is supported by the German Research Foundation (Deutsche Forschungsgemeinschaft – DFG) with funds from the Excellence Initiative of the German Federal and State Governments.



Imprint

Cluster of Excellence “Unifying Concepts in Catalysis” – UniCat
Technische Universität Berlin, Sekr. BEL 4
Straße des 17. Juni 135
10623 Berlin, Germany

Gerhard Ertl Center
at TU Berlin
Marchstr 6, 10587 Berlin

Contact – PR

Dr. Martin Penno and Dr. Ingo Zebger
Phone: +49 (0)30 314-28 590
E-mail: pr@unicat.tu-berlin.de