

LIKAT Symposium

Young Researchers in Catalysis

16 March 2021

6:00 – 7:40 pm

Virtual Satellite Event of the
Chemiedozententagung 2021

*The reward of the young scientist
is the emotional thrill of being the first person in the history of the world to
see something or to understand something.
Nothing can compare with that experience.*

Cecilia Payne-Gaposchkin

British-born American astronomer and astrophysicist (who proposed in her 1925 doctoral thesis that stars were composed primarily of hydrogen and helium).



Every year, young researchers from the chemistry faculties from Germany and neighboring countries come together for the Chemiedozententagung to find out about news in research and teaching and to exchange ideas at an international level. The topics of the conference include current knowledge and research results from all fields of chemistry.

More than 90% of the current chemical processes and thus the majority of all commodities produced involve catalytic transformations. Catalysis has become a key technology to face recent and future challenges concerning health, sustainability, energy and environmental matters.

The virtual satellite event "Young Researchers in Catalysis" is organized by the Leibniz Institute of Catalysis and wants to support the spirit of the Chemiedozententagung focussed on Catalysis.

Registration link https://veranstaltungen.gdch.de/tms/frontend/index.cfm?!=10726&sp_id=1

Scientific Program

Chair: Prof. Jennifer Strunk – LIKAT Rostock

- 6:00 pm Dr. Jola Pospesch
Pyrimidopteridines as *N*-Heterocyclic Photoredox Catalysts in Organic Synthesis
Leibniz Institute of Catalysis, Rostock
- 6:20 pm Dr. Ulrich Hintermair
Mechanistic Insight into Homogeneous Catalysis from Multi-Nuclear High Resolution FlowNMR Spectroscopy
University of Bath
- 6:40 pm Dr. Tatiana Otroshchenko
Development of unconventional ZrO₂-based catalysts for non-oxidative propane dehydrogenation
Leibniz Institute of Catalysis, Rostock
- 7:00 pm Dr. Matthias Schwalbe
Photocatalytic CO₂ reduction with homo and hetero dinuclear rhenium complexes
Humboldt-Universität zu Berlin
- 7:20 pm Prof. Franziska Hess
The search for a new Deacon catalyst: modeling catalyst stability across the periodic table
Technical University Berlin
- 7:40 pm Closing Remarks

Pyrimidopteridines as *N*-Heterocyclic Photoredox Catalysts in Organic Synthesis

*Jola Pospesch, Rostock/D, Tobias Täufer, Rostock/D, Firas El-Hage, Rostock/D,
Richy Hauptmann, Rostock/D*

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Tetraalkylated pyrimidopteridines-*N*-oxides, first introduced by the group of Maki in the 1980s are traditionally applied as a stoichiometric reagent in photo-mediated oxygen atom transfer reactions. Their utility have been for *N*-demethylation, C–H oxygenation and oxidative C–C bond cleavage.^[1] Derivatization and thorough characterization revealed a great potential of these flavin-related heterocycles as catalysts in oxidative photoredox catalysis.^[2] Excerpts from decarboxylative coupling chemistry and photo-mediated hydroamination of stilbenes will be discussed.^[3,4]

[1] A. Petrosyan, R. Hauptmann, J. Pospesch, *Eur. J. Org. Chem.* **2018**, 38, 5237–5252.

[2] R. Hauptmann, A. Petrosyan, F. Fennel, M. A. Argüello Cordero, A.-E. Surkus, J. Pospesch, *Chem. – Eur. J.* **2019**, 25, 4325–4329.

[3] F. El-Hage, C. Schöll, J. Pospesch, *J. Org. Chem.* **2020**, 85, 13853–13867.

Mechanistic Insight into Homogeneous Catalysis from Multi-Nuclear High Resolution FlowNMR Spectroscopy

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The development and optimization of homogeneous catalysts is often hampered by limited insight into the kinetics of the reaction and the transformation of the catalyst during turnover, in many cases requiring empirical optimization in practice. Rational catalyst and reaction development is only possible through thorough understanding of catalyst activation and deactivation mechanisms, potential resting or dormant states, and the kinetics of the productive cycle (i.e. rate-limiting steps).

We have built a setup in which a reaction vessel is coupled to a NMR flow tube via air-tight small diameter HPLC tubing. With this we can continuously circulate a reaction mixture through the spectrometer, thereby simultaneously follow the reaction progresses and catalyst transformation under realistic conditions in real time.¹

We have characterised the hydrodynamic characteristics of the setup and measured flow effects on continuous NMR acquisition to quantify changes in T_1 , T_2 and signal intensity as function of volumetric flow velocity.² Application in real-time reaction and catalyst monitoring under strictly inert conditions has been demonstrated, and multiple solvent suppression and selective excitation techniques allow the detection of minor intermediates even in non-deuterated solvents.³

The setup also allows monitoring reactions that require continuous delivery of a driving force for turnover, which are difficult to investigate by traditional techniques. For instance, we have recently demonstrated facile monitoring and mechanistic interrogation of a photocatalytic reaction.⁴

Complementary techniques such as UV-vis, HPLC, MS and GPC can be added to the sample flow path, and have allowed the investigation of asymmetric hydrogen transfer catalysis,⁵ the molecular weight evolution during a radical polymerization reaction,⁶ and dynamic organometallic catalysis under gas pressure.⁷

[1] <http://www.bath.ac.uk/research-facilities/dynamic-reaction-monitoring-facility/>

[2] A. Hall, J. Chouler, A. Codina, P. Gierth, J. Lowe, U. Hintermair; *Catal. Sci. Technol.* **2016**, *6*, 24, 8406-8417.

[3] A. Hall, P. Dong, A. Codina, J. Lowe, U. Hintermair; *ACS Catal.* **2019**, *9*, 2079-2090.

[4] A. Hall, R. Broomfield-Tagg, M. Camilleri, D. Carbery, A. Codina, D. Whittaker, S. Coombes, J. Lowe, U. Hintermair; *Chem. Commun.* **2018**, *54*, 1, 30-33.

[5] D. Berry, A. Codina, I. Clegg, C. Lyall, J. Lowe, U. Hintermair; *Faraday Discuss.* **2019**, *220*, 45-57.

[6] J. Vrijnsen, I. Thomlinson, M. Levere, C. Lyall, M. Davidson, U. Hintermair, T. Junkers; *Polym. Chem.* **2020**, *11*, 3546-3550.

[7] A. Bara-Estaun, C. Lyall, J. Lowe, P. Pringle, P. Kamer, R. Franke, U. Hintermair; *Faraday Discuss.* **2020**, doi: 10.1039/C9FD00145J.

Development of unconventional ZrO₂-based catalysts for non-oxidative propane dehydrogenation

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The catalytic non-oxidative propane dehydrogenation to propene is of increasing importance due to the growing demand for this olefin.^[1] Commercial Pt- and CrO_x-based catalysts have, however, disadvantages, which are high price of Pt and toxicity of Cr(VI) respectively. Against this background, we have, for the first time, introduced non-toxic and cheap bulk ZrO₂-based catalysts for this reaction a few years ago.^[2] They demonstrate high activity, propene selectivity, and durability, and can be considered as good alternatives to commercial Pt- or CrO_x-based catalysts. Their practical relevance was validated in a series of dehydrogenation/regeneration cycles between 550 and 625°C under industrially relevant conditions. Their activity, selectivity, and durability were established to be comparable with those of an analogues of industrial CrO_x-based catalyst tested under the same conditions.

The results of catalytic tests and thorough catalyst characterization including density functional theory calculations enabled us to conclude that coordinatively unsaturated Zr⁴⁺ cations (Zr_{cus}) are catalytically active sites. From a structural viewpoint, Zr_{cus} sites should have a lower coordination than the Zr⁴⁺ sites located on the top of an ideal flat surface. The concentration of such surface defects and accordingly dehydrogenation activity of ZrO₂-based catalysts can be increased through their reductive pre-treatment,^[3] doping of ZrO₂ with a proper promoter,^[3] supporting of tiny amounts of dehydrogenation-active metal,^{[2], [4]} and/or decreasing crystalline size of ZrO₂.^[5] All these effects are related to the ability of this metal oxide to release its lattice oxygen upon reductive pre-treatment or *in situ* during first minutes of the dehydrogenation reaction. Zr_{cus} sites are created, when lattice oxygen is removed. Not only the concentration of such sites but also their intrinsic activity can be controlled. It is affected by (i) the nature of metal oxide promoter for ZrO₂,^[3] (ii) the presence of supported hydrogenation-active metal,^[4] and (iii) phase composition of ZrO₂.^[5]

The above-mentioned aspects will be illustrated by examples, which demonstrate the importance of fundamental knowledge for the purposeful design of catalysts with industrially relevant performance.

[1] T. Otroshchenko, G. Jiang, V.A. Kondratenko, U. Rodemerck, E.V. Kondratenko, Chem. Soc. Rev. 2021, 50, 473 – 527.

[2] T. Otroshchenko, S. Sokolov, M. Stoyanova, V.A. Kondratenko, U. Rodemerck, D. Linke, E.V. Kondratenko, Angew. Chem. Int. Ed. 2015, 54, 15880 – 15883.

[3] T.P. Otroshchenko, V.A. Kondratenko, U. Rodemerck, D. Linke, E.V. Kondratenko, Catal. Sci. Technol. 2017, 7, 4499 – 4510.

[4] Y. Zhang, Y. Zhao, T. Otroshchenko, A. Perechodjuk, V.A. Kondratenko, S. Bartling, U. Rodemerck, D. Linke, H. Jiao, G. Jiang, E.V. Kondratenko, ACS Catal. 2020, 10, 6377 – 6388.

[5] Y. Zhang, Y. Zhao, T. Otroshchenko, S. Han, H. Lund, U. Rodemerck, D. Linke, H. Jiao, G. Jiang, E.V. Kondratenko, J. Catal. 2019, 371, 313 – 324.

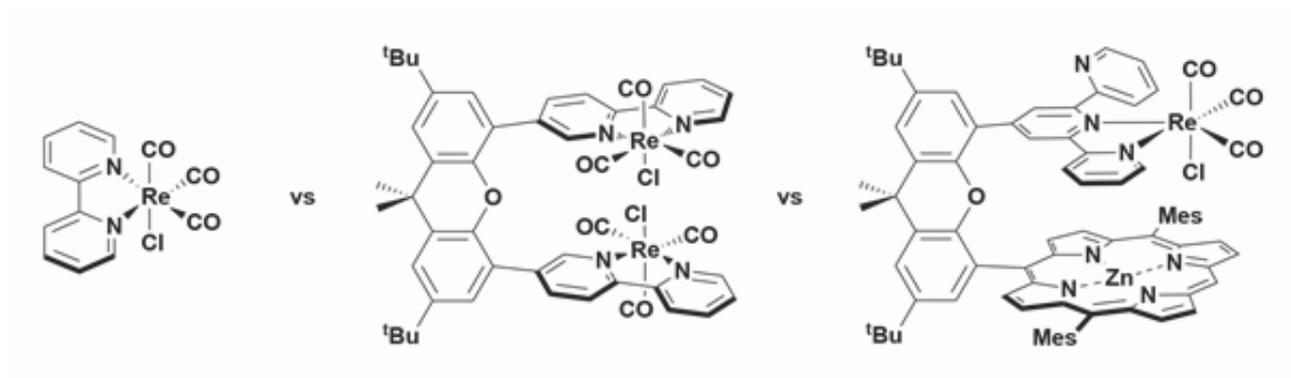
Photocatalytic CO₂ reduction with homo and hetero dinuclear rhenium complexes

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The enzyme carbon monoxide dehydrogenase (CODH) is able to catalyse the reversible transformation of carbon monoxide to carbon dioxide.^[1] The activation of the small molecules takes place at a hetero bimetallic Ni/Fe centre with both metals acting cooperatively. Resembling this reactive centre in detail with molecular building blocks could not be achieved yet by synthetic chemists, and there is no hetero dinuclear catalyst known that shows a similar activity and selectivity as the biological system.^[2]

Indeed, there are predominantly mononuclear metal complexes known, which can catalyse the selective transformation of CO₂ to either CO or HCOOH.^[3] In our own recent studies we could demonstrate that the well-known complex [Re(bpy)Cl(CO)₃] shows an unexpected wavelength-dependency of the catalytic activity in the light-driven CO₂-to-CO transformation.^[4] Spectroscopic as well as theoretical investigations suggest a dinuclear intermediate (with a Re-Re bond) to play an important role – especially when illuminating with low energy light. These results led to the development of homo and hetero dinuclear rhenium complexes,^[5] which clearly possess better catalytic properties than the analogous mononuclear starting compounds.



[1] M. Can, F. A. Armstrong, S. W. Ragsdale, *Chem. Rev.* **2014**, *114*, 4149.

[2] P. Lang, M. Schwalbe, *Chem. Eur. J.* **2017**, *23*, 17398.

[3] a) J. Schneider, H. Jia, J. T. Muckerman, E. Fujita, *Chem. Soc. Rev.* **2012**, *41*, 2036; b) H. Takeda, C. Cometto, O. Ishitani, M. Robert, *ACS Catal.* **2017**, *7*, 70.

[4] P. Lang, R. Giereth, S. Tschierlei, M. Schwalbe, *Chem. Commun.* **2019**, *55*, 600.

[5] a) P. Lang, M. Pfrunder, G. Quach, B. Braun-Cula, E. G. Moore, M. Schwalbe, *Chem. Eur. J.* **2019**, *25*, 4509; b) R. Giereth, P. Lang, E. McQueen, X. Meißner, B. Braun-Cula, C. Marchfelder, M. Obermeier, M. Schwalbe, S. Tschierlei, *ACS Catal.* **2021**, *11*(1), 390.

The search for a new Deacon catalyst: modeling catalyst stability across the periodic table

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Catalysts degrade over time, which means that they lose catalytic activity or selectivity due to a variety of aging processes. While catalyst screening (both experimental and theoretical) regarding activity and selectivity is well-established in catalysis research, screening with respect to stability is experimentally difficult due to the long time scales of catalyst degradation. Computational catalyst screening can complement experimental studies aiming at the identification of new catalyst materials that are stable under operating conditions.

In the HCl oxidation in the Deacon process using an oxide catalyst MO_x , the main catalyst degradation mechanisms are catalyst leaching in the form of volatile M-O-Cl compounds, as well as bulk phase transformation of oxide catalysts into less catalytically active chlorides. We present a catalyst screening approach based on experimental thermodynamic data for the compounds in the M-O-Cl system. In this approach, we divide the M-O-Cl system into four groups of compounds, oxides, chlorides, condensed and gaseous species.

It can address specific reaction conditions by computing the driving forces (ΔG) of chlorination and sublimation as a function of temperature, reactant feed composition and conversion. We apply it to the M-O-Cl compounds of 66 elements, regarding chlorination and volatility as separate descriptors. According to previous experimental studies, catalyst degradation starts at the reactor inlet and is driven by water formation [1]. At the target reaction conditions ($T < 650$ K, dry, $p(\text{HCl})/p(\text{O}_2) \approx 1$, conversion $< 1\%$), 13 oxides are identified as suitable candidates. While some of the candidates (TiO_2 , ZrO_2 , Al_2O_3 , and SiO_2) are inactive (but already employed as catalyst supports in the Deacon process), other candidates are ruled out for safety concerns (BeO , ThO_2 , UO_3). Catalytic activity of the remaining candidates is assessed preliminarily by employing the oxygen and binding energies at the surface as a descriptor.

[1] C. Li, F. Hess, I. Djerdj, G. Chai, Y. Sun, Y. Guo, B.M. Smarsly, H. Over. *J. Catal.* **2018**, 357, 257-262.