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Catalysis Science and Engineering, Lecture **69**

## Designing mono-and multifunctional Solid Catalysts

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In an approach to design selective solid catalysts we start from the knowledge, at the molecular level, of the reaction to be catalyzed. Then hypothesis are made on the nature of the active sites required. At this point we are ready to synthesize solid materials, in where the required active sites are introduced as well defined entities. On top of that the adsorption properties of the solid are taylored to optimize the interactions between reactants, catalyst and products.

Following this methodology will present solid catalysts in where the active sites correspond to well defined transition metal complexes and organocatalysts that are either grafted or structurally builded into solids. In this case, the role of the solid can go beyond a simple support, since it is designed to intervene in the reaction either by stabilizing transition states or by introducing additional active sites.

Well defined single or multiple active sites can also be introduced into crystalline nanoporous materials with controlled adsorption properties, and this allows to perform new acid and redox, one step or multistep reactions.

Finally will show that by depositing metal nanoparticles (Au, Pd, Pt) on proactive supports ($CeO_2$, $Fe_2O_3$, MgO, hydrotalcites, etc.) we can open new catalytic reaction routes for C-C bond formation, oxidations and reductions. These catalytic system allow the design of multifunctional solid catalysts, that are able to carry out multistep process through cascade type reactions that were not possible before.

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Catalysis Science and Engineering, Talk **70**

## Hierarchical Y and USY zeolites designed by post-synthetic strategies

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Y and USY zeolites could be considered as the most valuable catalysts in chemical reactions associated with the (petro)chemical and particularly oil refining industries. Nevertheless, a sub-optimal utilization of the active sites present in zeolites is often implied by limited access and slow intracrystalline diffusion in their micropores. Hierarchical (mesoporous) zeolites integrate the native microporosity with an auxiliary level of mesopores, increasing zeolite utilization substantially [1]. Herein, we present strategic combinations of affordable and scalable post-synthetic modifications to design a broad family of hierarchical Y and USY zeolites (Fig. 1) [2]. A thorough characterization showed the presence of extensive mesoporosity coupled to largely preserved intrinsic zeolite properties. Superior performance of the hierarchical zeolites in pyrolysis, alkylation, Knoevenagel condensation, and fluid catalytic cracking, revealed the tremendous implications for current and emerging applications in acid- and base-catalyzed reactions.

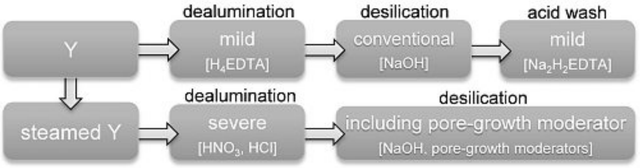

*Fig. 1. Strategies to design hierarchical FAU zeolites by post-synthetic modifications.*

[1] J. Pérez-Ramírez, C.H. Christensen, K. Egeblad, C.H. Christensen, J.C. Groen, *Chem. Soc. Rev.* **2008**, *37*, 2530.

[2] D. Verboekend, G. Vilé, J. Pérez-Ramírez, *Adv. Funct. Mater.* **2012**, *22*, 916.

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Catalysis Science and Engineering, Talk **71**

## Higher catalytic performance of well-defined heterogeneous catalysts by stabilization of active sites through secondary surface interactions.

D. Gajan,[1] M. Samantaray,[2] J. Alauzun,[3] S. Kavitake,[2] A. Mehdi,[3] L. Veyre,[2] M. Lelli,[4] A. Lesage,[4] L. Emsley,[4] C. Copéret,[1] C. Thieuleux.[2]*

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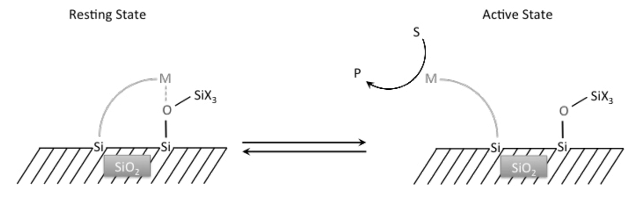
Secondary interactions, typically encountered in enzymatic systems, are demonstrated to exist and direct the stability of well-defined Ru-NHC based heterogeneous alkene metathesis catalysts. By providing key stabilization of the active sites, higher catalytic performance is achieved. Specifically, they can be described as interactions between the metal center (active site) and the surface functionality of the support, and they have been detected by Surface Enhanced $^{1}H$-$^{29}Si$ NMR spectroscopy[1] on the ligand. They are present only when the metal center is attached at the surface via a flexible linker, which allows the active site to either react with the substrate or relax – reversibly – to the surface, thus providing stability.



[1] M. Lelli *et al*. *J. Am. Chem. Soc*. **2011**, *133*, 2104-2107.

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Catalysis Science and Engineering, Talk **72**

## PtPd areogels as a new class of high surface area catalyst towards the oxygen reduction reaction

Wei Liu[2], Annett Rabis[1], Annette Foelske[1], Rüdiger Kötz[1], Jipei Yuan[2], Anne-Kristin-Herrmann[2], Paramaconi Rodriguez[1], Alexander Eychmüller[2], Thomas J. Schmidt[1].

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2 Physical Chemistry/Electrochemistry, Technische Universität Dresden, Bergstr. 66b, 01062 Dresden, Germany

Here we will present an approach in the preparation of highly active extended surface area electrocatalysts towards the oxygen reduction reaction (ORR). PtPd bimetallic aerogels with different composition ratios were prepared in-house using a newly developed synthesis method. Transmission Electron Microscopy images indicate that the aerogel is composed by porous necklace-like nanowires composed of small (ca. 3 nm) nanoparticles.

The maximum activity for the ORR takes place on the 8:2 Pt:Pd catalyst. At 0.9 V the mass activity of the $Pt_{80}Pd_{20}$ is 1180A/g which corresponds to 3.3 mass activity enhancement compared to the monometallic Pt aerogel and 5 times mass activity enhancement compared Pt/C commercial catalyst [1,2]. The mass activity of our aerogel catalyst is significantly improved in comparison to previous results on PtPd/C dispersed nanoparticles [3] and is comparable activity to the PtPd unsupported nanotubes [2,4]. The unsupported high-surface area aerogels are potentially applicable in polymer electrolyte fuel cells where extreme cathode catalyst is necessary.

[1] van der Vliet, D. et al. *Electrochim Acta* **2011**, *56*, 8695.

[2] Koenigsmann, C et al. *J. Am. Chem. Soc.* **2011**, *133*, 9783.

[3] Li, H. et al. *J. Phys Chem C* **2007**, *111*, 5605.

[4] Chen, Z et al. *Angew.Chem. Int. Ed* **2007**, *46*, 4060.

Catalysis Science and Engineering, Talk **73**

## Design, Synthesis, and Characterization of an α/β-Heterodimeric Chorismate Mutase

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Nature exploits sequence-specific biopolymers to store genetic information and to promote all the chemical reactions necessary for life. Recently, chemists and biologists have begun to consider building blocks other than the canonical nucleic acids and α-amino acids for constructing non-natural oligomers that adopt well-defined secondary and tertiary structures ("foldamers"). Here we examine the feasibility of building functional enzymes from β-amino acids. Specifically, we replaced a short helix in a heterodimeric chorismate mutase [1] with a synthetic α/β-foldamer to study the impact of backbone alterations on catalysis. To that end, we designed and synthesized a small library of peptides in which individual α-amino acids were replaced by their β-counterparts. Introduction of β-amino acids at solvent exposed positions were well tolerated, reducing activity by only an order of magnitude compared to the starting enzyme. Although more demanding changes at the helical interface and replacement of the catalytic Arg9 with its β-counterpart decreased catalytic efficiency even further, these experiments represent the first steps toward creating non-natural, yet functional polymers capable of mimicking the properties of highly active enzymes. This lecture will discuss the design principles and properties of these artificial catalysts.

[1] Muller, M. M.; Kries, H.; Csuhai, E.; Kast, P.; Hilvert, D., **2010,** *19*, 1000-1010.

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Catalysis Science and Engineering, Talk **74**

## Complementing Biocatalytic Processes with Streptavidin-Iridium-Pianostool-Hybrids

V. Köhler[1], E. Churakova[2], M. Dürrenberger[1], D. Ghislieri[3], D. Häussinger[1], F. Hollmann[2], L. Knörr[1], T. Quinto[1], N. J. Turner[3], T. R. Ward[1], Y. Wilson[1]

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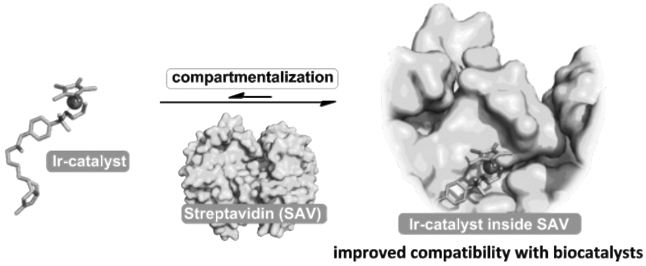
The intrinsic design constraints (aq. buffer, mild pH, moderate temperature) in the construction of transition metal – protein hybrid catalysts qualifies them in the first instance for combination with biocatalysts. A recently reported artificial transfer hydrogenase,[1] based on the biotin - (strept)avidin technology, has been combined with a range of enzymes such as monoamine oxidase variants to effect e.g. the deracemisation of cyclic amines.[2] The firm incorporation of the iridium complex by means of a biotin anchor is crucial to prevent the deactivation of the amine oxidase by the metal catalyst. A strong beneficial effect was confirmed for other enzymes.[3]



[1] M. Dürrenberger et al., *Angew. Chem. Int. Ed.* **2011**, *50*, 3026.
[2] N. J. Turner, *Chem. Rev.* **2011**, *111*, 4073.
[3] M.Poizat et al., *J. Mol. Catal. B: Enzym.* **2010**, *63*, 149.

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Catalysis Science and Engineering, Poster Talk **75**

## Mechanistic Investigations of Iridium-Catalysed Imine Hydrogenation

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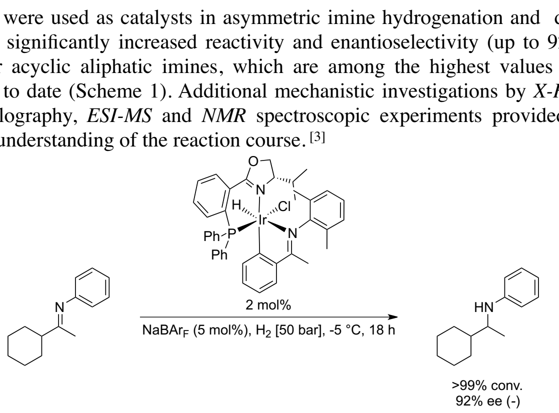
Transition metal-catalysed asymmetric hydrogenation of imines has emerged as a very powerful protocol for the preparation of chiral amine building blocks. However, among the different classes of imines, acyclic aliphatic imines have been particularly challenging substrates. Poor conversion and low enantioselectivites are often observed. [1], [2]

We commenced a mechanistic investigation of the asymmetric imine hydrogenation catalysed by Iridium P`N complexes and identified new iridium complexes that were formed under the reactions conditions. These complexes were used as catalysts in asymmetric imine hydrogenation and displayed significantly increased reactivity and enantioselectivity (up to 92% ee) for acyclic aliphatic imines, which are among the highest values reported to date (Scheme 1). Additional mechanistic investigations by *X-Ray* crystallography, *ESI-MS* and *NMR* spectroscopic experiments provided a better understanding of the reaction course. [3]



**Scheme 1:** asymmetric hydrogenation of acyclic aliphatic imines

[1] A. Baeza, A. Pfaltz, *Chem. Eur. J.* **2010**, *16*, 4003
[2] T. C. Nugent, M. El-Shazly, *Adv. Synth. Cat.*, **2010**, *352*, 753
[3] Y. Schramm, F. Barrios-Landeros, A. Pfaltz, *manuscript in preparation*

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Catalysis Science and Engineering, Poster Talk **76**

## Visible-light driven water oxidation reaction via polyoxometalate-photosensitizer complexes

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Over the past years, water splitting into $H_2$ and $O_2$ via artificial photosynthesis systems[1] turned into a most promising pathway to address the worldwide demands for clean and sustainable energy. The complexity of the water oxidation half reaction and the inevitable differentiation between homogeneous and heterogeneous water oxidation catalysts (WOCs) inspired us to investigate in depth the actual catalytic species involved in polyoxometalate (POM) assisted water oxidation. In search of insight into the challenging oxidative half reaction of water splitting, we synthesized two new all-inorganic POMs as WOCs:[2]
$\alpha\text{-}K_6Na_1[\{Ru_3O_3(H_2O)Cl_2\}(SiW_9O_{34})]\cdot 17H_2O$ and $\alpha\text{-}K_{11}Na_1[Co_4(H_2O)_2(SiW_9O_{34})_2]\cdot 26H_2O$. These new POMs have been fully characterized and the Ru-POM was analyzed with computational methods. Their potential as WOCs has been evaluated and results are in line with recent publications in the field.[3] Most importantly, our study revealed through spectroscopic techniques that the two new POMs form polyoxometalate-photosensitizer complexes which are most likely the active species of the catalytic reaction. They offer two important and promising properties for the construction of overall water splitting systems with low-cost components: recyclable complexes and constant oxygen production rates.

[1] S. Losse, J. G. Vos, S. Rau, *Coord. Chem. Rev.* **2010**, *254*, 2492.
[2] P.-E. Car, M. Guttentag, K. K. Baldridge, R. Alberto, G. R. Patzke, *Green Chem.* **2012**, DOI: 10.139/c2gc16646a.
[3] M. Orlandi, R. Argazzi, A. Sartorel, M. Carraro, G. Scorrano, M. Bonchio, F. Scandola, *Chem. Commun.* **2010**, *46*, 3152.

Catalysis Science and Engineering, Poster Talk **77**

### Biolubricants by lipase catalysis in a microwave barrel reactor

Fabian Fischer[1], Manuel Happe[1], Pascal Grand[2], Sébastien Farquet[2], Sandrine Aeby[3], Jean-Claude Héritier[2], François Corthay[2], Roger Marti[3], Ennio Vanoli[3], Alain-François Grogg[1], Samuel Nussbaum[4], François Tièche[4], Sam Salem[5], Carole Constantin[1], Esther Schmitt[1], Silvan Zahno[2], Christoph Ellert[2], Cristopher Treanor[1], Charles O'Doherty[1]

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3) Institute of Chemistry, HES-SO Fribourg, Fribourg.
4) Information and Communication Systems Institute, HE-arc, St Imier.
5) Institute of Economics, heig-vd, Yverdon.

A newly constructed microwave barrel reactor (MBR) was used in lipase mediated biolubricant synthesis. The lipase catalyzed transformation in the MBR was compared to a state of the art jacketed reactor with heat exchanger. Oleic acid and trimethylolpropane converted quantitatively (96%) into biolubricants using microwave irradiation. The heat dissipation in the MBR was ensured by rotating the reactor tube and a stirrer; and analyzed by thermo imaging. Turn over frequencies (TOF), rate constants $k_{rxn}$ and pseudo reaction orders $n$ were in line with conventional processing. The MBR is a versatile new reactor for bi- and multiphase biotransformation. It is in particular of interest for non solvent or minimal solvent processing in the microwave field. The reactor is designed to be scaled-up into a large batch reactor that can be used in eco-efficient processing of performance chemicals such as: lubricants, surfactants, polymers, but also specialty chemicals and pharmaceutical intermediates. A project Video can be viewed searching the acronym: "ECO2BioPro ST" on Youtube.

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Catalysis Science and Engineering, Poster Talk **78**

### Development of Ca-based $CO_2$ sorbents for the sorbent enhanced water-gas-shift and steam methane reforming reactions

Marcin Broda, Agnieszka M. Kierzkowska, Christoph R. Müller

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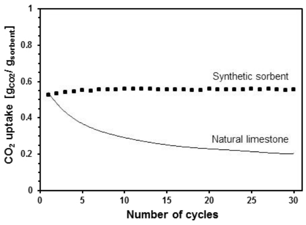
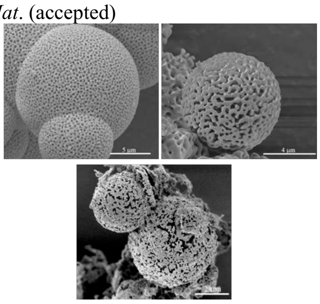
The sorbent enhanced water-gas-shift or steam methane reforming reactions are emerging processes to produce pure hydrogen from, respectively, CO or $CH_4$ in a single-step process with simultaneous $CO_2$ capture, e.g. $CO + H_2O + CaO \rightarrow CaCO_3 + H_2$. Owing to their low price and high availability, the use of natural Ca-based sorbents, *e.g.* limestone, has been proposed initially. However, most natural sorbents show a rapid decrease in the $CO_2$ uptake with cycle number. It has been argued that the drop in the $CO_2$ capture capacity is mainly caused by thermal sintering resulting in the reduction of the surface area and pore volume available in micro and meso pores and the blockage of small pores. Here, we report a technique to synthesize, micro- and nano-structured, Ca-based, $Al_2O_3$-stabilized materials with excellent $CO_2$ capture characteristics over 30 repeated carbonation and calcination cycles (including the presence of steam) [1]. A carbon-gel template was used to generate a thermally stable, highly porous structure.

[1] M. Broda and. C.R. Müller, *Adv. Mat.* (accepted)





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Catalysis Science and Engineering, Poster Talk **79**

### Aerobic Alcohol Oxidations Mediated by Nitric Acid

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Despite their industrial relevance, the mechanistic rationalization of selective oxidations often trails the industrial state-of-the-art. Nitric acid based oxidations are a classical example of a poorly understood process of tremendous industrial importance. The production of adipic acid (3 Mt/year), a building block for nylon-6,6, is just one example from bulk industry. The reason why $HNO_3$-based oxidations are so valuable is the fact that nitric acid is a rather inexpensive oxidant with no toxic potential. One disadvantage of this technology is the stoichiometric reduction of the $HNO_3$ to $NO_x$ and $N_2O$, a severe greenhouse gas, the formation of which is still poorly understood.

In this contribution, we unravel the reaction mechanism of $HNO_3$-induced alcohol oxidations, and illustrate how such stoichiometric reactions can be turned into catalytic systems in which $HNO_3$ initiates a selective oxidation with $O_2$ as terminal oxidant.[1]

Mass spectrometry and transmission IR spectroscopy were used to monitor the formation of $N_2O$ in the gas phase, stemming from HNO dimerization.[1,2] With the help of these measurements, the mechanism for the formation of $N_2O$ and the detrimental role of $H_2O$ that reduces the turnover of $(H)NO_x$ species in the system could be elucidated.

These micro-kinetic insights, combined with tailored reaction engineering, allow the design of a promising sustainable oxidation system for alcohols by reducing the amount of $N_2O$ formed and by boosting the turnover in $(H)NO_x$ species.

[1] C. Aellig, C. Girard, I. Hermans, *Angew. Chem. Int. Ed.* **2011**, *50*, 12355-12360
[2] C. Aellig, I. Hermans, *ChemCatChem* **2012**, *4*, 525-529

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Catalysis Science and Engineering, Poster Talk **80**

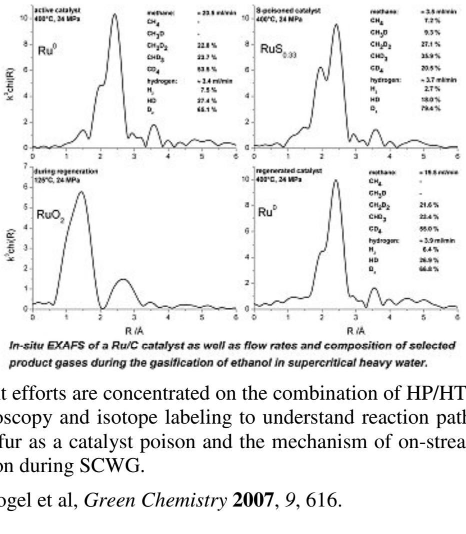
### Activation, Poisoning and Regeneration of a Ru/C Catalyst during the Gasification of Model Biomass in Supercritical Water

### - an in-situ EXAFS and Isotope Scrambling Study -

Marian Dreher, Maarten Nachtegaal, Jörg Wambach and Frédéric Vogel

Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland

The catalytic supercritical water gasification (SCWG) of wet biomass is a highly efficient way of producing synthetic natural gas from various types of biomass [1]. However, catalyst deactivation due to poisoning and sintering severely limits the lifetime of catalysts used in this process.



*In-situ EXAFS of a Ru/C catalyst as well as flow rates and composition of selected product gases during the gasification of ethanol in supercritical heavy water.*

Our current efforts are concentrated on the combination of HP/HT in-situ X-ray spectroscopy and isotope labeling to understand reaction pathways, the role of sulfur as a catalyst poison and the mechanism of on-stream catalyst regeneration during SCWG.

[1] F. Vogel et al, *Green Chemistry* **2007**, *9*, 616.

Catalysis Science and Engineering, Lecture **81**

## A nature-inspired approach to structuring porous catalysts from the nano- to the particle scale

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Guided by the way the nano-cage in GroEL/GroES chaperonins prevents protein aggregation and assists protein folding in *E. coli*, we design nanoporous silica SBA-15 with controlled nanopore diameter, surface charge and chemistry to boost the activity of immobilized enzymes, up to levels several times those of the free enzymes in solution [1, 2]. We also show how the hydroformylation activity, selectivity and stability of Rh-diphosphine complexes can be remarkably increased by nano-confinement in SBA-15 [3].

Transport limitations and catalyst deactivation by pore blockage are major issues in many processes involving zeolites and other nanoporous catalysts. We draw inspiration from the architecture of leaves and of pulmonary alveoli, and use theoretical and computational optimization methods to guide the hierarchical structure of the pore network of heterogeneous catalysts [1], hereby increasing activity [4], mitigating effects of catalyst deactivitation [5], and improve control over product distribution [6].

[1] M.-O. Coppens, *Curr. Opin. Chem. Eng.* **2012**, doi:10.1016/j.coche.2012.03.002 .

[2] L.C. Sang, M.-O. Coppens, *Phys. Chem. Chem. Phys.* **2011**, *13*, 6689.

[3] F. Marras, J. Wang, M.-O. Coppens, J.N.H. Reek, *Chem. Comm.* **2010**, *46*, 6587.
[4] G. Wang, M.-O. Coppens, *Ind. Eng. Chem. Res.* **2008**, *47*, 3847.
[5] S. Rao, M.-O. Coppens, *Chem. Eng. Sci.* **2011**, doi:10.1016/j.ces.2011.11.044 .
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Catalysis Science and Engineering, Talk **82**

## Structured Metal Fiber-based Catalysts for the Solvent-Free Hydrogenation of 2-butyne-1,4-diol: Role of the Oxide Support

Charline Berguerand, Igor Iouranov, Fernando Cárdenas-Lizana and Lioubov Kiwi-Minsker

Ecole Polytechnique Fédérale de Lausanne, GGRC-ISIC-EPFL, Lausanne CH-1015, Switzerland

2-butene-1,4-diol (B$_2$D), obtained by selective hydrogenation of 2-butyne-1,4-diol (B$_3$D), is an important chemical used in the manufacture of fine chemicals.[1] The conventional powder Lindlar catalyst (Pd/CaCO$_3$) presents drawbacks in terms of separation, lack of selectivity and intolerance to water. We have studied the viability of novel structured catalysts based on Pd *nano*-particles (NPs) supported on metal fibers coated by oxide layer for the solvent-free liquid phase hydrogenation of B$_3$D. The nature of the oxide support, as one of the key parameters affecting catalytic response in hydrogenations,[2] has been analyzed. For a series of oxide supports, *e.g.* SiO$_2$, MgO+Al$_2$O$_3$, ZnO+Al$_2$O$_3$, our results show that catalytic response can be controlled by modifying the acid-base properties of the carrier. We have achieved, for the first time, 99 % yield of B$_2$D over Pd/ZnO where activity and selectivity were maintained over consecutive runs. This is ascribed to the formation of inter-metallic PdZn alloy. Metal particle size has been confirmed by TEM analyses while alloy formation and modifications in the electronic properties have been established by XPS measurements. The reaction kinetics has been modeled using a Langmuir-Hinshelwood approach and a mechanism is proposed.

Our findings establish the potential of novel structured catalysts based on Pd-NPs supported on oxide-metal fiber composites for selective alkyne hydrogenation where product composition can be tuned through the choice of the oxide support.

[1] F. Cárdenas-Lizana *et al.*, *Catal. Sci. Technol.*, **2011**, *1*, 652
[2] M. G. Musolino *et al.*, *Appl. Catal. A: Gen.*, **2010**, *390*, 141.

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Catalysis Science and Engineering, Talk **83**

## Controlling the chemoselectivity via surface modification over supported Pt catalysts

[1]Martin Makosch, [1]Václav Bumbálek, [1,2]Jacinto Sá, [3]Will Medlin, [1]Konrad Hungerbühler and [1,2]Jeroen A. van Bokhoven

[1]Institute for Chemical and Bioengineering ETH Zurich, Wolfgang-Pauli Strasse, 8093 Zurich, Switzerland

[2]Paul Scherrer Institute (PSI), Villigen (Switzerland)

[3]Renewable and Sustainable Energy Institute (RASEI), Colorado at Boulder (USA)

Control of chemoselectivity in hydrogenation of multi-functionalized substrates for the production of fine chemicals is difficult over heterogeneous catalysts.[1] We show that the selectivity towards 4-aminostyrene in the liquid phase hydrogenation of 4-nitrostyrene can be completely reversed without the addition of promoters for phenylhydroxyl decomposition via a simple surface modification. The activity remained about 30 % of the non modified system. Catalyst characterization by means of TEM, FT-IR and in situ HERFD XANES measurements showed that the Pt surface is densely packed with the surface modifier which is stable under reaction conditions. The modification of the Pt nanoparticles using organic thiols leads to a changed adsorption mode of the substrate 4-nitrostyrene such that flat adsorption is prohibited but H$_2$ splitting can still occur on the metal surface. The reaction then proceeds on the uncovered Pt atoms at the rim of the nanoparticles. A strong dependence of thiol concentration during modification on activity and selectivity was observed. Chemically different surface modifiers did not have a significant impact on the selectivity, while H$_2$S treatment resulted in complete catalyst deactivation. This new system adds to the “heterogeneous tool box” and could also be applied for other selective hydrogenation problems.

[1] Blaser, H.-U.; Steiner, H.; Studer, M., *ChemCatChem* **2009**, *1*, 210.

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Catalysis Science and Engineering, Talk **84**

## Flame-made PdO/YFeO$_{3\pm\delta}$ as TWC for methane abatement from stoichiometric engines

Y. Lu[1], K. Michalow-Mauke[2], A. E. Maegli[1], A. Heel[3], M. Santhosh Kumar[1], T. Graule[2], A. Weidenkaff[1], D. Ferri[1]

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Natural gas (> 90% CH$_4$) is receiving increasing attention as an alternative fuel to gasoline. However, CH$_4$ present in the exhaust gas of the engine needs to be abated because of its massive greenhouse potential. Palladium is the precious metal of choice for catalytic after treatment but suffers from a number of issues including thermal aging [1]. Pd-based YFeO$_3$ catalysts have been prepared by flame spray synthesis (FSS) with the aim to provide more stable Pd-based formulations to present three-way catalysts with low Pd content. Activity tests were conducted with 7000 ppm CO, 1300 ppm CH$_4$, 1600 ppm NO$_x$ and 5300 ppm O$_2$ ($\lambda$= 1) to simulate natural gas engine exhaust conditions.

The 2 wt% PdO/YFeO$_{3\pm\delta}$ catalyst consisted of finely dispersed PdO particles supported on 20 nm YFeO$_{3\pm\delta}$ particles. The catalyst demonstrated interesting catalytic activity for CO, CH$_4$ and NO$_x$ abatement though remaining inferior to a conventional Pd/Al$_2$O$_3$-CeZrO$_2$ catalyst with similar Pd loading. Light-off for CH$_4$ oxidation was observed at 350°C. However, PdO and YFeO$_3$ nano-particles were stable against thermal aging to 900°C, thus providing potential for the development of a TWC catalyst. The Pd content could be reduced to 0.5 wt% without sacrificing catalytic activity for the three pollutants.

[1] A. Winkler, P. Dimopoulos, R. Hauert, C. Bach, M. Aguirre, *Appl. Catal. B* **2008**, *84*, 162.

Catalysis Science and Engineering, Lecture

**85**

## Hydroformylation Kinetics for Continuous Homogenous Catalysis with Integrated Membrane Separation#

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Hydroformylation is used on a large scale in industry to produce aldehydes from alkenes. These are important intermediates for polymer-softeners and surfactants. In homogeneous catalysis in general, catalyst separation and reuse is an important issue. We develop generic methods that aim at continuous homogeneous catalysis.[1] Recently we reported on the efficient continuous hydroformylation using a molecular weight enlarged phosphine in a loop membrane reactor.[2] For the further development of this approach we examined the kinetics of a highly active phosphite-modified catalyst [3] for neohexene and cyclooctene as model substrates for terminal and internal alkenes. Rate equations were determined applying a sequential experimental design. Deuterium labeling studies were carried out for further insight into the mechanism. The model derived was used in the design of a jet-loop reactor.

[#] This research is funded by the EC within the Integrated Project F3-Factory, grant agreement no 22886

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Catalysis Science and Engineering

**86**

## Gasification of biomass in SCW over Ru catalysts: *in situ* and deactivation studies

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Wet biomass, e.g. agricultural residues, and dry biomass (e.g. wood) are considered playing a major role in our future sustainable energy supply. Biogenic synthetic natural gas (Bio-SNG) is particularly interesting as it can be produced with a high efficiency from almost any kind of biomass applying a proper conversion technology. *Hydrothermal processing* under supercritical water (SCW) conditions does not require dry biomass and thus has a great potential for producing biofuels and bio-chemicals from various types of biomass.

At PSI a catalytic SCW process using a commercial Ru/active carbon catalyst was developed, which is operated at temperatures of 400-450°C and pressures of 25-35 MPa. We study the supercritical water gasification (SCWG) feeding relatively simple model compounds of wet biomass, e.g. ethanol or glycerol mixtures. Occasionally deactivation is observed, which is accompanied by a loss of surface ruthenium. Therefore we want to obtain an improved insight on the catalyst as well as on understanding the processes governing the catalytic reactions in the hydrothermal media.

We will present results on the modifications the catalyst undergoes during the reaction obtained from various spectroscopic methods like *in situ* XAS, respectively XPS, RBS, XRD, etc. applied *ex situ*. Some XANES data are already published [1].

[1] S. Rabe, M. Nachtegaal, T. Ulrich, F. Vogel; Angew. Chem. Int. Ed. **2010**, 49, 6434.

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Catalysis Science and Engineering

**87**

## Development of a bi-functional Ni-Ca-based catalyst/$CO_2$ sorbent for the sorbent enhanced steam methane reforming reaction

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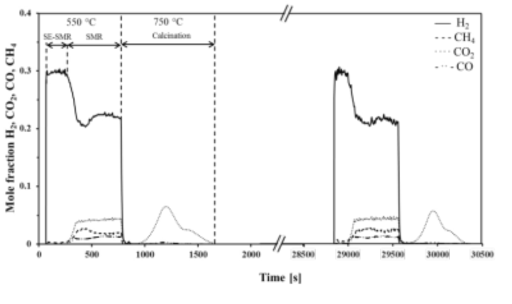
To reduce the operational complexity and the severeness of the operating conditions of the conventional steam methane reforming reaction, the so-called Sorbent Enhanced Steam Methane Reforming (SE-SMR) reaction has been proposed, viz. $CH_4 + 2\ H_2O + CaO \rightarrow CaCO_3 + 4\ H_2$. Here, a bi-functional catalyst/$CO_2$ sorbent (46 wt.% Ni; 21 wt.% CaO) was derived from a hydrotalcite-based precursor synthesized via a co-precipitation technique. The recorded mol fraction of hydrogen in the effluent stream was 99 vol.% (dry and without inert component) i.e. reaching thermodynamic equilibrium. The high and stable $CO_2$ uptake capacity and the fast carbonation kinetics of CaO in the material were attributed to its fine dispersion into the highly porous and thermally stable network, effectively limiting calcite particle sintering.



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Catalysis Science and Engineering

**88**

## Relation between surface properties and acidity of aluminosilicate materials obtained by grafting

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Amorphous aluminosilicates (ASAs) are widely used acidic catalyst supports in the field of heavy oil fractions conversion (hydrocracking). These mixed mesoporous oxides provide the moderate acidity required for high selectivity towards middle-distillates, for which demand is continuously increasing. Yet, the structure of ASAs (which depends on their synthesis route) and, more particularly, the nature, localization and number of the sites originating their acidity remain largely debated. The present study proposes to rationalize the role played by the catalyst surface. For this purpose, model-aluminosilicates have been synthesized using the grafting technique, i.e. the deposition of alkoxy species on the complementary oxide ($Al/SiO_2$ and $Si/Al_2O_3$). Since catalytic active sites are located on the surface, grafting allows to connect acidity rising to the presence of the deposited species according to their structure.

First observation is that the size of the precursor molecule seems to be the limiting factor of surface oxide reactivity. Maximum guest species concentration is attained once the whole oxide surface has been covered with precursor molecules. Yet, repetition of the grafting step can be performed provided that alkoxy groups of the deposited molecules have been converted into OH groups upon calcination. Correlation between the IR study of adsorbed CO molecules and *m*-xylene isomerization results evidences that deposition of guest species leads to acidity enhancement, thanks to the appearance of strong Lewis and Brönsted acid sites. Lutidine adsorption study confirms that acidic sites implied in *m*-xylene isomerization are the strongest Brönsted acid sites.

Catalysis Science and Engineering

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## Supported gold-nanoparticles in hydrogenation

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Gold nanoparticles on metal oxide supports are active and selective in the hydrogenation of nitroaromatic compounds[1]. Since hydrogen splitting is the rate limiting step in the reaction, it provides an opportunity to study the effects of particle size, oxidation state and support on hydrogenation reactions over gold nanoparticles. We determined particle size effects in gold on titania and gold on alumina by pretreating the catalysts at different temperatures and comparing activity and the particle size obtained by TEM after reaction. Within the tested range, no significant effect of pretreatment temperature was observed for gold on titania. For gold on alumina, high pretreatment temperatures led to strong sintering and reduced activity. In-situ high energy resolution fluorescence detected X-ray absorption spectroscopy (HERFD XAS) revealed that pretreatment at low temperatures was insufficient to completely reduce the gold precursors. The gold precursors were then reduced under reaction conditions, which also led to uncontrolled sintering and thus lower activity. On gold supported on alumina, the activity of the catalyst is proportional to the amount of gold particles that are smaller than 2 nm. Gold supported on titania is a more active catalyst than gold supported on alumina, since the titania support is able to assist in hydrogen splitting due to its stronger basic sites.

[1] A. Corma, P. Serna, *Science*, **2006**, *313*, 332-334.

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Catalysis Science and Engineering

**90**

## Fine chemical synthesis by photocatalysis

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Photocatalysis is often used for the removal of pollutants. A less common application is the synthesis of fine chemicals. We exploited the use of Au/TiO2 for ring closure and N-alkylation, under mild UV irradiation (350 nm) at room temperature and atmospheric pressure. The results show that with the addition of Au one can achieve high yield in N-alkylation and fairly high production of ring closure products such as Caprolactam, a precursor for the production of Nylon 6.

This opens new perspectives in the use of photocatalysis as a viable way to produce relevant fine chemicals.

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Catalysis Science and Engineering

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## Correlations between the geometric structure and the electronic properties of polyhedral ceria NPs

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Ceria-based materials have many interesting applications including catalysis, fuel cells, and biology.[1] The size- and shape-dependant changes in the catalytic properties of nano-ceria are often attributed to stabilization $Ce^{3+}$ defects on the NPs surface. We performed a systematic analysis of the structure of polyhedral $CeO_2$ NPs of 2-10 nm, under ambient conditions, using combination of transmission electron microscopy, X-ray diffraction and X-ray spectroscopy at Ce K- and L-edges.[2]

We reveal that the unit cell parameter increases when the NPs size decreases (up to 0.3% for 2 nm NPs) correlating to an effective negative Madelung pressure taking place in ionic crystals. The structural disorder, characterized by pseudo Debye-Waller factors, increases for smaller NPs. Under ambient conditions, the oxidation state of ceria NPs is always close to 4+ and there is no stabilization of $Ce^{3+}$ in smaller ceria nanoparticle.

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Catalysis Science and Engineering

**92**

## Single atom Rh catalysts for steam reforming of methane

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The steam reforming of methane (SRM) reaction is important for the large scale production of $H_2$. Previous reports found that the reaction rate in SRM increases with the dispersion of the active phase[1,2]. Hence, obtaining highly efficient catalysts with single-atom dispersion is crucial for achieving high activity. Jones et al.[1] confirmed that Rh is one of the most active metals for this reaction. Additionally, the properties of the support have crucial impact on the activity and stability of catalysts. Giving this, Rh catalysts supported on mixed oxides of $Sm_2O_3$-$CeO_2$-$Al_2O_3$ were investigated in order to clarify the role of the metal dispersion and specially the role of samaria and ceria dopant in the catalytic performance. 0.5%Rh/$x$$Sm_2O_3$-$y$$CeO_2$-$Al_2O_3$ ($x$ and $y$ = 0, 6 or 12 % wt., being x + y = 12 % wt.) catalysts were obtained by wet impregnation. STEM images of the samples showed clearly the formation of single-atom dispersed catalysts. The catalytic properties of Rh/$Al_2O_3$ and Rh/12$CeO_2$-$Al_2O_3$ were evaluated and the latter showed higher activity and stability. STEM images of Rh/$Al_2O_3$ catalyst after reaction showed the coexistence of small cluster and single atoms, showing that sintering took place in the absence of promoter.

[1] G. Jones, J. G. Jakobsen, S. S. Shim, J. Kleis, M. P. Andersson, J. Rossmeisl, F. Abild-Pedersen, T. Bligaard, S. Helveg, B. Hinnemann, J. R. Rostrup-Nielsen, I. Chorkendorff, J. Sehested, J. K. Nørskov, *Journal of Catalysis*. **2008**, *259*, 147.
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Catalysis Science and Engineering **93**

## Hydrogen production from formic acid decomposition

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The catalytic decomposition of liquid hydrocarbons to form hydrogen has several advantages over using $H_2$ directly, such as avoiding the need for large compression tanks and the hazard of handling an explosive gas. Formic acid is a safe and non-toxic chemical that has received increasing attention as a potential $H_2$ source material [1]. However, the competing dehydration to CO and $H_2O$ and formation of formaldehyde require that all product species be taken into account.

The vapor-phase decomposition of formic acid on 0.7 wt% gold supported on $TiO_2$ and $Al_2O_3$ was studied between 24 and 350 ºC with the goal of forming $H_2$ selectively. A setup that allowed the detection of HCOOH, $H_2$, $CO_2$, $H_2O$, and CO, as well as most liquid products, including HCHO, was developed. Above 350 ºC thermal non-catalytic decomposition became significant and reached full conversion around 500 ºC.

While selectivity to $H_2$ did not exceed 40% over the Au/$TiO_2$ samples, the decomposition over Au/$Al_2O_3$ proceeded predominantly to $H_2$ and $CO_2$ between 150 and 250 ºC. However, formation of HCHO was observed over all catalysts. Our results show the importance of detecting all species in the product stream to obtain more complete information about the reaction. The presence of liquid products suggests that formic acid can decompose by reaction paths other than dehydrogenation and dehydration [2].

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Catalysis Science and Engineering **94**

## Selective conversion of lignin to chemicals via catalytic fast pyrolysis

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The catalytic fast pyrolysis of alkaline lignin to useful chemicals was investigated using zeolite catalysts of different acidity and pore size. Fine-tuning the properties of the catalyst lead to high yields of liquid and selectivity to aromatic hydrocarbons was obtained. Notably, the amount of coke was significantly decreased. Using no catalyst yielded 40 wt.% of liquid, which mainly consisted of 6 wt.% (carbon yield) of phenols and 19 wt.% (carbon yield) of phenol alkoxy species. The highest yield of phenol alkoxy species was obtained over H-ZSM5 of extremely low number of acid sites; liquid yield of 51 wt.% and carbon yield of 24 wt.%. The highest yield of liquid (75 wt.%) was obtained over H-USY, which had the largest pore size and lowest Si/Al ratio, thus the largest number of acid sites among all the catalyst tested; the carbon yield of aromatic hydrocarbons was around 40 wt.% at 650 °C. Analysis of the mechanism lead to the conclusion that the catalyst plays a dual role in this process. They transform the depolymerized intermediates into desirable products, and they also stabilize the depolymerized intermediates and prevent the repolymerization and thus coke formation. Understanding the chemistry of catalytic fast pyrolysis combined with the development of improved catalysts, which are specifically designed for selective lignin conversion, leads to further process improvement.

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Catalysis Science and Engineering **95**

## Homogeneous Asymmetric Hydrogenation Enhanced by Metal-Organic Frameworks

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Asymmetric hydrogenation of olefins is one of the most important catalytic processes in the fine chemicals industry. It can be catalyzed by homogeneous catalysts based on rhodium diphosphine complexes in high activity and selectivity[1] and the reaction mechanism is well accepted.

Metal-organic frameworks (MOFs) are becoming more and more popular in the area of catalysis.[2] MOFs with $NH_2$ groups can be functionalized with organometallic precursors to form heterogeneous catalysts with single-atom active sites.

In this work, we present the use of MOFs in the asymmetric hydrogenation of olefins (methyl 2-acetamidoacrylate, dimethyl itaconate and methyl 2-acetamidocinnamate) catalyzed by [Rh(Me-BPE)(COD)]OTf (Me-BPE = 1,2-Bis((2*S*,5*S*)-2,5-dimethylphospholano)ethane; COD = 1,5-cyclooctadiene; OTf = triflate). The addition of MOFs (IRMOF-3, $NH_2$-MIXMOF-5, $NH_2$-UMCM-1 and UMCM-1)[2] into a homogeneously catalyzed reaction generally increases the turnover number of the catalyst and allows selectivities above those described in the literature.

If toluene is used as solvent, the MOF absorbs the homogeneous catalyst and thus reduces the contamination of products with Rh. Moreover, under these conditions, the heterogeneous catalyst thus formed can be recycled.

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[2] M. Ranocchiari, J. A. van Bokhoven, *Phys. Chem. Chem. Phys.* **2011**, *13*, 6388.

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Catalysis Science and Engineering **96**

## Synthesis of novel phosphine substituted metal-organic frameworks and their use in enantioselective hydrogenation

Flavien L. Morel[1,2], Marco Ranocchiari[1*], Jeroen A. van Bokhoven[1,2*]

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Metal-organic frameworks (MOFs) are porous, crystalline materials whose recent development is leading to exciting applications in catalysis and gas storage [1]. Recent works showed the possibility to incorporate framework-bridging organophosphine species into MOF via synthetic routes [2]; however, MOFs containing “free” phosphine moieties, i.e. non-coordinated to the inorganic unit, are rarities and they have not yet found application in catalysis.

Phosphines are commonly used class of ligands in homogeneous catalysis, well-known for their metal coordination capabilities. Our work focuses on the preparation of a new class of organophosphine linkers which allows the synthesis of MOFs with non-coordinated phosphine species inside their framework. We will present the synthesis of biphenyl and terphenyl dicarboxylic acids with bearing diphenylphosphino groups. Moreover we will describe the synthesis of the corresponding MOFs and their post-functionalization with chiral organometallic catalysts to create their heterogeneous enantioselective counterparts. Preliminary results in asymmetric hydrogenation will be presented to illustrate the potential of this class of catalyst.

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Catalysis Science and Engineering **97**

### New Metal-Organic Framework for Heterogeneous Catalysis

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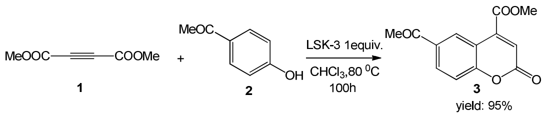
We have designed a method to control the local structure of the active site in a heterogeneous catalyst. The ultimate aim is to control the local environment of an active site in the pockets of a metal-organic framework. Our group has recently developed a novel structure[1], which has free diphenylphosphine (DPP) groups connected to the linkers (LSK-3). We have explored its catalytic properties by employing its Lewis basicity. We thus synthesized coumarin methyl 6-acetyl-2-oxo-2H-chromene-4-carboxylate (**3**) from 4-hydroxyacetophenone and (**1**) dimethyl-acetylenedicarboxylate (**2**) in the presence of LSK-3. The conversion exceeded 99% and the GC yield 95%.[2]



The DPP moieties of LSK-3 make it a versatile, crystalline, and heterogeneous catalyst for reactions that are usually catalyzed by soluble organic phosphines.

[1] S. Rummelt, X. Xu, M. Wörle, M. Ranocchiari and J. A. van Bohoven, unpublished results.
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Catalysis Science and Engineering **98**

### LSK-1: A Novel, Phosphorus-functionalized Metal-Organic Framework Applicable in Au(I) Catalysis

Jiří Václavík[1], Marco Ranocchiari[1,*], Christian Lothschütz[1], Jeroen A. van Bokhoven[1,2]

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During the last two decades, metal-organic frameworks (MOFs) have been extensively studied in various areas of application, out of which catalysis belongs to the most significant ones.[1] Phosphine-functionalized MOFs (*P*-MOFs) possess excellent preconditions for the use in catalysis since phosphines are known to be very good ligands in the field of homogeneous catalysis. Designing a MOF containing free phosphine groups can thus bring together the advantages of homogeneous and heterogeneous catalysis, because the MOF serves both as a solid ligand and a support.

We present here the synthesis, metal-functionalization, and catalytic application of LSK-1, a novel *P*-MOF which is composed of zirconium inorganic units and tris(4-carboxyphenyl)phosphine as the organic linker. The material is exceptionally thermally and chemically stable, with a BET surface area of 1024 $m^2/g$.

LSK-1 was successfully functionalized with Au(I) active sites that efficiently catalyze hydration of terminal alkynes and cyclization of propargylcarboxamides to oxazoles. Both reactions have been reported previously with $PPh_3$-Au-X homogeneous catalysts (X = a weakly coordinating anion), whose chemistry was applied to LSK-1 accordingly.

[1] M. Ranocchiari and J. A. van Bokhoven *Phys. Chem. Chem. Phys.* **2011**, *13*, 6388-6396.

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Catalysis Science and Engineering **99**

### Cu-$Al_2O_3$ oxygen carrier for chemical looping combustion: synthesis, redox stability and reaction pathways

Q. Imtiaz[1], M. Broda[1], A. Kierzkowska[1], C. Koenig[2], O. Safonova[2], M. Nachtegaal[2], T. J. Schildhauerand[2] and C. R. Müller[1]

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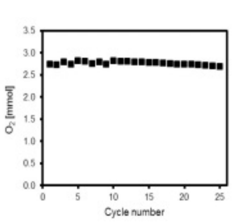
Copper oxide is a commonly used catalyst for various important chemical reactions such as the water-gas shift reaction or methanol synthesis from CO. In addition, copper oxide is also a very promising oxygen carrier for chemical looping combustion (CLC), an emerging process for carbon dioxide capture and storage (CCS).[1] In CLC lattice oxygen of the oxygen carrier is used to oxidize a carbonaceous fuel, *e.g.*: $CH_4 + 4CuO \rightarrow 4Cu + CO_2 + 2H_2O$. Subsequently, Cu is re-oxidized with air to close the cycle. Here, we develop a Cu-rich (82 wt. % CuO), $Al_2O_3$ stabilized oxygen carrier using a co-precipitation technique. The redox stability of the oxygen carrier was evaluated at 800 °C in a fluidized bed reactor (Figure 1). In-situ XAS measurements indicate that both the reduction and oxidation of $Al_2O_3$-stabilized CuO occurs *via* the $Cu_2O$ intermediate at the temperature investigated.



[1] Q. Imtiaz, A. Kierzkowska, C. R. Müller, *ChemSusChem*, **2012**, DOI: 10.1002/cssc.201100694

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Catalysis Science and Engineering **100**

### Manganese Oxide for high temperature sulfur removal from synthesis gas - a time-resolved XAS study

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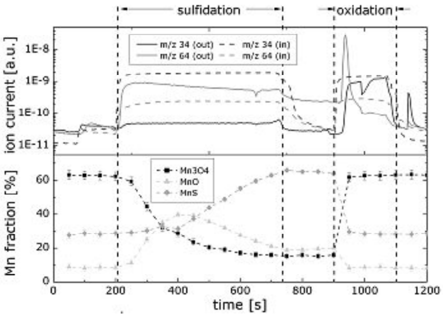
Catalytic conversion of biomass into chemicals, such as methane, is a promising route for sustainable energy supply. However, biomass contains sulfur, which needs to be removed from the gas stream to protect catalysts from poisoning. High temperature sulfur removal is desired to improve overall efficiency. [1]



We studied the mechanism of sulfur transport at high temperatures over a Mn-based material under cyclic sulfidation and oxidation conditions *in situ*, by using time resolved, fluorescence detected X-ray absorption spectroscopy (XAS) and mass spectrometry. Sensitivity of XAS was increased by using a modulated excitation approach [2]. The results allow proposing a mechanism, in which $Mn_3O_4$ is reduced by $H_2S$ to MnS via an MnO intermediate species.

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[2] D. Ferri et al, *Phys. Chem. Chem. Phys.* **2010**, *12*, 5634 - 5646

Catalysis Science and Engineering **101**

## A novel approach to combine *In situ* X-ray Absorption (XAS) and Infrared (DRIFT) Spectroscopies for catalytic applications

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*In situ* DRIFTS and XAS are two complementary techniques in catalysis, allowing a deeper insight into reaction mechanisms and the dynamic of redox processes. However, XAS provides only bulk information due to the penetration depth of X-rays. The combination with modulated excitation spectroscopy (MES) through periodic switch of gas composition, and phase sensitive detection (PSD) [1], has demonstrated to be a powerful tool to bring surface sensitivity to XAS [2]. MES exploits the PSD algorithm used to demodulate the time-resolved data to filter the signals of spectator species and the noise present in the time domain. This approach is here used to enhance the response of time-resolved XAS (and DRIFTS) to the subtle variation of the surface of metal oxides.

Existing examples of combined IR-XAS setups are adaptations of commercial DRIFT cells to X-rays [3,4], whose use is limited to transmission and to selected materials because of the long optical path length. Our new cell, consisting of a plug-flow design, offers a wide surface for IR collection and a variable thin sample thickness for transmission measurements of difficult highly absorbing materials. Moreover, MES is facilitated by the absence of dead volume around the sample contrary to commercial DRIFT cells. The IR beam will be shined over the samples by means of a proper set of mirrors and positioning motors, placed along the X-ray beam. Preliminary results will be presented for oxidation of volatile organic compounds on metal oxides.

[1] D. Baurecht, U.P. Fringeli, *Rev. Sci. Instr.* **2001**, *72*, 3782.
[2] D. Ferri, et al., *PCCP*, **2010**, *12*, 5634.
[3] M. A. Newton, *Top. Catal.* **2009**, *52*,1410.
[4] Marinkovic et al., *Nucl. Instrum. and Meth. A*, **2011**, *649*, 204.

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Catalysis Science and Engineering **102**

## Sorption enhanced $CO_2$ hydrogenation for the production of renewable fuels

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In the Sabatier process $CO_2$ can be reduced by $H_2$ over a catalyst producing eventually methane and water. If hydrogen is produced from renewable energy sources by electrolysis and carbon dioxide is extracted from the atmosphere, the methane from such a process represents a $CO_2$ neutral synthetic fuel. The reduction of $CO_2$ by hydrogen eventually forming hydrocarbons depends on the interaction of $CO_2$ and $H_2$ with a catalyst surface, i.e. ad- and desorption of hydrogen, $CO_2$ and products [1]. The Sabatier principle indicates that an optimal catalyst has intermediate binding energy to the adsorbent, because an enhanced bonding strength increases the adsorption, but decreases the desorption reaction. To overcome this limitation we control the surface reaction by enhanced product desorption upon forced removal of water within a sorption catalyst [2]. As a proof-of-concept, an improvement of the reaction yield of more than 100% is realized using Ni-zeolite catalysts. The reaction mechanism is investigated by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and is correlated to the structural properties of the catalyst as measured by XPS, XRD, SEM and TEM. Two Ni species are present in the catalyst: Ni-ions located at the cationic sites of the zeolite and metallic Ni clusters. While the latter ones show the desired effect, Ni-ions in the zeolite are basically inefficient catalysts for the Sabatier reaction.

[1] J. K. Nørskov, et al., *Nature Chem.* **2009**, *1*, 37.
[2] B. T. Carvill, et al., *AIChE J.* **1996**, *42*, 2765.

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Catalysis Science and Engineering **103**

## Studies on thermal and chemical aging of model three-way catalysts by operando spectroscopy

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New fuel concepts like compressed natural gas (CNG) and new EURO VI legislations impart greater challenges to the three-way catalytic (TWC) performance of CNG fuelled vehicles. Thermal aging caused by high temperature excursions in the TWC and chemical aging due to phosphorus (P) originating from engine oil additives result in the catalyst deactivation. However, the deactivation mechanism, especially P induced one is not completely understood [1]. To this end, operando XAS/Mass spectrometry is employed to gain insight into the thermal and P induced deactivation mechanisms.

Characterization results reveal that chemical aging with P at 700°C decreases drastically both surface area and pore volume, while this is not the case with simple thermal aging. Chemical aging leads to the formation of $AlPO_4$ and $CePO_4$ like species in the catalysts [1]. From operando spectroscopic data, it emerges that P alters the redox properties of $PdO_x$ species in the catalysts, which reduces the oxidation and reduction efficiency of the catalysts. Thermal aging affects to some extent only oxidation efficiency.

[1] S.K. Matam, E. Otal, M. Aguirre, A. Winkler, A. Ulrich, D. Rentsch, A. Weidenkaff, D. Ferri, *Catal. Today.* **2011**, doi.org/10.1016/j.cattod. 2011. 09.030.

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Catalysis Science and Engineering **104**

## Modulated excitation spectroscopy coupled with XAS and XRD to capture dynamic structural changes in supported Pd catalysts

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Automotive catalysts operate under severe conditions of temperature and of fast transients that are challenging to reproduce for in situ structural studies. Improved data evaluation of the spectroscopic data is required to separate the contribution of dynamic signals from that of typically overwhelming static signals. This can be achieved by a demodulation technique [1], based on phase sensitive detection (PSD), that has been applied to typical bulk synchrotron techniques, i.e. energy dispersive EXAFS, quickEXAFS and hard-XRD, in an effort to capture the structural changes under fast transient conditions. The PSD algorithm generates a new set of phase-resolved data in which static signals and other features responding at a different frequency than the external stimulation are removed. This processing massively reduces noise. Small features in the EXAFS and XRD data can be then clearly resolved.

The data reveal that during the CO-NO pulses a likely thin oxide layer is periodically formed and reduced on $Pd/Al_2O_3$. Additionally, $PdC_x$ forms under reducing conditions [2]. In the time-resolved XRD experiment, obvious reflections of reduced Pd appear only in the phase-resolved data set of Pd on ceria-zirconia, apparently exceeding the detection threshold of conventional XRD for particles in the nano-scale. The data allow recognizing that the observed subtle changes occur at different rates thus uncovering the detailed structural-dynamic behaviour of the systems with unprecedented surface sensitivity for these synchrotron based techniques.

[1] D. Baurecht, U.P. Fringeli, *Rev. Sci. Instr.* **2001**, *72*, 3782.
[2] D. Ferri, M. Santhosh Kumar, R. Wirz, A. Eyssler, O. Korsak, P. Hug, A. Weidenkaff, M.A. Newton, *PCCP* **2010**, *12*, 5634.

Catalysis Science and Engineering

## 105

### Foam and honeycomb structured catalytic converters for automotive pollution control

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Among structured catalyst carriers, monoliths are widely employed, in particular in pollution control applications, since they allow low pressure drops while decreasing diffusion limitations [1]. The objective of this work is to compare those conventional substrates with $Al_2O_3$-based foams prepared at Empa. Foam carriers are known for generating increased turbulences in the stream, then improving the mass transfer to the catalytic layer. For automotive pollution control this may result a suitable strategy to decrease the precious metal loading without sacrificing efficiency [2].

Washcoating procedures for catalysts consisting of Pt/$\gamma$-$Al_2O_3$, Pd/$\gamma$-$Al_2O_3$ and Pd-based perovskite-type oxides are being developed. Both sol-gel and slurry coating procedures are considered and compared in terms of washcoat layer adherence and of performances. Catalytic activity measurements were carried out under typical stoichiometric reaction conditions of three-way catalysts for natural gas exhaust after treatment in dry, high flow rate, close to real application conditions. Preliminary results obtained with cordierite indicate that though conventional catalysts are more efficient, Pd-based perovskite-type oxides may present an alternative for catalytic converters with reduced precious metal loading especially when coupled to foam substrates.

[1] J. Chen, H. Yang, N. Wang, Z. Ring, T. Dabros, *Appl. Catal. A: Gen.*, **2008**, *345*, 1.
[2] D.N. Tsinoglou, D.P. Eggenschwiler, T. Thurnheer, P. Hofer, *Proc. IMechE D*, **2009**, *223*, 819.

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Catalysis Science and Engineering

## 106

### $LaCoO_3$-based catalysts for preferential oxidation of CO

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The $H_2$-rich effluent gas exiting a reformer upstream a PEM fuel cell contains typically 10-30 vol.% CO. Beside a water gas shift step to diminish the concentration of CO (0.5-1 vol.%), an additional preferential oxidation (PrOx) catalyst is required to obtain the required low levels of CO. The primary requirement for PrOx catalysts is the selectivity in the presence of hydrogen. Thus, the ideal PrOx catalyst i) needs to adsorb CO, ii) must provide activated oxygen, and iii) must be inactive for hydrogen oxidation in the temperature regime where CO is oxidized (100-200 °C). Such properties can be found in perovskite-type mixed oxides, e.g. $LaCoO_3$.

In this work we study the effect of doping of $LaCoO_3$ with typical active metals (e.g. Cu, Ru, Pt) for PrOx. Perovskites-type catalysts based on $LaCoO_3$ were synthesized by ultrasonic spray combustion (USC) [1]. Micro-droplets of an aqueous precursor solution created by ultrasonic nebulization are transported inside a furnace at the synthesis temperature and decompose into particles via evaporation, combustion and sintering. The hollow pseudo-spherical particles with variable size (>0.5 µm) are composed of nano-particles. The catalytic materials were characterized by XRD, SEM, BET, $H_2$-TPR, *in situ* XRD and tested under PrOx conditions. $LaCoO_3$ exhibits an activity window for PrOx between 200°C and 350°C. Preliminary studies revealed the incorporation of coinage and precious metals into the perovskite lattice. This substitution influences the thermal stability, the redox properties and finally the reaction mechanism.

[1] X. Wei, et al., *Appl. Catal. B.* **2010**, 94, 27.

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Catalysis Science and Engineering

## 107

### ***Operando*** **XAS and APPES experiments over $LaNi_{1-x}Co_xO_3$ (x=0, 0.5, 1) perovskites as precursor for $CH_4$ reforming reactions**

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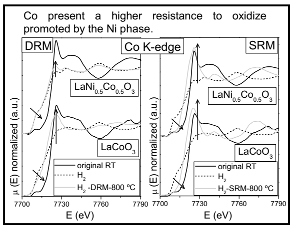
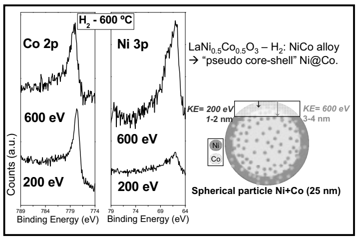
La-supported Ni and Co catalysts were investigated by "operando" techniques for $CH_4$ reforming reactions. The precursors ($LaNi_{1-x}Co_xO_3$) were prepared by the spray pyrolysis method [1] and contain homogeneously distributed metals (Ni, Co) in the crystal structure (perovskite), which, on further reduction, result in the formation of $Ni_{1-x}Co_x/La_2O_3$. The monometallic samples ($LaNiO_3$, $LaCoO_3$) have been compared with a bimetallic system of composition $LaNi_{0.5}Co_{0.5}O_3$. This "operando" study has allowed obtaining important conclusions about the bimetallic particles and the metal-support interactions. The data revealed the formation of bimetallic particles (NiCo) where the Ni avoids the Co oxidation during the reaction.





But, this protection does not induce an improvement in the activity, which presents an intermediated behavior between Ni/$La_2O_3$ and Co/$La_2O_3$. These bimetallic particles form a pseudo-alloy in which the surface is enriched in Co (after reduction), resulting nearly in a core-shell structure (Ni@Co).

[1] R. Pereñíguez, et al., *Appl. Catal. B: Env.* **2010**, 93, 346-353.

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Catalysis Science and Engineering

## 108

### Micro algae cultivation and enzymatic biodiesel synthesis

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Carbondioxid available from combustion engines, industrial processes and air is a resource for bio-fuels. Micro algae as photosynthetic organisms fix $CO_2$ under phototrophic conditions and metabolize it into vegetable oil [1].

Green micro algae can be cultivated under phototrophic and heterotrophic conditions. It accumulates under heterotrophic conditions good quantities of triacylglycerols what is less the case for autotrophic conditions. The objective is to examine process variants for productive algae oil production under phototrophic and heterotrophic conditions. The carbon source is $CO_2$ from the air, fermentations, fume exhausts or glucose. A torus shaped photobioreactor is well suited to examine in a controllable manner diverse cultivation conditions [2]. The reactor is constructed from Plexiglas and illuminated by artificial light. In a cell extraction procedure the triacylglycerols are recovered and the composition analyzed by gas chromatography. The recovered oil is converted in lipase mediated catalysis into biodiesel. An enzymatic transesterification is developed as non-solvent respectively minimal solvent process at room temperature [3]. In particular it is examined how methanol and other reaction conditions influence the enzymatic transesterification rates.

[1] C-Y. Chen, K-L. Yeh, R. Aisyah, D-J. Lee, J-S. Chang, *Bioresour. Technol.* **2011**, *102*, 71.
[2] L. Pottier, J. Pruvost, J. Deremetz, J.-F. Cornet, J. Legrand, C.G. Dussap, *Biotechnol. Bioeng*. **2005**, *91*, 569.
[3] M.S. Antczak, A. Kubiak, T. Antczak, S. Bielecki, *Renew. Energy* **2009**, *34*, 1185.

Catalysis Science and Engineering **109**

## Scale-up Studies and Process optimization of the Synthesis of $\beta^2$-Amino acids by Organocatalysis

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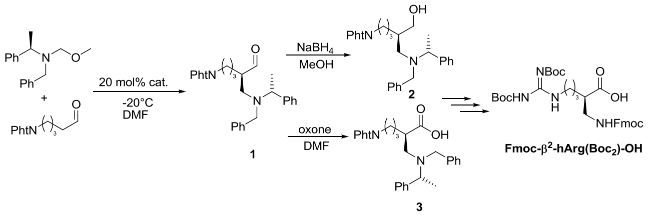
Synthesis of $\beta^2$-amino acids is still a big challenge and only a few of them are commercially available [1]. There is a need for a simple, fast and cheap synthesis. We were interested in the large scale synthesis of $\beta^2$-arginine and evaluated the organocatalytic Mannich reaction reported by Gellman [2] regarding scale-up and process optimization.



We found that the organocatalytic Mannich reaction occurs with excellent conversion (>98%) and offers aldehyde **1** in good selectivity (94:6 d.r.). We report our results on the optimization of the organocatalytic Mannich reaction and our process optimization on the critical steps (protecting group strategies, racemization, and purification steps) for scale-up.

The prepared $\beta^2$-amino acids will be used for synthesis of new bioactive peptides.

[1] Seebach at al. *Synthesis* **2009**, 1-32.
[2] Gellman at al. *J. Am. Chem. Soc.* **2007**, *129*, 6050-6055.

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Catalysis Science and Engineering **110**

## Methane catalytic combustion at differently oxidized $Pd_9/\gamma\text{-}Al_2O_3$

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Palladium catalysts are frequently used for the total oxidation of hydrocarbons. Experimental and theoretical investigations have shown that palladium is especially suited for demanding methane complete combustion applications [1].

The catalyst has been modelled by cluster of $Pd_9$ at $\gamma\text{-}Al_{64}O_{142}H_{92}$, which represents support. The electronic structure of the catalysts was investigated using ab initio density functional theory (DFT) calculations with a cluster model and using grid implementation of the projector augmented wave (PAW) method.

After analyzing the oxidation process of Pd-nanoparticles, it is suggested that different oxidations of nanoparticles can lead to different methane oxidation paths (and therefore hysteresis in oxidation loop) due to different location and access to the oxygen at Pd-nanoparticles [2]. In case of low oxidation of Pd-nanoparticle activation of methane is observed, where hydrogen is adsorbed at one oxygen atom. Due to the lack of oxygen, $Pd_3C$ is formed and after additional adsorption of oxygen $CO_2$ is produced. However, when the Pd-nanoparticle is more strongly exposed to oxidative conditions, adsorption of methane is also possible, but will succeed in carbonic acid production at the interface between Pd-nanoparticles and support.

[1] M. M. Wolf, H. Zhu, W.H. Green, G. S. Jackson, Appl. Catal. A: Gen. **2003**, *244* , 323.
[2] K.A. Kacprzak, I. Czekaj and I. Mantzaras, DFT studies of common Oxidation of $Pd_9$ cluster supported on γ-alumina, submitted to Phys. Chem. Chem Phys. (Mar. 2012).

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Catalysis Science and Engineering **111**

## Particle size effect in the low temperature reforming of methane by carbon dioxide on silica-supported Ni nanoparticles.

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The influence of nickel particle size in the range of 1.6-7.3 nm on the performance in low temperature $CO_2$ reforming of methane synthesis has been investigated using well-defined catalysts based on neutral silica support. XAS and XPS studies indicated a reduction degree greater than 90%. The intrinsic $Ni/SiO_2$ performances were found to be independent of nickel particle size in dry reforming at 773K using a $CH_4/CO_2$ ratio of 1.3 at 1 atm, both at early stage and in steady state conditions. The $H_2/CO$ ratio measured was as well not structure sensitive but controlled by thermodynamic through the faster reverse water gas shift.

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Catalysis Science and Engineering **112**

## The effect of hydrogen coverage and particle size on CO adsorption on supported Ruthenium nanoparticles

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Controlled growth of metal nanoparticles supported on high surface area supports plays an important role in the design of heterogeneous catalysts. Fischer – Tropsch (FT) synthesis is a good example where the parameters of a catalyst such as nanoparticle size and distribution influence its performances. For instance, the decrease of particle size below ca. 6-8 nm leads to a sharp decrease of activity, which is attributed to a stronger interaction of CO with the metal.[1] However, the influence of particle size on CO adsorption on the metal at a molecular level remains unclear as well as its effect on FT reaction mechanism. Of various metals, Ruthenium exhibits a very high activity and a high selectivity into formation of long hydrocarbon chains in FT reaction [2], while its physico-chemical properties enable for instance NMR studies.

Here, we described the steps towards the preparation of Ru nanoparticles with narrow size distribution over a broad range of sizes (from ca. 2 to 20 nm) as well as their characterization by TEM, $H_2$ and CO chemisorption. We also present NMR investigation focused on the understanding of CO adsorption as a function of hydrogen coverage and particle size.

[1] J. P. den Breejen et al., *J. Am. Chem. Soc.*, **2009**, *131*, 7197.
[2] J. M. G. Carballo et al., *J. Catal.*, **2011**, *284*, 102

Catalysis Science and Engineering **113**

## Active sites in Re-based alkene catalysts supported on $\gamma$-$Al_2O_3$ : Structure and Density.

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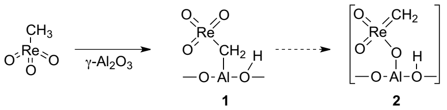
[2]Institute of Chemistry, University of Lyon, Ecole Normale Supérieure of Lyon, 46, Allée d'Italie, 69364 Lyon 07, France.

While $Re_2O_7$/$\gamma$-alumina is an active room temperature catalyst in alkene metathesis, the structure of the active sites is still unknown despite forty years of research. [1] Previous studies on the model system $CH_3ReO_3/Al_2O_3$ have revealed that the active site is based on Al-$CH_2$-$ReO_3$ ("Al-$CH_2$") (**1**), formed by the activation of the C-H bond of $CH_3ReO_3$ on the defect sites of alumina, [2] and generating the catalytically active carbene (**2**) in the presence of alkenes. [3]



Here, we address the structure and the density of active sites in alumina supported Re-based alkene metathesis, in particular as a function of the pretreatment temperature of $Al_2O_3$.

[1] A. Salameh, C. Copéret, J.-M. Basset *et al*., *Adv. Synth. Catal.* **2007**, 349, 238 – 242

[2] R. Wischert, C. Copéret, F. Delbecq, P. Sautet, *Angew. Chem. Int. Ed.*, **2011**, *50*, 3202-3205.

[3]A. Salameh, Jérôme Joubert, Anne Bauouin *et al., Angew. Chem. Int. Ed.,* **2007**, 46, 3870 –3873

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Catalysis Science and Engineering **114**

## How Selective are Probe Molecules for Defect Sites on $\gamma$-Alumina?

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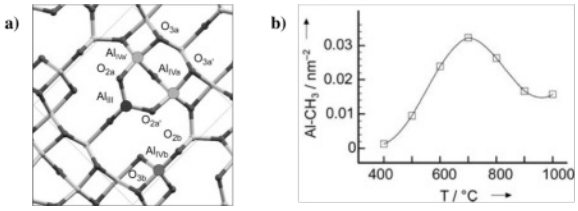
Transition aluminas are widely used as catalysts or catalyst supports in heterogeneous catalysis. It is thought that specific sites at the surface are responsible for the reactivity of alumina towards substrate molecules, including $H_2$ and alkanes.[1] However, the structure of these sites, often present in small amounts and referred as defect sites, is not known.

While probe molecules have been used in heterogeous catalysis to investigate surface sites, we present here how selective are probe molecules ($H_2$, $CH_4$, $N_2$, CO, NO, $N_2O$…) toward the surface sites of alumina via a combination of experimental and theoretical approaches.



**a)** Surface Al sites on a bare 110 surface as an illustration. **b)** Titration of defect sites by methane as a function of thermal treatment.

[1] Wischert et al., *Chem. Commun.* **2011**, *47*, 4890. Wischert *et al. Angew. Chem. Int. Ed.* **2011**, *50*, 3202. Rascón et al., *Chem. Sci.* **2012**, *2*, 1449.

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Catalysis Science and Engineering **115**

## Preparation of silica supported well-defined iridium and rhodium surface complexes and their conversion into nanoparticles.

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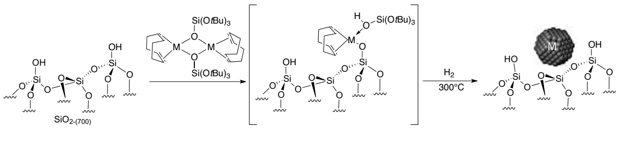
Supported metallic nanoparticles can been prepared by incipient wetness impregnation of a precursor on a support and its subsequent decomposition. During this process, the metallic precursor is dissolved in a solvent to achieve uniform dispersion on the support, and after drying the solid, the ligands are decomposed by thermal treatment and the metal is reduced by reaction with hydrogen. Another preparation route consist in the grafting of the metallic precursor on the support, i.e. the formation of a bond between the metal center and the surface, with a better control of the nature and density of surface sites.

In this study, we prepared iridium and rhodium nanoparticles *via* Surface Organometallic Chemistry (SOMC): where the first step consists in the controlled grafting on partially dehydroxylated silica of an iridium molecular precursor, here $[(cod)MOSi(O^tBu)_3]_2$ (M = Rh or Ir), followed by the subsequent treatment under hydrogen at 300 °C. This controlled surface chemistry leads to the formation of small nanoparticles with a mean size of 2 nm, where the intermediate and the final object have characterized by $^1H$ and $^{13}C$ solid state NMR, infrared transmission spectroscopy, elemental analysis, transmission electronic microscopy and gas adsorption.



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Catalysis Science and Engineering **116**

## Remarkable selectivity and thermal durability of $Au/TiO_2$ for the generation of $NH_3$ used for the selective catalytic reduction of $NO_x$

O. Kröcher, M. Elsener, D. Peitz

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The selective catalytic reduction (SCR) with urea is an efficient process for the reduction of $NO_x$ in diesel vehicles. In this process, a 32.5% aqueous urea solution is injected into the hot exhaust gas, where it is catalytically decomposed to yield ammonia ($NH_3$), which is the actual reducing agent on the SCR catalyst. There are a number of severe problems associated with urea solution, which led to the proposal of guanidinium formate (GuFo), ammonium formate and methanamide solutions as interesting alternatives, which can be stored safely between -30 and 60°C, while they contain up to the double amount of $NH_3$.[1]

The use of commercial $TiO_2$ anatase led to complete conversion of GuFo, but the decomposition temperature of 300 °C was relatively high and side-products were formed. While the guanidinium cation was quantitatively converted to $NH_3$, the formate anion was released as CO and formic acid. Formic acid condensated with $NH_3$ to create methanamide, which reacted further to yield traces of HCN.[2]

By doping of the $TiO_2$ anatase with gold the decomposition temperature could be significantly reduced and side-product formation was completely suppressed without oxidation of the desired reaction product $NH_3$. Moreover, the catalyst stability upon hydrothermal aging and sulfur poisoning was remarkable.[3,4]

[1] O. Kröcher, M. Elsener, E. Jacob, *Appl. Catal. B* **2009**, *88*, 66.

[2] T. Todorova, D. Peitz, O. Kröcher, A. Wokaun, B. Delley, *J. Phys. Chem. C* **2011**, *115*, 1195.

[3] D. Peitz, M. Elsener, O. Kröcher, *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* **2011**, *56*, 19741.

[4] D. Peitz, M. Elsener, O. Kröcher, *Angew. Chem.* **2012**, *submitted.*

Catalysis Science and Engineering **117**

### Outstanding selective character of $CeO_2$ in alkyne hydrogenation

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Mostly used as an oxidation (co)catalyst and as a support not only in the hydrogenation of different functional groups [1], we report for the first time the outstanding properties of pure $CeO_2$ as *highly* selective catalyst for hydrogenation reactions. Ceria has been systematically tested in the gas-phase hydrogenation of terminal alkynes (ethyne, propyne, and 1-pentyne), attaining olefin selectivities up to *ca*. 90% at a conversion of *ca*. 95% (Table 1). The specific surface area and the degree of reduction play a key role on the catalytic performance. *Operando* infrared spectroscopic studies, combined with DFT calculations in the literature, enabled to derive a consistent reaction mechanism. Specifically, molecular hydrogen is activated and adsorbed into two OH groups. The alkyne undergoes dissociative adsorption with the hydrogen onto subsurface oxygen. Therefore, (sub)surface oxygen takes active part in the reaction, and vacancies are detrimental on the catalytic performance, since they favor the formation of by-products. These unprecedented results are of practical interest in the chemical industry and open exciting opportunities for exploring hydrogenation of other functional groups on this metal oxide.

*Table 1. Performance of $CeO_2$ in the hydrogenation of different alkynes.*

| Alkyne | $X$(alkyne) / % | $S$(alkene) / % |
|---|---|---|
| Ethyne | 82 | 84 |
| Propyne | 94 | 91 |
| 1-Pentyne | 50 | 81 |

[1] A. Trovarelli, *Catal. Rev. Sci. Eng*. **1996**, *38*, 439.

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Catalysis Science and Engineering **118**

### Selective hydrogenation of propyne over supported silver nanoparticles

Gianvito Vilé[1], Crisa Vargas-Fuentes[2], Emma Oakton[1], Blaise Bridier[1], Núria López[2], Christophe Copéret[1], Javier Pérez-Ramírez[1]

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The selective hydrogenation of alkynes to the corresponding olefins is the most attractive process for upgrading alkene streams [1]. Here, the gas-phase hydrogenation of propyne to propene was investigated over a series of Ag-based catalysts. The propene selectivity reached up to 97% at a degree of propyne conversion of 30% (Fig. 1). The properties of the support and its interaction with the active phase were explored employing various supports and preparation routes, such as spray-drying, incipient wetness impregnation, and controlled surface chemistry. In all of these cases, the type of support and the synthesis method did not affect the catalytic behavior of the active metal. Finally, the experimental data were combined with density functional theory (DFT) calculations in order to understand the structure-activity and selectivity relationships. The findings led to an improved understanding of hydrogenation of unsaturated hydrocarbons and open new routes to design more selective catalysts.

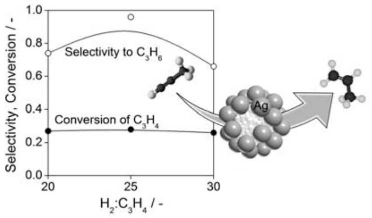

*Fig. 1. Conversion of propyne ($C_3H_4$) and selectivity to propene ($C_3H_6$) over 1 wt.% Ag/$SiO_2$ at different $H_2$:$C_3H_4$ ratios.*

[1] B. Bridier, N. López, J. Pérez-Ramírez, *Dalton Trans*. **2010**, *39*, 8412.

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Catalysis Science and Engineering **119**

### Zeolite-based composite engineering through spray drying

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ETH Zurich, Wolfgang-Pauli-Strasse 10, CH-8093 Zurich, Switzerland

One-step assembly of multimodal composites comprising a surfactant-templated binder matrix containing mesoporous zeolite particles was achieved using spray drying. The levels of porosity include: the silica binder matrix (13-25 nm), zeolitic micropores (0.6 mm) and intracrystalline mesopores (7 nm), and interparticle space (7 µm). Evaporation-induced assembly of different binder particles into a mesoporous matrix was directed by surfactants during the spray drying process (Fig. 1). The technique was applied to diverse zeolite structures (MFI, USY, MOR, and FER) and zeolite-related structures, with no impact in the characteristics of either the matrix or the catalytically active material. The composite design is aimed towards improvement of the material properties by spatial confinement of single crystals allowing optimized mass transfer, while moderating the acidity of unselective surface sites. This use of spray drying constitutes a powerful scalable route for production of highly structured, multifunctional composites with adjustable porous properties and enhanced agglomeration.

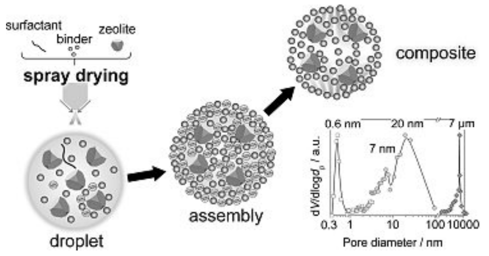

*Fig. 1. Composite assembly and porous properties.*

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Catalysis Science and Engineering **120**

### Impact of substrate size in the design of hierarchical ZSM-5 catalysts for liquid-phase alkylations

Maria Milina, Sharon Mitchell, Javier Pérez-Ramírez

ETH Zurich, Wolfgang-Pauli-Strasse 10, CH-8093 Zurich, Switzerland

Desilication is an effective method to prepare hierarchical zeolites through the introduction of intracrystalline mesopores. Alkaline and acid treatments can be combined to obtain mesoporous zeolites with varying porosity and composition. Here the liquid-phase alkylations of toluene with benzyl alcohol or isopropanol (access- or transport-limited reactions, respectively) are used as model reactions to understand key parameters in the design of hierarchical zeolite catalysts. In the former, restriction of alkylation activity to the external surface provides excellent sensitivity to the mesoporosity introduced (Fig. 1) [1]. The interplay between the mesoporous surface developed and the preservation of intrinsic microporosity is more significant in the latter, where reaction can also occur within the micropores. The removal of aluminium-rich debris by acid washing has a positive impact in both cases.

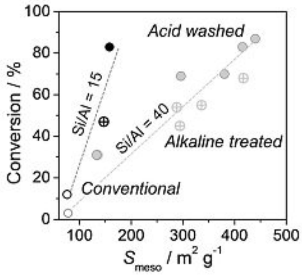

*Fig. 1. Decoupling the impacts of porosity and composition in the alkylation of toluene with benzyl alcohol.*

[1] M. Milina, S. Mitchell, Z. Domínguez Trinidad, D. Verboekend, J. Pérez-Ramírez, *Catal. Sci. Technol.* **2012**, *2*, 759.

Catalysis Science and Engineering **121**

## Scale up of hierarchically-structured zeolite catalysts

Nina-Luisa Michels, Maria Milina, Sharon Mitchell, Javier Pérez-Ramírez

ETH Zurich, Wolfgang-Pauli-Strasse 10, CH-8093 Zurich, Switzerland

To practically benefit from the enhanced properties exhibited by hierarchical zeolite powders, they must be scaled up into mm-sized macroscopic bodies. The adjustment of laboratory protocols, inclusion of binders, and forming step required can profoundly influence the catalytic performance. This work aims at understanding how hierarchical zeolite catalysts are assembled and function in industrial reactors. Granules and extrudates have been prepared and characterized using advanced techniques [1]. Particular emphasis has been placed on visualizing the structural origins of the multiple porosity levels. The superiority of hierarchical zeolites in technical form is demonstrated in the conversion of methanol to olefins.

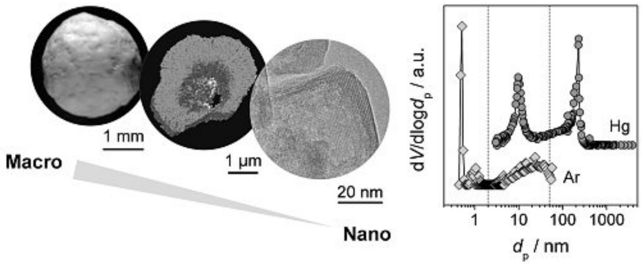

*Fig. 1. Visualization of multi-porosity in hierarchical zeolite bodies from the macro- to the nanoscale.*

[1] N.-L. Michels, S. Mitchell, M. Milina, K. Kunze, F. Krumeich, F. Marone, M. Erdmann, N. Marti, J. Pérez-Ramírez, *Adv. Funct. Mater.* **2012**, doi: 10.1002/adfm.201103120.

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Catalysis Science and Engineering **122**

## Quantification of mass transfer in conventional and hierarchical zeolite powders and shaped bodies

Maria Milina, Laurent Gueudré, Sharon Mitchell, and Javier Pérez-Ramírez

ETH Zürich, Wolfgang-Pauli-Strasse 10, CH-8093 Zürich, Switzerland

While indispensable to their unique properties, micropores limit the performance of zeolitic materials by constraining accessibility and diffusion of reactants/products. Catalytic function can be greatly improved through the introduction of interconnected intracrystalline mesopores [1]. Rationalized in terms of improved molecular transport, the latter has only been demonstrated for zeolite powders and the results vary widely depending on the probe molecule, measurement technique, and materials studied. This work aims at quantifying diffusion properties in conventional and mesoporous ZSM-5 powders and shaped bodies (Figure 1a). The technical forms were obtained by standard shaping techniques with inorganic binders. Comparing the diffusivities of bulky paraffin molecules measured by gravimetry enables quantification of the impacts of mesoporosity development and of structuring on mass transfer. It will be shown that despite significantly reducing the sorption kinetics, the superior properties evidenced for the mesoporous zeolite powder (Figure 1b) are retained following structuring.

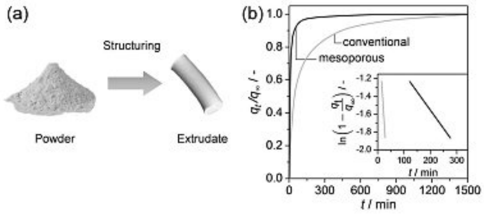

*Figure 1. (a) Schematic representation of powder and technical forms (b) Uptake curves of 2,2-dimethylbutane (338 K, 2 mbar) by ZSM-5 powders.*

[1] J. Pérez-Ramírez, *Nat. Chem.* **2012**, *4*, 250.

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Catalysis Science and Engineering **123**

## Supported $CeO_2$ catalysts for HCl oxidation

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The catalyzed oxidation of HCl, a sustainable route to recycle chlorine in the chemical industry, has for long suffered from the lack of sufficiently stable catalysts till the introduction of $RuO_2$-based materials [1]. In spite of their outstanding performances, these catalysts are costly. $CeO_2$ has been recently identified as an alternative active phase. Herein, we have addressed the selection of a suitable support for $CeO_2$ in view of a practical implementation. $ZrO_2$ resulted a better carrier than $Al_2O_3$ or $TiO_2$, the chlorine production level for $CeO_2/ZrO_2$ being 2.5 times higher than for the other catalysts (Fig. 1, left). The Ce loading was optimized at 7-10 wt.% (Fig. 1, right). Textural and structural characterization data indicate that the higher activity of $CeO_2/ZrO_2$ might be related to the fine dispersion of $CeO_2$ nanostructures on this carrier and that the loading limitation is likely caused by blockage of the $ZrO_2$ pores. Preliminary results of a long-term testing at the pilot scale for a Ce (9 wt.%)/$ZrO_2$ catalysts appear very promising, highlighting the potential for industrial application.

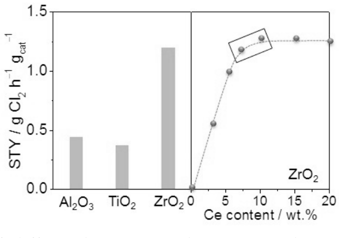

*Fig. 1. Activity of differently supported $CeO_2$ catalysts (left) and activity versus Ce content for the $ZrO_2$-supported catalyst (right).*

[1] J. Pérez-Ramírez, C. Mondelli, T. Schmidt, O. F.-K. Schlüter, A. Wolf, L. Mleczko, T. Dreier, *Energy Environ. Sci.* **2011**, *4*, 4786.

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Catalysis Science and Engineering **124**

## Kinetic aspects and deactivation behavior of chromia-based catalysts in hydrogen chloride oxidation

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ETH Zurich, Wolfgang-Pauli-Strasse 10, CH-8093 Zurich, Switzerland

The heterogeneously catalyzed oxidation of HCl is a sustainable way to recycle chlorine in the chemical industry [1]. Herein we have gathered fundamental aspects of this reaction on bulk and supported $Cr_2O_3$ catalysts. $Cr_2O_3$ exhibited high activity (*ca.* 30% HCl conversion). Upon use, the bulk composition remained unaltered (Fig. 1a), while the surface chromium species in higher (V and VI) oxidation states evidenced for the fresh catalyst reduced to $Cr^{3+}$ and the surface chlorinated to some extent (Fig. 1b). The positive dependence of HCl conversion on inlet $O_2$ content suggests that catalyst re-oxidation is rate determining. $SiO_2$ was identified as a better carrier for $Cr_2O_3$ than $Al_2O_3$ and $TiO_2$-anatase. Nevertheless, all supported catalysts underwent substantial chromium loss, ultimately resulting in dramatic activity deterioration. Among the various labile $Cr^{6+}$ species possibly responsible for the metal depletion, $CrO_2Cl_2$ seems to play a predominant role, as suggested by the significant decrease in the deactivation rate at higher inlet $O_2$/HCl ratios (Fig. 1c). The features evidenced represent critical reasons for the restricted industrial implementation of chromium-based catalysts for chlorine recycling.

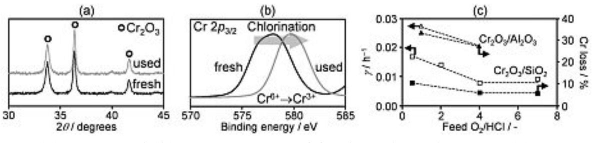

*Fig. 1. (a) XRD and (b) XPS spectra of fresh and used $Cr_2O_3$. (c) Deactivation constant (γ) and Cr loss versus the feed $O_2$/HCl ratio for supported $Cr_2O_3$.*

[1] J. Pérez-Ramírez, C. Mondelli, T. Schmidt, O.F.-K. Schlüter, A. Wolf, L. Mleczko, T. Dreier, *Energy Environ. Sci.* **2011**, *4*, 4786.

Catalysis Science and Engineering **125**

### Preparation of bio-derived lactic acid by isomerization over hierarchical zeolites

Pierre Y. Dapsens, Cecilia Mondelli, Javier Pérez-Ramírez

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In recent years, biomass is attracting much interest as a renewable feedstock for the production of chemicals [1]. In spite of the chemical diversity of bio-derived (high O content) with respect to fossil raw materials, remarkable versatility and tunability render zeolites attractive candidates to be amended for its conversion. Recent studies have indicated that they are able to catalyze the isomerization of dihydroxyacetone (DHA) into lactic acid (LA), a valuable commodity chemical, and that this reaction requires the presence of Lewis acid sites. Herein, we show that porosity and acidity of ZSM-5, Y, and beta zeolites can be modified by alkaline treatment [2], thus rendering hierarchical materials which attain superior selectivity to lactic acid with respect to their parent samples. In view of its flexibility, ZSM-5 was selected to investigate in details the correlation between textural and acid properties and performance. Indeed, an increase in mesoporous surface as well as Lewis acidity (confirmed by pyridine adsorption) determined enhanced DHA conversion and, more remarkably, LA selectivity (Fig. 1).

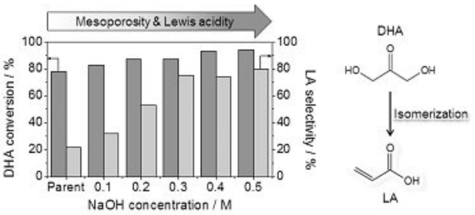

*Fig. 1. DHA conversion and LA selectivity over parent and alkaline-treated H-ZSM5.*

[1] M.S. Holm, S. Saravanamurugan, E. Taarning, *Science* **2010**, *328*, 602.
[2] D. Verboekend, J. Pérez-Ramírez, *Catal. Sci. Technol.* **2011**, *1*, 879.

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Catalysis Science and Engineering **126**

### Potential of tin oxide-based support materials for durable cathode catalysts in PEFCs

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Electrochemistry Laboratory, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland

Polymer Electrolyte Fuel Cells (PEFCs) have been intensively studied as alternative power source for stationary and mobile applications. At present, the most feasible electrocatalyst system for oxygen reduction reaction (ORR) in acidic medium is Pt supported on carbon. However, recent investigations showed corrosion of the carbon support under fuel cell operating conditions. [1] Therefore, metal oxides, with their high thermodynamic stability in acidic medium, have recently become of interest as alternative support materials. Thermochemically calculated pH-potential diagrams have shown that only few oxides are stable at pH=0, 80 °C, and with an applied potential of 1.0 V vs. standard hydrogen electrode. [2] Among the stable oxides, we have selected tin-based compounds as a novel, durable supports for PEFC catalysts.

In this contribution we will report on the electrochemical properties of doped $SnO_2$-supported Pt electrocatalysts. To investigate the potential of tin oxides as support we have prepared model thin film electrodes by reactive sputtering of doped tin oxide on glassy carbon discs. Films have been characterized by X-ray photoelectron spectroscopy (XPS), X-ray diffraction analysis (XRD) and scanning electron microscope (SEM). Cyclic voltammetry and rotating disc electrode measurements were performed in liquid electrolyte to evaluate the electrochemical stability and activity of oxide support materials and model tin oxide-based Pt catalysts towards the oxygen reduction reaction.

[1] Mathias M.F. et al. *Electrochem. Soc. Interf.* **2005**, *14*, 24.

[2] Sasaki K. et al. *ECS Trans.* **2010**, *33*, 473.

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Catalysis Science and Engineering **127**

### Laboratory evolution of an intrinsically disordered enzyme

Cindy Schulenburg and Donald Hilvert

Laboratory of Organic Chemistry, ETH Zürich, 8093 Switzerland

For efficient biocatalysis enzymes need to find a balance between folding to a stable tertiary structure and retaining sufficient flexibility for proper function. How these properties are optimized during biological evolution and how fold flexibility influences the capacity to evolve is poorly understood, however. To assess how the catalytic activity of flexible proteins responds to evolutionary pressure we are investigating a circularly permuted variant of *E. coli* dihydrofolate reductase (cpDHFR).[1] This enzyme is about 1000-fold less active than wild-type DHFR and intrinsically disordered. Thermal and chemical denaturation studies show that cpDHFR is substantially less stable than its parent. Addition of methotrexate, a competitive inhibitor of DHFR, leads to greater stability and, judging from the concomitant decrease in affinity for ANS, an increase in structural order. We are now optimizing this enzyme by directed evolution. The cpDHFR gene has been randomly mutated by error-prone PCR, and selection experiments are being carried out in an *E. coli* host in which the DHFR gene, *fol A*, has been replaced by a kanamycin resistance determinant. The coupling of enzyme activity to cell growth allows the selection of (more) active enzyme variants. Improved variants of the first three rounds of selection are being fully characterized with respect to their catalytic activity and biophysical properties to gauge how substitutions of specific amino acid residues enhance function and stability of the protein and hence evolutionary development.

[1] Protasova, Kireeva, Murzina, Murzin, Uversky, Gryaznova, Gudkov, *Protein Eng.* **1994**, *7,* 1373-1377

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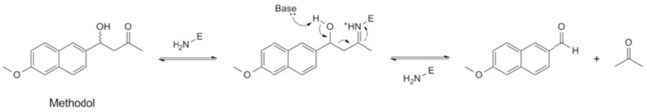
Catalysis Science and Engineering **128**

### Mechanistic Insights into a Computationally Designed Retro-Aldolase

Reinhard Zschoche[1], Lars Giger[1,2], Donald Hilvert[1]

[1]Laboratory of Organic Chemistry, ETH Zurich, 8093 Zurich, Switzerland
[2]University of California Berkeley, Berkeley, CA 94720-1462, United States

The increasing demand for green chemical processes and enantiopure chemical building blocks drives the development of novel biocatalysts. Recently, computational *de novo* designs of retro-aldolases were published [1] and subsequently the moderate starting activities of the designed enzymes were improved in the laboratory by directed evolution [2]. Currently, our best evolved variant RA95.5-8 shows more than twofold higher catalytic activity for methodol cleavage than the most efficient catalytic antibody for this reaction.



In order to further improve the enzyme's efficiency and explore its utility for enantioselective chemical synthesis, mechanistic studies have been performed. The rates of acetone-binding and release as well as enolate formation were determined by following $^{18}$O-exchange by mass spectrometry and deuterium incorporation by time-resolved NMR spectroscopy. Steady-state kinetic measurements were conducted to investigate the stereoselectivity and substrate inhibition for the synthetic aldol reaction.

Analysis of active site mutations, isotopically labeled substrates and transient-state kinetic measurements will provide further insight into the catalytic mechanism.

[1] L. Jiang et al, *Science* **2008**, *319*, 1387.
[2] L. Giger, Ph.D. Thesis, ETH Zürich, 2011

Catalysis Science and Engineering **129**

## Elucidation of the P450cam cytochrome reaction mechanism using selenium as a mechanistic probe

An Vandemeulebrouke and Donald Hilvert

Laboratory of Organic Chemistry, ETH Zurich, 8093 Switzerland

Cytochrome P450 enzymes are versatile ubiquitous heme-containing monooxygenases that activate dioxygen for insertion into organic substrates. The ability of these enzymes to perform difficult chemistry with high selectivity and specificity has kept them at the forefront of engineering efforts. Despite the fact that the P450 enzymes have been investigated for more than 4 decades, there is still controversy regarding their catalytic mechanism.

We embarked on further investigation of the catalytic mechanism of cytochrome P450 enzymes, focusing on P450cam, the isozyme from the soil bacterium *Pseudomonas putida*. To probe this system, a unique mutant of P450cam has been generated in which the proximal cysteine, coordinating the heme in the enzyme, has been replaced with selenocysteine [1]. This substitution is conservative and preserves the activity of the enzyme. Moreover, quantum chemical calculations suggest that the greater electron donating capacity of selenolate compared to thiolate should stabilize the elusive compound I, a highly reactive ferryl-oxo ـضcation porphyrin radical in the P450 catalytic cycle [2].

Here we present a comparative pre-steady state kinetic analysis by using stopped flow spectroscopy of the cysteine P450cam and its selenocysteine variant. The determination of the critical rate constants for the intermediary steps allows us to map the effects of the sulfur-to-selenium substitution on the individual steps of the catalytic cycle.

[1] Aldag C, Gromov IA, García-Rubio I, von Koenig K, Schlichting I, Jaun B, Hilvert D, *Proc Natl Acad Sci U S A.* **2009**, *106*, 5481-6.

[2] Cohen S, Kumar D, & Shaik S, *J. Am. Chem. Soc.,***2006***, 128***,** 2649-2653.

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Catalysis Science and Engineering **130**

## Testing the Two State Reactivity Hypothesis for Cytochrome P450cam Using a Selenium-Substituted Enzyme Variant, Deuterated Camphor Derivatives, and Radical Clocks

Claudio Signorell and Donald Hilvert

Laboratory of Organic Chemistry, ETH Zurich, 8093 Zurich, Switzerland

Cytochrome P450 enzymes utilize a heme cofactor coordinated by an axial thiolate ligand (C357) to activate dioxygen and perform various reactions, including epoxidations and C-H hydroxylations, regio- and stereoselectively. The resting state of P450 enzymes and the various intermediates occurring during catalysis can be either low or high spin, which are close in energy but separated by large energy barriers. Shaik and coworkers hypothesized that the low and high spin species also exhibit different reactivity ( two state reactivity ) [2]. To test this proposal, enzyme variants in which the axial thiolate ligand is substituted by a more electron donating selenoate ligand (C357U) could be useful. This conservative substitution leaves the environment of the heme almost unaffected [1], but alters the ratio of high and low spin states in the resting enzyme [1]. In the current work, the proposed two state reactivity is being tested by comparing reaction products of the wild-type and selenium-substituted enzymes with 5-deuterated camphor and radical clocks such as س and سthujone. The results of our kinetic studies will be presented in this poster.

[1] Aldag C, Gromov IA, García-Rubio I, von Koenig K, Schlichting I, Jaun B, Hilvert D, *Proc. Natl. Acad. Sci. USA* **2009**, *106***,** 5481-5486.

[2] Shaik S, de Visser SP, Ogliaro F, Schwarz H, & Schröder D, *Curr. Opin. Chem. Biol.* , **2002**, *6*, 556-567

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Catalysis Science and Engineering **131**

## Directed Evolution of a Computationally Designed Diels-Alderase

Nathalie Preiswerk[1], Donald Hilvert[1]

[1]ETH Zürich, Wolfgang-Pauli Strasse 10, 8093 Zürich

Directed evolution is a powerful tool for tailoring protein properties. It consists of iterative cycles of genetic diversification and identification of variants with enhanced properties. This approach has successfully been used to improve catalytic activity, enantioselectivity, protein stability and organic solvent tolerance. Its combination with computational design, which provides starting points with initial activity for evolutionary optimization, is emerging as a promising strategy to generate biocatalysts for reactions unprecedented in Nature. Currently, the major challenge in the field is the development of robust high-throughput assays specific to every reaction for which a catalyst is coveted. In this work, we set out to evolve a Diels-Alderase computationally designed by the Baker lab and FoldIt players [1] and developed a screening assay consisting of three consecutive steps. First, the desired reaction is carried out in cell lysate. The product of the reaction is then extracted in a solvent compatible with electrospray ionization (ESI) and finally analyzed without further work-up by tandem mass spectrometry. This tandem-MS technique is simple, robust, has high-throughput and could be generalized to any reaction in which the product can be extracted into an organic solvent. This screening assay is currently being used for the evolution of the Diels-Alderase towards higher activity. By using a combination of random mutagenesis and semi-rational approaches in the generation of sequence diversity we expect to reach acceleration rates not yet accomplished for this Diels-Alder reaction.

[1] C.B. Eiben *et al.*, *Nature Biotechnology* **2012**, *30*, 190.

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Catalysis Science and Engineering **132**

## The Interplay of Catalytic Efficiency and Substrate Promiscuity for Intrinsically Disordered Staphylococcal Nuclease

Amanda Stouffer[1,2], Linda Bengtsson[1], Michael Sheremet[1] and Donald Hilvert[1]

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[2] Hoffman-La Roche Inc., New Jersey, U.S.A

In order to investigate the effect that intrinsic disorder has on catalytic activity and enzyme-substrate promiscuity, we chose to study the N- (11-N), C- (C-13) and N- and C-terminally truncated variants containing residues 1-3, 13-140 (Δ131Δ) of staphylococcal nuclease (SNase). SNase is small globular 3’ endo-exonuclease of 149 amino acids that folds into a mechanically and thermally stable structure comprising three α-helices and five β-sheets. Wild type SNase is well characterized, hence, rational comparative analyses of the effects of truncations on stability and catalytic activity are possible.

Here we show that sequence truncations increase the degree of intrinsic disorder, as proven by using circular dichroism and ANS fluorescence. Additionally the catalytic activity on natural (Adenine 16-mer (A16), Cytosine 10 and 4-mer (C10, C4)), and non-natural (A16 with complete or alternating phosphothioate linkages ($PTO_{all}$, $PTO_{alt}$) or 2’O methylated ribose (OMe)) substrates was investigated. Here we found that WT SNase, and Δ131Δ – the most intrinsically disordered variant – had the overall highest catalytic efficiencies. The easiest substrate to cleave was FAM-A16-TAMRA. Interestingly the variants displayed more substrate promiscuity, i.e. higher relative catalytic efficiencies for substrates that are typically difficult to hydrolyze.

The results from this study serve as a good primer, enabling the choice of substrates with suitable turnover rates, for future single molecule FRET analyses into intrinsically disordered SNase.

Catalysis Science and Engineering **133**

## Directed Evolution of Computationally Designed Chorismate Mutases

Narupat Hongdilokkul[1], Florian Richter[2], David Baker[2], Peter Kast[1], and Donald Hilvert[1]

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[2]University of Washington, Seattle, WA 98195, USA

Enzyme design is an exciting new area of chemistry. Recent studies have demonstrated that computationally designed enzymes can be generated for various chemical reactions [1][2][3]. The chorismate mutase reaction is a particularly challenging target for protein designers as multiple polar and charged active site residues are required for efficient catalysis in the natural enzymes. To achieve this, we used Rosetta methodology to screen for scaffolds with backbone geometries that allow four catalytic residues, two arginines, one lysine, and one aspartate or glutamate, and the transition state from a set of approximately 3,500 proteins. Eleven of the best designs were chosen for kinetic characterization. *In vivo* complementation has been employed to further optimize the activity of the designed enzymes.

[1] J. B. Siegel, A. Zanghellini, H. M. Lovick, G. Kiss, A. R. Lambert, J. L. St.Clair, J. L. Gallaher, D. Hilvert, M. H. Gelb, B. L. Stoddard, K. N. Houk, F. E. Michael, D. Baker, *Science*. **2010**, *329*, 309-313.
[2] D. Röthlisberger, O. Khersonsky, A. M. Wollacott, L. Jiang, J. DeChancie, J. Betker, J. L. Gallaher, E. A. Althoff, A. Zanghellini, O. Dym, S. Albeck, K. N. Houk, D. S. Tawfik, D. Baker, *Nature*. **2008**, *453*, 190-195.
[3] L. Jiang, E. A. Althoff, F. R. Clemente, L. Doyle, D. Röthlisberger, A. Zanghellini, J. L. Gallaher, J. L. Betker, F. Tanaka, C. F. Barbas, D. Hilvert, K. N. Houk, B. L. Stoddard, D. Baker, *Science*. **2008**, *319*, 1387-1391.

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Catalysis Science and Engineering **134**

## Directed evolution of *de novo* retro-aldolases with a microfluidic screening assay

Richard Obexer[1], Alexei Godina[2], Andrew Griffiths[2], Donald Hilvert[1]

[1]ETH Zürich, CH-8093 Zürich, [2]ISIS, F-67083 Strasbourg

Directed evolution is a powerful tool to improve enzyme properties such as catalytic efficiency. In principle it is an iterative random search algorithm in sequence space, which means that the number of hits correlates with the number of analyzed mutants. Since *de novo* enzymes display low catalytic activities in comparison to natural enzymes, it is important to identify highly beneficial and synergistic mutations that are rare. In this work are evolving a *de novo* retro-aldolase[1] with a microfluidic screening assay in order to create an enzyme that has a similar or even higher catalytic activity than a natural aldolase. The assay is based on co-encapsulation of a fluorogenic substrate and a single *E. coli* cell containing a retro-aldolase variant in a droplet. Each droplet serves as miniature reaction vessels that ensures linkage of genotype and phenotype. Droplets are sorted according to their fluorescence with a sorting frequency of ca. 700 droplets per second, which enables screening of up to $10^7$ variants per day. Various model sorts have demonstrated the feasibility of our screening system. In this poster we will present results on the isolation of improved retro-aldolases from large random protein libraries.

[1] E.A. Althoff *et al*., *Prot. Sci*. **2012**, *21*, 717.

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Catalysis Science and Engineering **135**

## Pt nanoparticles to mitigate stress corrosion cracking in boiling water reactors.

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In boiling water reactors radiolysis products of water ($O_2$/$H_2O_2$) generate a highly oxidizing environment which may result in an increased susceptibility to stress corrosion cracking (SCC) of reactor components. General Electric-Hitachi has developed a technology (NobleChem$^{TM}$) where noble metal compounds are injected into reactor feed water to mitigate SCC on reactor internals and recirculation systems. Upon injection into the hot water (220-290 °C), $Na_2Pt(OH)_6$ decomposes to form Pt nanoparticles. These nanoparticles deposit on all water wetted reactor components, and in presence of $H_2$, catalyze the reduction of $O_2$/$H_2O_2$, thus decreasing the electrochemical corrosion potential [1].

To better understand the influence of particle size and distribution on the catalytic power, an elaborate lab-scale hydrothermal loop has been built at PSI. Precise control of water flow rate, $O_2$ and $H_2$ concentrations, temperature and pressure, and Pt injection rate is achieved to simulate reactor water conditions. Stainless steel specimens, either pre-oxidized or used as received where exposed to these specific conditions. At the end of each run, specimens were studied by SEM & TEM and Laser Ablation-ICP-MS to determine size, distribution and surface loading of Pt on the specimens' surface.

It was found that higher $H_2$ concentration results in a more efficient Pt nanoparticles deposition. Also pre-oxidized specimens exhibit a higher Pt concentration on their surface. Further it was observed that a lower Pt injection rate yields smaller particles and provides a more homogenous distribution.

[1] Wood, C. J., Water Chemistry Control in LWRs. In *Comprehensive Nuclear Materials*, Konings, R.J.M., Ed. Elsevier: Oxford, 2012; pp 17-47.

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Catalysis Science and Engineering **136**

## New Penta-coordinate Iron(III) Aryloxide as Initiators for Ring-Opening Polymerization

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In addition to the development of new energy-producing processes, finding new energy-saving procedures offers a promising solution to meet our energy needs in the long run. Indeed, catalysis is one of the key technologies for energy saving. A wide variety of metal alkoxides/aryloxides[1] has been used as initiators and catalysts for ring-opening polymerization (ROP). Due to the use of cyclic esters in the tailoring synthesis of biodegradable and bioresorbable materials, interest in the development of well-defined initiators and catalysts has increased. Iron-based catalysts offer many advantages, such as their abundance, their low toxicity and even their biocompatibility[1].

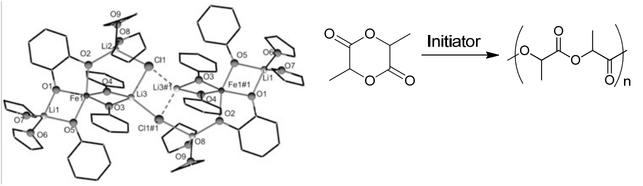

Figure 1: pentacoordinated Iron(III) Complex used as initiator(left), and ring-opening polymerization of the *rac*-lactide(right).

For this purpose, the authors will present their first results on a new and cheap hetero-bimetallic Li-Fe based aryloxide complex[2] as an initiator for ring-opening polymerization(ROP) of lactide.

[1] M. Ouchi, T Terashima, M. Sawamoto, Chem. Rev. 2009, 4963-5050
[2] Y. Chérémond, A. Crochet, K. M. Fromm, Eur. J. Inorg. Chem. 2012, DOI: 10.1002/ejic.

Catalysis Science and Engineering **137**

### SENS NMR Characterization of a Highly Active Single-Site Heterogeneous Catalyst for the Selective Semi-Hydrogenation of Alkynes

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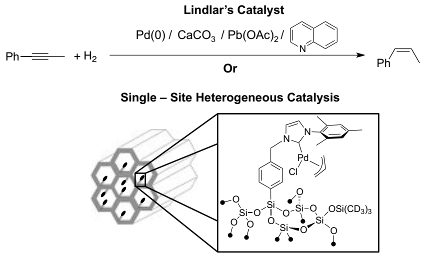
The selective hydrogenation of alkynes to yield *cis*-olefins is usually performed using Lindlar's catalyst,[1] which consists of a $Pb(OAc)_2$ doped Pd black material supported on $CaCO_3$ that is poisoned with quinoline. Less than 10% of the palladium sites are catalytically relevant due to the unselective catalyst poisoning.



We show the design, preparation, and SENS NMR[2] characterization of a single-site heterogenous Pd-catalyst. This catalyst is very active and selective in the semi-hydrogenation of 1-phenyl-1-propyne.

(1) Lindlar, H. *Helvetica Chimica Acta* **1952**, *35*, 446.
(2) Lesage, A. *et. al. J. Am. Chem. Soc.* **2010**, 132, 15459.

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Catalysis Science and Engineering **138**

### Compounds with the Structural Motif N–C–C–O Catalyze the Disproportionation of Peroxynitrite to Nitrite and Peroxynitrate

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The oxidizing and nitrating agent peroxynitrite (PN), $ONOO^-$ and ONOOH ($pK_a = 6.6$), is formed *in vivo* [1], which has stimulated studies of its reactions with biomolecules. PN is unstable and decomposes in a 1st-order process by isomerization to nitrate and in a 2nd-order process by disproportionation to nitrite and peroxynitrate [2]. The buffer Tris(hydroxymethyl)aminomethane (Tris) catalyzes this disproportionation:

$$\mathrm{ONOOH + ONOO^- + Tris \rightarrow NO_2^- + O_2NOO^- + H^+ + Tris}$$

The decomposition of PN in phosphate buffer at pH = 6.8, in absence and presence of Tris or structural analogues, was studied by stopped-flow spectrophotometry. The amine fragment alone, $^t\mathrm{BuNH_2}$, does not accelerate; $t_{½}$ has the characteristic value of 1.42 s at pH = 6.8. The corresponding alcoholic substructure 2,2-bis(hydroxymethyl)propanol, and also its 1:1 mixture with $^t\mathrm{BuNH_2}$, even decelerate the decay: $t_{½} = 1.65$ s and 1.55 s respectively.

Tris, 2-methoxyethylamine and 2-aminoethanol all catalyze PN disproportionation: $t_{½} = 0.93$ s, 1.15 s, and 0.73 s respectively. We conclude that (H–)N–C–C–O is the special substructure required for this capability. This structural motif is widespread among biomolecules, e.g. amino acids like serine and 2-aminoethylphosphates, a class of phospholipids occurring in cell membranes. The catalytic efficiency seems to be diminished by steric hindrance, the simple 2-aminoethanol is the best accelerator.

[1] J. S. Beckman, T. W. Beckman, J. Chen, P. A. Marshall, B. Freeman, *Proc. Natl. Acad. Sci. USA* **1990**, *87*, 1620
[2] D. Gupta, B. Harish, R. Kissner, W. H. Koppenol, *Dalton Trans.* **2009**, *29*, 5730

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Catalysis Science and Engineering **139**

### Artificial Metalloenzyme for Aqueous Olefin Metathesis

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Artificial metalloenzymes based on Biotin-(strept)avidin technology insure the incorporation of an active catalyst in a protein scaffold which provides a chiral environment. Our previous works proved that incorporation of a biotinylated Hoveyda-Grubbs catalyst into (strept)avidin affords artificial metalloenzyme which display multiple turnovers for ring closing metathesis of N-tosyl diallylamine in aqueous solution [1]. Current efforts are concentrated on the design of new type of NHC based catalysts to increase turnovers and running catalysis in cell free extracts.

[1] Lo C.; Ringenberg M.; Gnandt D.; Wilson Y.; Ward T. *Chem. Commun.* **2011**, *47*, 12065.

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Catalysis Science and Engineering **140**

### Expanding the Scope of Artificial Metathetase Based on Biotin-Streptavidin Technology

Mark R. Ringenberg, Cheikh Lo, Anamitra Chatterjee, Raphael Reuter and Thomas R. Ward[1]

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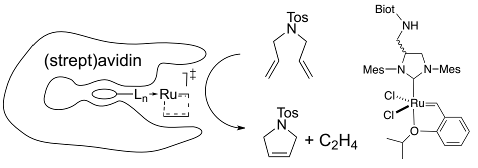
Artificial metalloenzymes have emerged as a new class of catalysts that is distinct from naturally occurring metalloenzymes. Incorporation of a catalytically active, organometallic moiety within a biomacromolecule (e.g. protein or DNA) leads to artificial enzymes with reactivity not found in nature.[1]



Building on the library of hybrid catalysts that utilize the biotin-(strept)avidin interaction (Figure 1), we present the latest developments towards the implementation of artificial metathesases. Olefin metathesis is distinctly a bio-orthogonal transformation which limits the possible side reactions with cell contaminants and thus is an ideal reaction to implement in chemical biology.[2]

[1] Mark R. Ringenberg, and Thomas R. Ward, *Chem. Commun.,* **2011**, 47, 8470.
[2] Cheikh Lo, Mark R. Ringenberg, David Gnandt, Yvonne Wilson and Thomas R. Ward, *Chem. Commun.,* **2011**, 47, 12065.

Catalysis Science and Engineering

## 141

### Aerobic Oxidation of Alcohols Catalyzed by Palladium Complexes Containing Redox-Active Moiety Appended NHC Ligands.

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Oxidation of organic substrates using environmentally benign oxidants such as $O_2$ or $H_2O_2$ is of immense interest [1]. In this context, palladium catalyzed aerobic oxidation of alcohols to the corresponding aldehydes is an important reaction [2]. In order for the reaction to become catalytic and efficient, the facile re-oxidation of Pd(0) to the catalytically active Pd(II) species is vital. However, in many cases, the re-oxidation reaction is very difficult to achieve due to a large kinetic barrier. To this end, we have synthesized several monomeric and dimeric palladium(II) complexes bearing redox-active moiety appended *N*-heterocyclic (NHC) ligands. These redox-active ligands are expected to act as electron transfer mediators between $O_2$ and Pd(0), and hence to lower the kinetic barrier for the re-oxidation reaction. We have investigated benzyl alcohol oxidation using these palladium complexes and compared their kinetic and catalytic activities to that of Pd(II) complexes containing a non-redox active NHC ligand. The results of detailed kinetic and thermodynamic oxidation studies will be presented. In addition, the effects of several additives on the reaction rates and activity have been investigated, and will be highlighted.

[1] Piera, J.; Bäckvall, J-E, *Angew. Chem. Intl. Ed.* **2008**, *47*, 3506.
[2] Stahl.S. S, *Angew. Chem. Intl. Ed.* **2004**, *43*, 3400.

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Catalysis Science and Engineering

## 142

### Developing the potential of an iridium-pianostool catalyst

**M. Dürrenberger[1], Y. Wilson[1], V. Köhler[1], D. Ghislieri[2], D. Häussinger[1], L. Knörr[1], N.J. Turner[2], T.R. Ward[1]**

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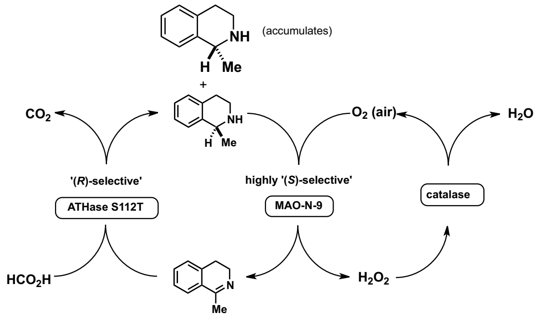
The incorporation of a biotinylated iridium piano stool complex into streptavidin (SAV) variants affords artificial transfer hydrogenases (ATHases) previously shown to be effective catalysts for the enantioselective reduction of prochiral imines[1]. Compartmentalization of the organometallic moiety inside the protein allows combination with natural enzymes in one-pot cascade reactions such as the double stereoselective amine deracemisation using monoamine oxidase (MAO-N) variants shown below. Further examples will be given. The absence of SAV typically leads to inhibition of the biocatalyst and partial deactivation of the Ir-center.



[1] M. Dürrenberger, T. Heinisch, Y. M. Wilson *et al.*, *Angew. Chem. Int. Ed.* **2011**, *50*, 3026

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Catalysis Science and Engineering

## 143

### Bioorthogonal Scissors: Artificial Metalloenzymes for the Selective Cleavage of Protecting Groups *in Vivo*.

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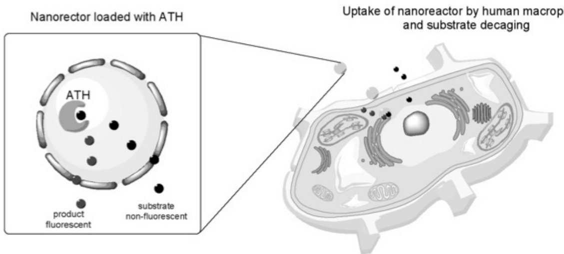
The efficiency of drugs often is hampered by side effects. A key problem very often is an insufficient drug target specificity. Prodrug-strategies are based upon the administration of non-active drug precursors that are activated either by the patients metabolism or by the application of external stimuli such as radiation, heat or magnetic fields. Herein we present research on a bioorthogonal protecting group that releases its cargo upon activation by an artificial metalloenzyme. The latter is guided to target cells using a vesicle-based delivery system.



[1] Dürrenberger, M., Heinisch, T., Wilson, Y., Rossel, T., Nogueira, E., Knörr, L., Mutschler, A., Kersten, K., Zimbron, J. M., Pierron, J., Schirmer, T., Ward, T. R., *Angew. Chem. Int Ed.*, **2011**, *50*, 3026.
[2] Ben-Haim, N., Broz, P., Marsch, S., Meier, W., Hunziker, P., *Nano Lett.*, **2008**, *8*, 1368.

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Catalysis Science and Engineering

## 144

### Artificial Metalloenzymes for the *in situ* regeneration of NADH

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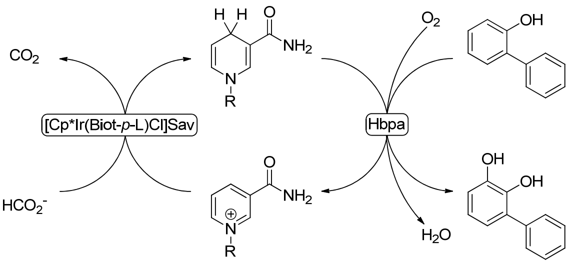
NAD(P)H-dependent oxidoreductases are useful tools for the preparation of fine chemicals. Nicotinamide cofactor regeneration is mandatory as its cost is prohibitive.[1] Among the non-enzymatic regeneration approaches, $[Cp^*Rh(bpy)H_2O)]^{2+}$ has been the system of choice. A critical drawback of this catalyst however, is the mutual inactivation with the enzyme.[1] Herein we provide a new concept for *in situ* NADH-regeneration, which overcomes this problem. [Cp*Ir(biotin-*p*-L)Cl] was incorporated within streptavidin to afford an artificial transfer hydrogenase for the regeneration of $NAD^+$ to NADH. The system was successfully employed in the 2-hydroxybiphenyl 3-monooxygenase (Hbpa) catalyzed oxidation of 2-hydroxybiphenyl.



1. M. Poizat et al., *J.Mol.Catal.B: Enzym.*,**2010**,*63*, 49-156.

Catalysis Science and Engineering **145**

## Activated Carbon Fibers as Effective Adsorbent for VOCs Removal

Guillaume B. Baur, Oliver Beswick, Micaela Crespo-Quesada, Igor Yuranov and Lioubov Kiwi-Minsker

Group of Catalytic Reaction Engineering, Station 6, Ecole Polytechnique Fédérale de Lausanne, CH-1015

Commonly found in emissions of industrial processes, volatile organic compounds (VOCs) are harmful and toxic for humans even at low concentrations. During the last few decades, particular effort has been devoted to remove them by adsorption processes. Activated carbon (AC) are often used for this application since they present high SSA (up to 2000 m$^2$ g$^{-1}$) and that their surface chemistry can be easily modified [1]. Indeed, SSA and surface oxygen content are known to be key parameters for VOCs abatement [2]. However, a high pressure drop through the packed bed can be caused especially at large gas flow rates. Having the same properties than AC, activated carbon fibers (ACF) represent a valuable alternative due to lower pressure drop through the arranged catalytic bed even at high gas velocities.

Herein, the adsorption capacity of ACF with different SSA and amount of surface oxygen containing groups was studied for acetaldehyde and toluene removal. Toluene adsorption was increased by increase in the SSA whereas acetaldehyde adsorption was influenced by the surface oxygen-containing groups. Based on these findings, an optimal adsorbent was identified and subsequently the dynamics and the mode of adsorption for both compounds were studied through transient response method and temperature programmed desorption (TPD).

[1] K. L. Foster, R. G. Fuerman, J. Economy, S. M. Larson, M. J. Rood *Chem. Mater.* **1992**, *4*, 1068.
[2] M. A. Lillo-Ródenas, D. Cazorla-Amorós, A. Linares-Solano, *Carbon*, **2005**, *43*, 1758.

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Catalysis Science and Engineering **146**

## Shape and Size-Tailored Supported Pd Nanoparticles as a Model Catalyst for Acetylene Hydrogenation

Micaela Crespo-Quesada, Clément Voisard, Artur Yarulin and Lioubov Kiwi-Minsker

Group of Catalytic Reaction Engineering, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne

Acetylene hydrogenation is a key unit operation in the ethylene process. Traces of acetylene can poison the catalysts used for polyethylene production. Pd-based catalysts are usually employed for the study of this reaction. Much effort has been devoted to study the structure sensitivity of acetylene hydrogenation, and it is now unanimously accepted to be linked to carbide formation on the subsurface of Pd. Most of the studies, however, were performed either theoretically or over single crystals, which are far removed from the real catalysts used in industry (material and pressure gaps).

In this work, we used well-defined size and shape-tailored Pd nanoparticles, already proven to be an invaluable tool for unveiling the reaction mechanism of catalytic reactions [1], to study the structure sensitivity of acetylene hydrogenation in terms of the active sites involved and carbide phase formation. Subsequently, the effect of the nature of the nanoparticle's stabilizing agent, and its removal, was elucidated [2]. We also assessed the influence and characteristics of the macrostructured supports used to immobilize the active phase. Finally, the long term morphological stability of the nanoparticles under reaction conditions was studied.

In conclusion, we believe that this work shows a new generation of model catalysts capable of bridging the material and pressure gaps of catalysis.

[1] Crespo-Quesada, M.; Yarulin, A.; Jin, M.; Xia, Y.; Kiwi-Minsker, L. *J. Am. Chem. Soc.* **2011**, 133, 12787.
[2] Crespo-Quesada, M.; Andanson, J.-M.; Yarulin, A.; Lim, B.; Xia, Y.; Kiwi-Minsker, L. *Langmuir* **2011**, 27, 7909.

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Catalysis Science and Engineering **147**

## Monodispersed Pd-containing Nanoparticles for Liquid-Phase Alkynol Hydrogenation: How to Improve Selectivty?

Artur Yarulin, Igor Iouranov, Fernando Cárdenas-Lizana and Lioubov Kiwi-Minsker

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Pd-catalyzed selective partial -C≡C- hydrogenation is a critical reaction in the manufacture of fine chemicals.[1] In this type of reactions, controlled modifications in metal particle size and a move from *mono*- to *bi*-metallic catalysts have been identified as effective means of influencing catalytic response.[1,2] However, an explicit link between catalytic performance and Pd dispersion is difficult to establish since conventional powder catalysts show a broad metal size distribution.[2] Moreover, catalytic response over *bi*-metallic systems is influenced by the spatial distribution of both metals within the metal nanoparticle (NP), *e.g.* alloy or core-shell structure.[1] We have analyzed the effect of Pd particle size in the liquid phase hydrogenation of a series of alkynols, *e.g.* methylbutynol and butynediol. We have established a correlation between specific hydrogenation rate and metal dispersion for a series of monodispersed polymer-stabilized Pd NPs (2-12 nm) where a mean size of 3 nm was found to be critical. The incorporation of Cu or Ag in colloidal Pd-NPs served to increase selectivity (by up to 98% at full conversion) to the target olefin product.

Our findings over model monodispersed colloidal systems establish the basis for the development of Pd-based catalysts for selective hydrogenations where product distribution can be controlled by the incorporation of a second metal.

[1] N. López and C. Vargas-Fuentes, *Chem. Comm.*, **2012**, *48*, 1379.

[2] N. Semagina and L. Kiwi-Minsker, *Catal. Rev.-Sci. Eng.*, **2009**, *51*, 47.

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Catalysis Science and Engineering **148**

## Maximising Nanoparticle Efficiency: Chemoselective Hydrogenation over Polymer-based Catalysts

Fernando Cárdenas-Lizana, Charline Berguerand, Igor Iouranov, and Lioubov Kiwi-Minsker

Ecole Polytechnique Fédérale de Lausanne, GGRC-ISIC-EPFL, Lausanne CH-1015, Switzerland

Heterogenization of metal complexes *via* inmobilization in porous solid materials is an optimum alternative for the synthesis of metal nanoparticles (NPs) with tailored size and electronic properties.[1] We report, for the first time, 100% yield of *p*-chloroaniline with multiple industrial applications[2] through the liquid phase hydrogenation of *p*-chloronitrobenzene over *quasi*-monodispersed Pt NPs confined within a structured polymeric matrix. Activity and selectivity were fully maintained in repeated reaction cycles. The polymeric network is characterized by uniform *nano*-sized (4.6 nm) pore distribution and large surface area (1065 m$^2$ g$^{-1}$). Controlled *pre*-treatment led to the gradual descomposition-reduction of the metal precursor and synthesis of Pt nanoclusters within the cavities of the polymer structure. After activation metallic (based on XPS) Pt clusters with a mean particle size 3.3±0.2 nm (from TEM and CO chemisorption) entrapped in the cages of the polymeric structure were formed. Under the same reaction conditions, two benchmark Pt/C and Pt/$\gamma$-Al$_2$O$_3$ catalysts delivered lower activity (by a 3-fold) and selectivity ($\leq$ 95 %), promoting dechlorination with the formation of aniline, and suffering deactivation over consecutive runs. The results established the potential of polymer-based materials for tailoring metal *nano*-scale particle size and the viability of the newly developed system as a promising catalyst for amine production.

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[2] C. Xiao *et al.*, *Curr. Org. Chem.* **2012**, *16*, 280.

Catalysis Science and Engineering **149**

## Catalytic Hydrogenation over $Mo_2N$: A Consideration of Crystal Phase ($\beta$- *vs.* $\gamma$-) and Surface Area

Daniel Lamey, Fernando Cárdenas-Lizana, and Lioubov Kiwi-Minsker

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The use of molybdenum nitrides in hydrogen mediated reactions has been considered to a limited extent with evidence of significant hydrogenation activity[1] and a distinct selectivity response relative to conventional supported metal (*e.g.* Pd or Pt) catalysts[2]. In this work we investigate, for the first time, the independent effect of nitride crystallographic phase (tetragonal $\beta$-$Mo_2N$ *vs.* cubic $\gamma$-$Mo_2N$) and surface area (7-66 $m^2$ $g^{-1}$) on the catalytic response in terms of *chemo-* and *partial*-selective hydrogenation of $-NO_2$ (*p*-chloronitrobenzene (*p*-CNB)) and C≡C (acetylene), respectively. The formation of $\beta$-$Mo_2N$ and $\gamma$-$Mo_2N$ was confirmed by XRD and HR-TEM. $\gamma$-$Mo_2N$ exhibits a platelet morphology whereas $\beta$-$Mo_2N$ is characterised by an aggregation of small crystallites. Hydrogen chemisorption and TPD analyses have established a greater hydrogen uptake capacity (per unit area) for $\beta$-$Mo_2N$ relative to $\gamma$-$Mo_2N$, which is associated with an increase nitrogen deficient surface component, *i.e.* higher surface Mo/N from XPS. Both $\beta$-$Mo_2N$ and $\gamma$-$Mo_2N$ catalyzed the exclusive hydrogenation of *p*-CNB (to *p*-chloroaniline) and the preferential ($S \sim 80\%$) formation of the olefin product where $\beta$-$Mo_2N$ delivered a higher specific (per $m^2$) rate; specific rate over $\gamma$-$Mo_2N$ was independent of surface area. The results establish the potential of $Mo_2N$ as a bulk catalytic material for selective hydrogenations.

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[2] F. Cárdenas-Lizana, D. Lamey, N. Perret, S. Gómez-Quero, L. Kiwi-Minsker, M. A. Keane, *Catal. Commun.* **2012**, *21*, 46.

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Catalysis Science and Engineering **150**

## Carbon Based Structured Catalysts for Bromate Reduction

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The increased demand of water purity in both industrial and domestic use leads to a strict regulation of the water pollutants. The presence of toxic by-products due to water disinfection has to be controlled. Bromate is one of the ozonation by-products detected in drinking water from bromide-containing source. There are different techniques for the bromate removal such as membrane processes or ion exchange. These techniques present some limitations due to a post-treatment of the effluent or high exploitation cost. Therefore, an alternative technology development is warranted.

Recently, it has been shown that suitable way to remove bromates is to reduce them to $Br^-$ via catalytic liquid phase hydrogenation [1]. In technical applications the use of fine powdered catalysts is limited either due to a high pressure drop in fixed beds or by filtration in a batch mode. To overcome such problems in water treatment, we have suggested using structured fibrous catalysts [2-3].

Structured Pd-containing catalysts based on Activated Carbon Fibers (ACF) and Carbon Nano-Fibers grown on Sintered Metal Fibers (CNF/SMF) were prepared, characterized and tested in both a batch and in an open-flow reactor. The support nature, metal content and catalyst preparation were optimized for effective bromates removal in a broad range of working conditions. The influence of the contact time, the water composition, the pH, the initial pollutant concentration, the catalyst stability in long-term experiments and the catalyst regeneration were studied.

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[2] L. Kiwi-Minsker, *Chimia*, **2002**, 56, 159.
[3] T.Yuranova, C.Franch, A.E.Palomares, E.Garcia-Bordejé, L.Kiwi-Minsker, *Appl. Catal. B*, **2012**, in print

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Catalysis Science and Engineering **151**

## Temperature monitoring of rapid and highly exothermic reactions in MSR using infrared thermometry

J. Haber[1], A. Kumar[1], M. N. Kashid[1], B. Jiang[2,3], T. Maeder[2], A. Renken[1], L. Kiwi-Minsker[1]

[1]Group of Catalytic Reaction Engineering (GGRC)
[2]Laboratory of Microengineering for Manufacturing (LPM)
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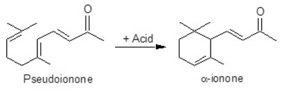
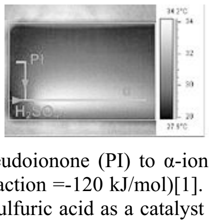
The local temperature rise (hot spot) in highly exothermic reactions often leads to loss in selectivity towards the target product. Microstructured reactors (MSR), reactors with at least one dimension in submillilimeter range, have been successfully used to carry out such reactions leading to increased yield due to their high heat removal efficiency. However, homogeneous catalytic reactions that require high concentrations of catalyst accelerate the reaction leading to unwanted temperature rise even in MSR.





In the present work, the cyclisation of pseudoionone (PI) to α-ionone (α) was studied as a model reaction (heat of reaction =-120 kJ/mol)[1]. The reaction was carried out using concentrated sulfuric acid as a catalyst leading to significant heat production rate. The temperature profiles for various operating conditions were monitored using an infrared thermometry based technique. The magnitude of the hot spot was analyzed and the reaction conditions were optimized for the highest yield.

[1] M.N. Kashid, I. Yuranov, P. Raspail, P. Prechtl, J. Membrez, A. Renken, L. Kiwi-Minsker, *Ind. Eng. Chem. Res*, **2011,** 50, 7920.

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Catalysis Science and Engineering **152**

## Catalytic and mechanistic aspects of the low-temperature catalytic conversion of methane to methanol over Cu-Fe-ZSM-5

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Methane is a highly abundant alternative resource to crude oil, present as the major component of many fossil resources. Although already utilised as an industrial feedstock, its conversion to value added products first requires the energy- and capital-intensive manufacture of *syngas*. Thus, there is significant interest in the development of a one-step conversion of methane to value added derivatives under mild reaction conditions.

Amongst potential routes for methane upgrading, its direct partial oxidation to methanol is one of the most promising, given methanols versatility as a chemical building block (*e.g.* MTO technology). However, although a number of routes have been thoroughly investigated, to date these are limited by low selectivity, non-closed catalytic cycles or low catalytic rates (*i.e.* turnover frequencies < 10 $h^{-1}$).[1]

Recently, it was demonstrated that a Cu- and Fe-containing zeolite is able to selectively oxidise methane to methanol at high selectivity (> 90 %), yield (*ca.* 10 %) and TOFs (≤ 14,000 $h^{-1}$).[2] The key to this process is the heterolytic activation of $H_2O_2$, which yields a highly-selective and oxidative species capable of activating methane under mild reaction conditions (50 ºC, aqueous phase). During this presentation, the nature of the active species within the catalyst will be discussed, along with their specific role(s) in some elementary aspects of the reaction mechanism. In closing, the implication of this work in the wider field of selective oxidation chemistry, and the challenges that remain, will be highlighted.

[1] G. I. Panov *et al.*, *Catalysis Today* **1998**, *41*, 365-385; P. Vanelderen *et al.*, *Journal of Catalysis* **2011**, *284*, 157-164; R. A. Periana *et al.*, *Science* **1998**, *280*, 560-564.
[2] C. Hammond *et al.*, *Angew. Chem. Int. Ed.* **2012,** *Accepted Article,* doi: 10.1002/anie.201108706

Catalysis Science and Engineering **153**

## Thermal Restructuring of Silica-Grafted Ti$^{IV}$ Lewis Acid Sites

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Epoxidation of olefins is an important chemical reaction throughout the chemical value-chain. Most of the currently operated catalysts use Ti$^{IV}$ as the catalytically active species, the microporous TS-1 catalyst for propylene to propylene oxide probably being the most studied system. However, until today, the true nature of the active site – and hence the catalytic action – is poorly understood. Therefore development of well define Ti$^{IV}$ model catalysts is desirable in order to compare different active sites with TS-1.

Chemical Vapor Deposition (CVD) is one approach to synthesize heterogeneous catalysts in a very convenient and precise way. This solvent free technique matches the sustainable and environmentally friendly technology demands of today. The reaction of a volatile metal precursor (e.g. $TiCl_4$, $VOCl_3$) with OH-groups on a support (e.g. silica) creates chemically bound metal sites on the surface which can be further modified by post-synthesis procedures. In order to characterize the resulting catalyst a variety of spectroscopic tools are necessary to elucidate the active sites and therewith setting the starting point for drawing conclusions about the chemical mechanism of the underlying reaction

In this contribution, we present the synthesis of well-defined silica supported Ti$^{IV}$ Lewis Acid catalysts which are stabilized by post-synthesis methods and investigated by various characterization techniques. Furthermore, a few preliminary results on the catalytic performance will be given.

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Catalysis Science and Engineering **154**

## Understanding the homolytic activation of alkyl peroxides by homogeneous and heterogeneous cobalt catalysts

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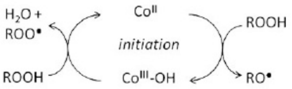
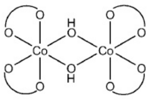
Kinetic information extracted from the deperoxidation of a model alkyl peroxide by dissolved cobalt(II)acetylacetonate led to new mechanistic hypotheses. Even under anaerobic conditions, the Haber-Weiss cycle **1** initiates a radical chain destruction of ROOH. At high cobalt concentrations, a remarkable decrease of the rate was observed which could be explained by the hitherto overlooked chain termination of two Co$^{III}$-OH species **2** [1].



**1**



**2**

The deperoxidation reaction was also studied under heterogeneous conditions by aerobic oxidation of cyclohexane at 130°C in the presence of a $Co/SiO_2$ catalyst, synthesized by flame-spray pyrolysis. Catalytic experiments demonstrated high activity causing a complete *in situ* deperoxidation of the intermediate cyclohexylhydroperoxide [2].

$$ROOH \rightarrow RO^{\bullet} + {}^{\bullet}OH \qquad (1)$$

$$ROOH + RH \rightarrow RO^{\bullet} + H_2O + R^{\bullet} \qquad (2)$$

Recently, the thermal and catalytic initiation rate for the oxidation of the renewable olefin α-pinene was quantified, providing evidence for a substrate-assisted thermal initiation (2) rather than the unimolecular O-O bond cleavage (1) [3]. The kinetics of the catalytic initiation is in good agreement with studies under model conditions mentioned above.

[1] N. Turrà et al., *Chem. Eur. J.* **2010**, *16*, 13226.
[2] N. Turrà et al., *Top Catal* **2011**, *54*, 737.
[3] U. Neuenschwander, I. Hermans, *J. Catal.* **2012**, *287*, 1.