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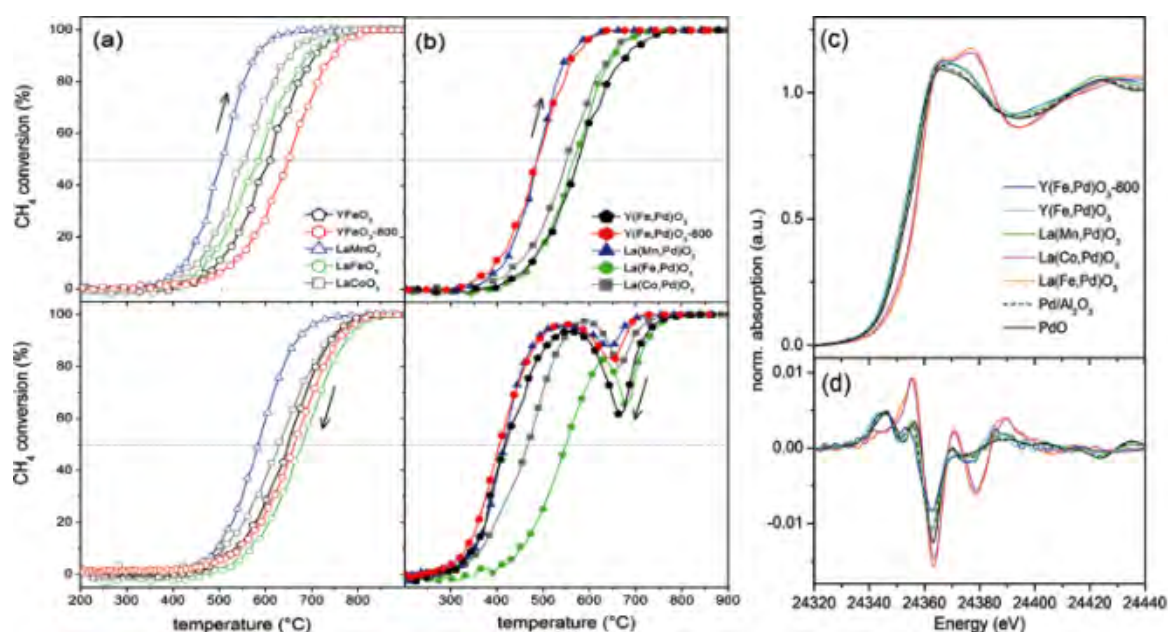
Effect of the Pd-state in perovskite-type $A(B,Pd)O_{3\pm\delta}$ ($A = La, Y$; $B = Mn, Fe, Co$) oxidation catalysts in terms of CH_4 -oxidation activity

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Pd-doped perovskite-type oxides are a promising class of catalysts for the exhaust after-treatment of natural gas vehicles (NGV) [1]. It has been shown for the $LaFe_{0.57}Co_{0.38}Pd_{0.05}O_3$ perovskite [2], that cycles of oxidative and reductive conditions force the incorporation (oxidation) of the noble metal into and the segregation (reduction) of the metal out of the perovskite lattice. This "self-regenerating property" is capable of limiting precious metal particle sintering under periodic redox fluctuations occurring on conventional catalysts.

Pd-containing perovskite-type oxides of nominal formula $LaB_{1-x}Pd_xO_{3\pm\delta}$ ($B = Mn, Fe, Co$) and $YFe_{1-x}Pd_xO_{3\pm\delta}$ ($x = 0.0435-0.0463$) have been prepared by the amorphous citrate method [3]. EXAFS measurements on fresh prepared samples and XANES during in situ H_2 -TPR revealed palladium in solid solution (Pd^{3+} in octahedral coordination state [4]) within the perovskite structure for $La(Co,Pd)O_3$ and $La(Fe,Pd)O_3$. Whereas $La(Mn,Pd)O_3$ and $Y(Fe,Pd)O_3$ revealed palladium present as fine dispersed PdO particles on their surface (Pd^{2+} species in square-planar coordination state). Our results show that such catalysts can only express high catalytic activity during CH_4 -conversion when palladium is present as highly dispersed PdO nanoparticles on the surface of the support. Depending of the B-site cation, palladium can form a solid solution with the support during oxidative atmosphere, whereas reductive atmosphere forces its segregation to the surface. Consequently, repeated pulses of rich and lean atmosphere will trigger the "self-regenerative" function which guarantees the long term stability of these catalysts.



[1] D. Fino et al, Progr. Solid State Chem. 35 (2007) 501

[2] Y. Nishihata, J. Mizuki, T. Akao, H. Tanaka, M. Uenishi, M. Kimura, T. Okamoto, N. Hamada, Nature 418 (2002) 164

[3] Baythoun, M. S. G.; Sale, F. R. J. Mater. Sci. 17 (1982) 2757.

[4] Uenishi, M.; Taniguchi, M.; Tanaka, H.; Kimura, M.; Nishihata, Y.; Mizuki, J.; Kobayashi, T. App. Catal., B 57 (2005) 267 Environmental 84 (2009) 607

Hydrogen Storage in Formic Acid/Carbon Dioxide Systems -Solvent Effects: Heat of Mixing and pH of the Reaction Media

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The massive exploitation of fossil fuels by mankind endangers the whole ecosystem on earth.^[1] They account for the majority of our energy needs, such as heat, electricity, and transportation.^[2] On this way, vast amounts of carbon dioxide are produced. The reduction of carbon dioxide (CO₂), captured at the origin, with hydrogen (H₂), generated from renewable energy sources, to formic acid (FA) can contribute to mitigate the negative effect of CO₂ on our climate. The chemical industry has a strong demand for formic acid and its high content of hydrogen (53 g/L) makes it attractive as a secondary energy vector for a future hydrogen-based society.^[3]

The direct synthesis of formic acid from CO₂ and H₂ in gas phase is thermodynamically not favored ($\Delta G^\circ = +33$ kJ/mol), whereas using water as reaction media shifts it already in a slightly exergonic ($\Delta G^\circ = -4$ kJ/mol) region. The equilibrium can be shifted even further to formate formation by using basic additives.^[4, 5] Beller et al. and others developed several iron^[6, 7] and ruthenium^[8] catalysts, operating in basic solutions or with formic acid-amine mixtures, reaching extremely high TOFs. A clear drawback when using additives is the more laborious purification of the H₂/CO₂ gas mixtures or FA due to the strong intermolecular interactions.^[9] Moreover, formate salts or widely used 5(HCOOH):2(NEt₃) adducts have lower hydrogen content per weight unit (e.g. 2.3 wt%) as formic acid, which is another apparent disadvantage.

Recently, we have reached unprecedentedly high concentrations of FA (2.2 M) with a Ru based catalyst in dimethyl sulfoxide.^[10] No additives were required in this reaction.

In the present work, we quantify the enthalpy of mixing when formic acid is dissolved in different solvents and additives under similar conditions as are used in the experimental procedures. The goal is to measure the energy conversion and to determine the interactions and structures in these reaction media.

Acknowledgement:EPFL and SCCER are thanked for financial support

[1]EPA. *Climate Change*. 2015; Available from: <http://www.epa.gov/climatechange>.

[2] D. Mori, K. Hirose, *International Journal of Hydrogen Energy* **2009**, 34, 4569-4574.

[3] M. Grasemann, G. Laurenczy, *Energy Environmental Science* **2012**, 5, 8171-8181.

[4] G. Papp, J. Csorba, G. Laurenczy, F. Joo, *Angew. Chem. Int. Ed.*, **2011**, 50, 10433-10435.

[5] A. Boddien, C. Federsel, P. Sponholz, D. Mellmann, R. Jackstell, H. Junge, G. Laurenczy, M. Beller, *Energy Environmental Science*, **2012**, 5, 8907.

[6] A. Boddien, D. Mellmann, F. Gaertner, R. Jackstell, H. Junge, P. J. Dyson, G. Laurenczy, R. Ludwig, M. Beller, *Science*, **2011**, 333, 1733.

[7] C. Ziebart, C. Federsel, P. Anbarasan, R. Jackstell, *J. Am. Chem. Soc.* **2012**, 134, 20701-20704.

[8] C. Fellay, P. J. Dyson, G. Laurenczy, *Angew. Chem. Int. Ed.*, **2008**, 47, 3966.

[9] B. Loges, A. Boddien, H. Junge, M. Beller, *Angew. Chem. Int. Ed.*, **2008**, 47, 3962-3965.

[10] S. Moret, P.J. Dyson, G. Laurenczy, *Nature Comm.* **2014**, 5, 4017.

Insights into the Ionic Liquid-Promoted Electrochemical Reduction of CO₂G. Lau¹¹EPF Lausanne

Ionic liquids (ILs) are fascinating materials with properties unlike most organic solvents. They typically possess high ionic conductivities, wide electrochemical windows, and negligible vapor pressure¹⁻⁴. These features make them ideally suited for various electrochemical applications; for example, as electrolytes in dye-sensitized solar cells, batteries, and supercapacitors⁴⁻⁶. In recent years, ionic liquids have also been found to be helpful in lowering the overpotential required for the electrochemical reduction of carbon dioxide⁷. Work in our research group has focused on determining the factors responsible for the beneficial effects of the ionic liquid, by thoroughly and systematically screening different ILs. Our results show that not all cation families are able to mediate the electrochemical reduction of CO₂, as some cations are inherently unstable at such reducing potentials. Among the cation families that are stable at the potentials required for CO₂ reduction, we find that the imidazolium salts perform much better than the tetraalkylammonium salts. Furthermore, we can conclude that residual water impurity in the ILs is not responsible for the observed catalytic effect.

¹ Fei, Z.; Geldbach, T. J.; Zhao, D.; Dyson, P. J. *Chem.-Eur. J.* **2006**, 12, 2122-2130.

² Zhang, S. J.; Sun, N.; He, X. Z.; Lu, X. M.; Zhang, X. P. *J. Phys. Chem. Ref. Data* **2006**, 35, 1475-1517.

³ Wang, P.; Zakeeruddin, S. M.; Humphry-Baker, R.; Grätzel, M. *Chem. Mater.* **2004**, 16, 2694-2696.

⁴ Zakeeruddin, S. M.; Graetzel, M. *Adv. Funct. Mater.* **2009**, 19, 2187-2202.

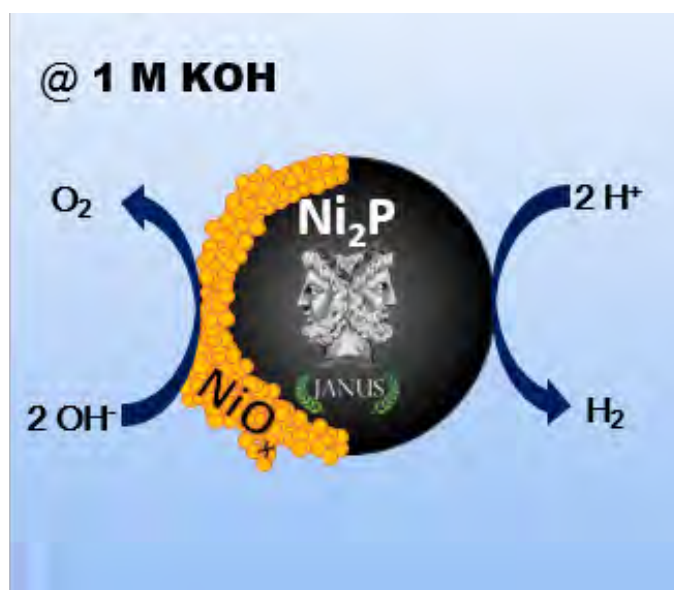
⁵ Lau, G. P. S.; Tsao, H. N.; Zakeeruddin, S. M.; Grätzel, M.; Dyson, P. J. *ACS Appl. Mater. Interfaces*, **2014**, 6, 13571-13577.

⁶ MacFarlane, D. R.; Tachikawa, N.; Forsyth, M.; Pringle, J. M.; Howlett, P. C.; Elliott, G. D.; Davis, J. H.; Watanabe, M.; Simon, P.; Angell, C. A. *Energy Environ. Sci.* **2014**, 7, 232-250.

⁷ Sun, L.; Ramesha, G. K.; Kamat, P. V.; Brennecke, J. F. *Langmuir* **2014**, 30, 6302-6308.

Ni₂P nanoparticles as Janus catalyst for electrochemical water splittingL.-A. Stern¹, L. Feng¹, F. Song¹, X. Hu^{1*}¹EPF Lausanne

Electrochemical water splitting into hydrogen and oxygen is a promising method for solar energy storage. The two half reactions of water splitting, the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER), both require catalysts to take place in a practical rate. The development of efficient electrocatalysts for water splitting, particularly those based on Earth-abundant metals, has drawn much attention.^[1] However, catalysts that are active for both the hydrogen evolution and oxygen evolution reactions are rare. Such bifunctional, Janus catalysts might be attractive for a water splitting device because the integration of only one rather than two catalysts need to be considered.^[2] Herein, we show for the first time that nickel phosphide (Ni₂P), an excellent hydrogen evolving catalyst,^[3] is also highly active for oxygen evolution. A current density of 10 mA cm⁻² is generated at an overpotential of only 290 mV in 1 M KOH, ranking among the most active non precious OER catalysts. The high activity is attributed to the core-shell (Ni₂P/NiO_x) structure that the material adopts under catalytic conditions. The Ni₂P nanoparticles can serve as both cathode and anode catalysts for an alkaline electrolyzer, which generates 10 mA cm⁻² at 1.63 V.



[1] Timothy R. Cook, Dilek K. Dogutan, Steven Y. Reece, Yogesh Surendranath, Thomas S. Teets, Daniel G. Nocera, *Chem. Rev.*, **2010**, 110 (11), 6474-6502.

[2] S. Cobo, J. Heidkamp, P.-A. Jacques, J. Fize, V. Fourmond, L. Guetaz, B. Josselme, V. Ivanova, H. Dau, S. Palacin, M. Fontecave and V. Artero, *Nat. Mater.*, **2012**, 11, 802-807.

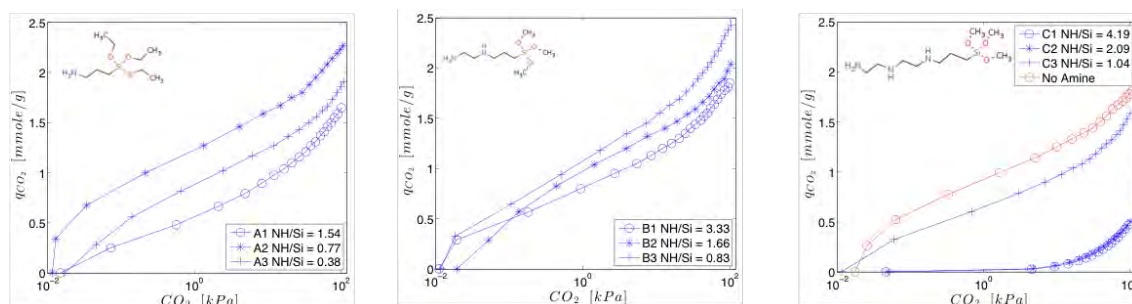
[3] E. J. Popczun, J. R. McKone, C. G. Read, A. J. Baccchi, A. M. Wiltrout, N. S. Lewis and R. E. Schaak, *J. Am. Chem. Soc.*, **2013**, 135, 9267-9270.

Aerogels for CO₂ Capture

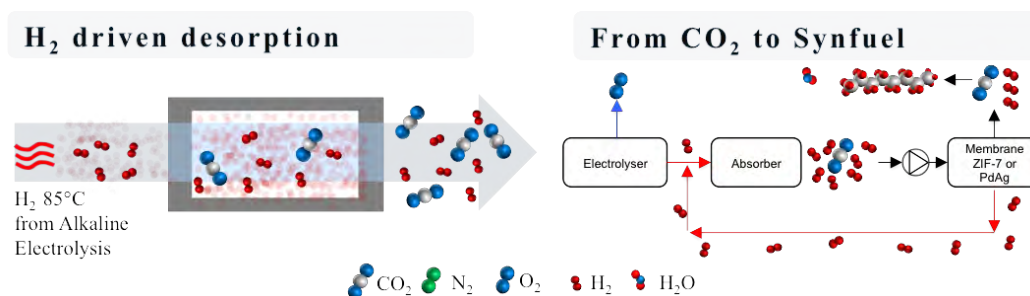
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Aerogels were synthesized and functionalized with three different amines. They exhibit a high specific surface area and a low gravimetric density. The CO₂ adsorption isotherms were measured and analyzed. An adsorption of up to 0.8 mmole/g, already at 40 Pa, consequently CO₂ may be captured from the atmosphere. Primary amine show advanced performance for CO₂ adsorption at low pressure contrary to secondary amines.



The selectivity of the sorbent is subject of further investigations. We plan to investigate the isotherms beside CO₂ also for H₂O and N₂. The desorption of the adsorbed gases is endothermic and therefore, the low density of the aerogels is favorable in view of heat requirement. Furthermore, we intend to use the heat of an electrolyser and Hydrogen at elevated temperature as a purge gas to regenerate the sorbent and to produce a H₂/CO₂ mixture, which can be directly used to synthesise hydrocarbons.



- K. S. Lackner, S. Brennan, J. M. Matter, a-H. A. Park, A. Wright, and B. van der Zwaan, "The urgency of the development of CO₂ capture from ambient air.," *Proc. Natl. Acad. Sci. U. S. A.*, vol. 109, no. 33, pp. 13156-62, Aug. 2012.
- C. Gebald, J. a Wurzbacher, A. Borgschulte, T. Zimmermann, and A. Steinfeld, "Single-component and binary CO₂ and H₂O adsorption of amine-functionalized cellulose.," *Environ. Sci. Technol.*, vol. 48, no. 4, pp. 2497-504, Feb. 2014.
- C. Gebald, J. a Wurzbacher, P. Tingaut, and A. Steinfeld, "Stability of amine-functionalized cellulose during temperature-vacuum-swing cycling for CO₂ capture from air.," *Environ. Sci. Technol.*, vol. 47, no. 17, pp. 10063-70, Sep. 2013.

Selective dehydrogenation of formic acid over sub-nanometric gold particles supported on silica

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The dehydrogenation of formic acid is considered a feasible process to obtain hydrogen.[1,2] Active and selective catalysts are necessary to reach a performance relevant for application. The size of gold clusters is a determining factor on alumina [3] and zirconia [4]. Using mesoporous SBA-15 for catalysis is advantageous due to its high surface area, highly ordered structure, and inertness. However, the synthesis of small gold particles on silica by conventional methods is challenging due to its low isoelectric point.[5]

We introduce a new synthetic route to synthesize sub-nanometer-sized gold particles on SBA-15 by a combination of modifying the silica surface with amine groups (N-SBA) and controlling the solution pH during preparation. This procedure yielded highly active and selective catalysts in the dehydrogenation of formic acid. Figure 1a shows the conversion of formic acid over gold on modified and non-modified SBA-15 prepared at pH 11. Catalysts on N-SBA showed improved conversion at lower temperature compared to using SBA-15 as a support. Figure 1b depicts the selectivity to hydrogen of the two catalysts, showing that the catalyst performing at low temperature is more selective. A strong correlation between performance and particle size was determined. Figure 1c,d shows the transmission electron micrographs of both catalysts, underlining the positive effect of the surface modification and preparation method on the gold particle size.

Multiple gold catalysts were synthesized using different bases and pH conditions and their performance in the dehydrogenation of formic acid was investigated. The smaller the particles, the more active was the catalyst. Selectivity exclusively to hydrogen and carbon dioxide was achieved.

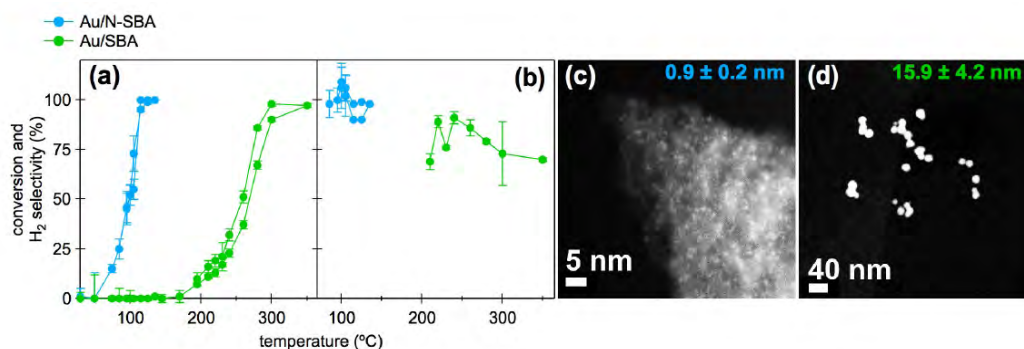


Figure 1. (a) Formic acid conversion and (b) H₂ selectivity over Au/N-SBA and Au/SBA prepared at pH 11. STEM images of (c) Au/N-SBA and (d) Au/SBA. The average size and standard deviation is indicated on the micrographs.

[1] Björn Loges, Albert Boddien, Henrik Junge, Matthias Beller, *Angewandte Chemie International Edition in English*, **2008**, 47, 3962-3965.

[2] Ferenc Joó, *ChemSusChem*, **2008**, 1, 805-808.

[3] Manuel Ojeda, Enrique Iglesia, *Angewandte Chemie International Edition*, **2009**, 48, 4800-4803.

[4] Qing-Yuan Bi, Xian-Long Du, Yong-Mei Liu, Yong Cao, He-Yong He, Kang-Nian Fan, *Journal of the American Chemical Society*, **2012**, 134, 8926-8933.

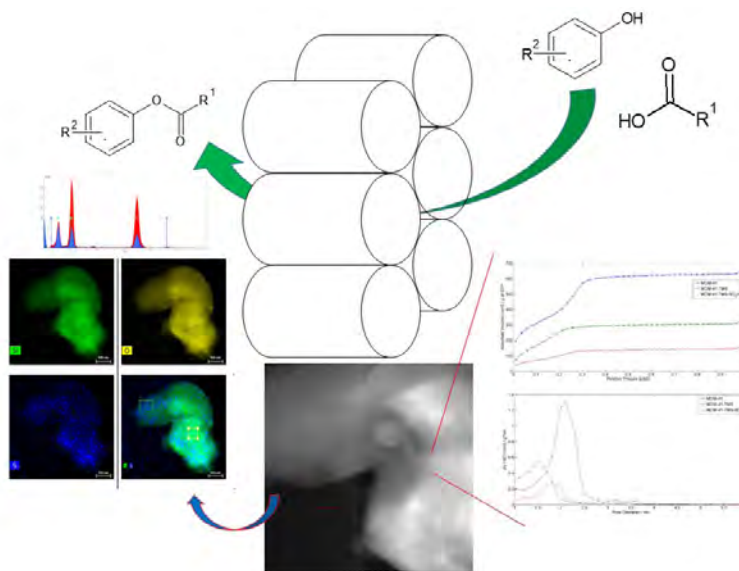
[5] Rodolfo Zanella, Alberto Sandoval, Patricia Santiago, Vladimir A. Basiuk, José M. Saniger, *Journal of Physical Chemistry B*, **2006**, 110, 8559-8565.

Esterification of 2-Methoxyphenol and Octanoic Acid over modified MCM-41 for Biomass Conversion

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Lignin is a promising, renewable, and oxygen-rich resource for phenol and phenol-derivative compounds. Pyrolysis of lignin yields bio-oil and contains lignin monomers, dimers and derivative thereof. The properties of bio-oil are disadvantageous, as it is with low value, acidic and unstable. Too many compounds in bio-oil makes the separation cost inefficient¹. The idea is to chemically catch the most abundant lignin monomers by reacting them with other low value chemicals to produce new chemicals. This can be done by esterification and acylation of the lignin monomers with other biomass resources, such as long chain fatty acid. These acid-catalyzed reactions were tested using commercial zeolites with and without modification with heteroatoms and modified mesoporous silicas, such as SBA-15 and MCM-41.



The micro- and mesopore containing SBA-15² yielded 44% of ester product in the esterification reaction of 2-methoxy phenol and octanoic acid. Even better yields were obtained over MCM-41³. The high stability of the structure was confirmed after its modification to sulfonated MCM-41. This modified MCM-41 shows an ester yield of 55%, which is close to the yield with homogeneous sulfuric acid catalyst, which is 60%. The easy separation of this solid acid from the product mixture makes its usage preferred.

[1] Zhao C., Lercher J. A., *ChemCatChem* **2012**, 4, 64-68.

[2] Ordonsky V. V., Ivanova I. I., Knyazeva E. E., Yuschenko V. V., Zaikovskii V. I. *Journal of Catalysis* **2012**, 295, 207-216.

[3] Kresge, C. T., Leonowicz M. E., Roth W. J., Vartuli J. C., Beck J. S. *Nature* **1992**, 359, 710 – 712.

Simple One-Pot Synthesis of Iridium-Titanium Oxide Composites

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The wider application of Polymer Electrolyte Fuel Cell (PEFC) technology is largely limited by short operation lifetimes due to oxidative degradation of the carbon-based catalyst layer. Consequently, current research is directed towards the development of oxidation stable catalyst supports based on conductive metal oxides. The application of iridium titanium oxide composites has been previously demonstrated¹, with improved corrosion resistance with respect to common carbon-based materials.²

Sol-gel chemistry is well developed for the preparation of a variety of pure and mixed metal oxides.³ Nevertheless these methods commonly employ expensive organic solvents and require long reaction times. Therefore there is an incentive to move towards simpler protocols. Here we report the one-pot preparation of an iridium oxide-titanium oxide composite using Adams Fusion Method.⁴ With a view towards application in PEFC technology, the variation of morphology and electronic conductivity with iridium content is explored.

[1] Suchsland et al. *ECS Trans.* **2012**, 50, 1659-1667.

[2] Binninger et al. *ECS Trans.* **2013**, 58, 1835-1841.

[3] Livage et al. *Prog. Solid State Ch.* **1988**, 18, 259-341.

[4] Adams and Shriner, *J. Am. Chem. Soc.* **1923**, 45, 2171-2179.

Silver-indium catalysts for the electrochemical reduction of carbon dioxideG. Larrazábal¹, A. J. Martín-Fernández¹, J. Pérez-Ramírez^{1*}¹ETH Zurich

The electrochemical conversion of carbon dioxide into fuels and bulk chemicals is one of the most attractive strategies for mitigating CO₂ emissions. In particular, the selective reduction of CO₂ to CO provides a valuable commodity chemical which is a stepping stone towards more complex products, such as liquid fuels and plastics, but the practical applicability of this reaction is hampered by the high overpotential required and concerns over the productivity and stability of existing metal electrocatalysts.¹ DFT calculations suggest that more active catalysts for the reduction of CO₂ to CO may be obtained by engineering sites that favor the stabilization of a COOH intermediate over that of CO.² Recently, a bimetallic Cu-In catalyst with remarkable selectivity towards CO at decreased overpotentials has been reported,³ although the mechanism behind the synergistic role of indium remains unclear. We have since evaluated an indium-decorated silver electrode with improved selectivity towards CO at low overpotentials (Fig. 1), suggesting the possible existence of bifunctional active sites in which metastable indium oxide favors the stabilization of the COOH intermediate adsorbed on the silver surface.⁴ In this work, we report the further development of silver-indium catalysts with nanoengineered architectures aimed at optimizing such bifunctional sites and unraveling the role of indium in the enhancement of the selectivity towards CO at decreased overpotentials.

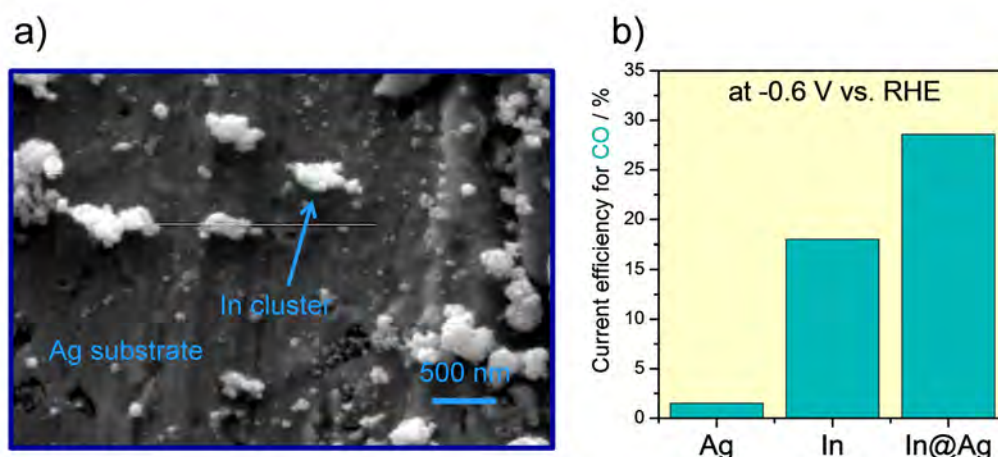


Figure 1. (a) SEM micrograph of the indium-decorated silver electrode. (b) The enhanced selectivity towards CO achieved compared to both component metals.

[1] E.V. Kondratenko, G. Mul, J. Baltrusaitis, G.O. Larrazábal, J. Pérez-Ramírez, *Energy Environ. Sci.*, **2013**, 6, 3112.

[2] H.A. Hansen, J.B. Varley, A.A. Peterson, J.K. Nørskov, *J. Phys. Chem. Lett.*, **2013**, 4, 388.

[3] S. Rasul, D.H. Anjum, A. Jedidi, Y. Minenkov, L. Cavallo, K. Takanabe, *Angew. Chem. Int. Ed.* **2015**, 54, 2146.

[4] Z.M. Detweiler, J.L. White, S.L. Bernasek, A.B. Bocarsly, *Langmuir* **2014**, 30, 7593.

Highly selective basic zeolites for the dehydrogenation of ethanol to acetaldehydeG. M. Lari¹, K. Desai¹, C. Mondelli¹, J. Pérez-Ramírez^{1*}¹ETH Zurich

With a market of over 10^6 tony⁻¹, acetaldehyde belongs to the top 50 chemicals worldwide. Currently, this compound is obtained by oxidation of ethylene. Herein, in view of a greener manufacturing route, we propose its alternative production through the dehydrogenation of bio-ethanol over basic zeolites. Based on the reported activity of sodium-impregnated high-silica zeolites,¹ we developed highly performing alkali-activated FAU zeolites adapting synthetic protocols recently reported by our group.² In particular, we tuned the concentration of the alkali hydroxide solution used for the treatment of the high-silica commercial materials to maximize Na incorporation while preserving the crystallinity (Fig.1a). The mild basic sites developed are supposed to favor the formation of ethoxide species, which have been postulated as intermediates of the transformation.¹ Upon optimization of the temperature and O₂:ethanol ratio (Fig.1b), an acetaldehyde yield as high as 60% was achieved over the best catalyst (Fig.1a). Preliminary longer-term tests of the latter indicate a substantially stable behavior with minimal coke formation.

b

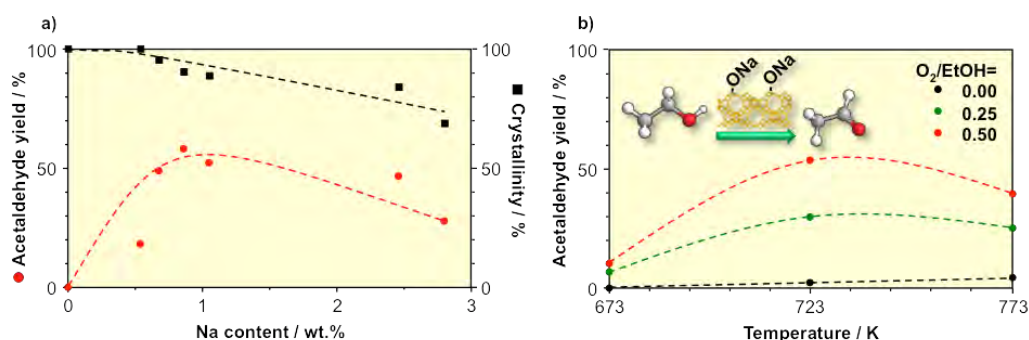


Figure 1. a) Acetaldehyde yield and crystallinity *versus* sodium content. b) Acetaldehyde yield *versus* temperature at different oxygen/ethanol ratio.

[1] Y. Matsumura, K. Hashimoto, S. Yoshida, *J. Catal.* **1990**, 122, 352.

[2] T.C. Keller, E.G. Rodrigues, J. Pérez-Ramírez, *ChemSusChem* **2014**, 7, 1729.b

Stability of tin-containing zeolites in continuous biomass conversions

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Tin-containing zeolites comprise outstandingly active and selective Lewis-acid catalysts for the upgrading of bio-derived substrates to commodity chemicals and polymer building blocks through isomerization.^{1,2} However, their stability under reaction conditions, most relevant in view of a prospective large scale implementation of these processes, has been infrequently explored. Herein, we investigate the deactivation behavior of tin-containing BEA, MFI, MOR, and FAU zeolites prepared by hydrothermal synthesis and alkaline-assisted metallation in the isomerization of dihydroxyacetone and xylose in aqueous and alcoholic media. For this purpose we couple studies in a continuous-flow fixed-bed reactor with in depth characterization. Preliminary results indicate that multiple mechanisms contribute to the deactivation of these materials. Specifically, tin redistribution and leaching and crystallinity loss dominate in the aqueous reactions, while fouling prevails in methanol-based conversions.

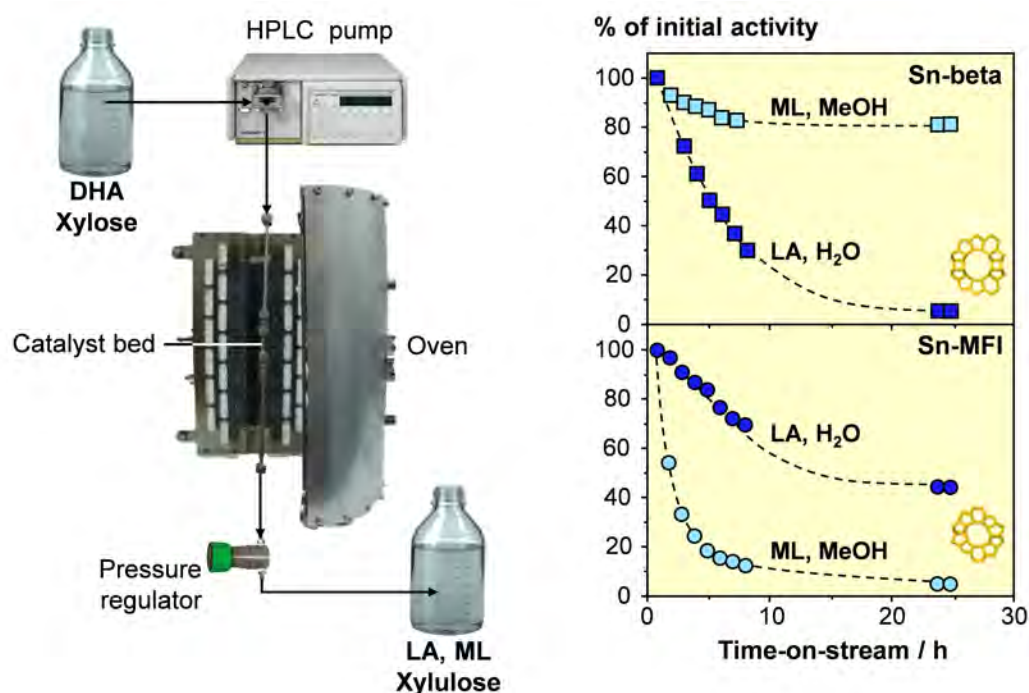


Figure 1. Scheme of the continuous-flow fixed-bed reactor setup used for the isomerization of triose and hexose sugars and deactivation of stannated BEA and MFI during the isomerization of DHA to lactic acid and to methyl lactate.

[1] M. Morales, P.Y. Dapsens, I. Giovinazzo, J. Witte, C. Mondelli, S. Papadokonstantakis, K. Hungerbühler, J. Pérez-Ramírez, *Energy Environ. Sci.* **2015**, 8, 558.

[2] M. Moliner, *Dalton Trans.* **2014**, 43, 4197.

Structure-performance relationships of hybrid nanocatalysts for selective hydrogenation

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Recently, a new generation of hybrid catalysts featuring supported inorganic (Pd and Pt) nanoparticles functionalized with an organic ligand (hexadecylhydroxydimethyl ammonium dihydrogen phosphate) has been commercialized with the trade name of NanoSelectTM.¹ An improved understanding of these nanostructured materials, which are tangible alternatives to the archetypal Pb-poisoned catalysts applied in alkyne and nitroarene hydrogenation, is of foremost relevance. In this work, we have assessed their complex structure, using advanced characterization methods, and obtained a comprehensive understanding of the role and optimal concentration of the ligand (Fig. 1). The materials were applied in the hydrogenation of functionalized alkynes and nitroarenes using a continuous micro-reactor. The derived kinetic fingerprints of the catalysts were compared with those of state-of-the-art Pd and Pt catalysts and rationalized by Density Functional Theory (DFT) and Molecular Dynamics (MD). This integrated approach provided a deeper knowledge on the ligand-modified catalysts for selective hydrogenations as well as distinct strategies to tackle eventual drawbacks derived from the presence of an organic shell at the active metal interphase.

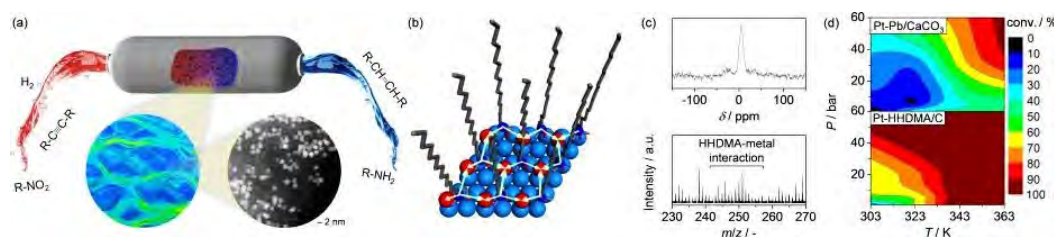
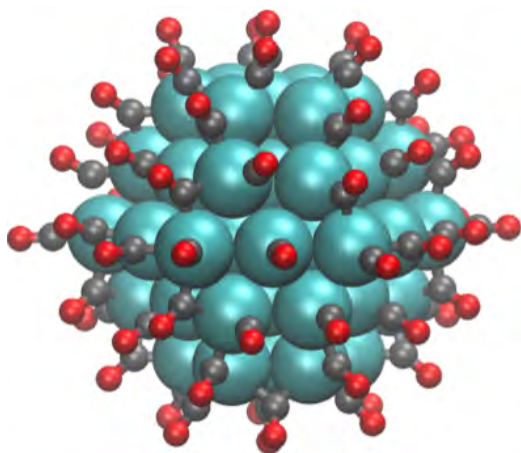


Figure 1. Representation of the flow chemistry hydrogenation (a). DFT-calculated structure (b) and NMR and ToF-SIMS characterization (c) of the hybrid catalyst. Color maps for the hydrogenation of 4-chloronitrobenzene at various temperatures and pressures (d).

[1] Witte, Patent WO096783, **2009**.

CO activation on Ruthenium Nanoparticles: Ab Initio calculations under reaction conditions.L. Foppa¹, C. Copéret¹, A. Comas-Vives^{1*}¹ETH Zurich

The Fischer-Tropsch synthesis (FTS) converts syngas (CO/H₂) to liquid hydrocarbons of various molecular weights through a sequence of elementary reaction steps. There are various transition metals able to catalyze FTS reaction such as Fe, Ru or Co. Ruthenium is of particular scientific interest since it is the most active catalyst and enables FTS with the lowest reaction temperature producing high molecular weight hydrocarbons.[1] Numerous experimental studies showed the dependence of the catalytic performance of these metal catalysts on its particle size and topology, which boosted theoretical investigations on the reactivity of specific active sites for CO activation specially for Ru systems. Density Functional Theory (DFT) calculations on periodic surfaces suggest that CO direct cleavage occurs more likely on stepped sites at low adsorbate coverages such as the referred as “B₅” sites, whereas an H-assisted CO dissociation path is proposed to be preferred on flat Ru and Co surfaces.[2] Nevertheless, high pressures and temperatures as well as nanoparticles are employed in the experiments, conditions that are often not fully accounted for on theoretical investigations although they may significantly change the understanding of the FTS reaction mechanism.[3] Herein, we report improved model systems to study CO activation reaction on Ru nanoparticles. We used both static DFT and *ab initio* molecular dynamics simulations on periodic surfaces and nanoparticle systems in order to evaluate direct and H-assisted CO cleavage under conditions as realistic as possible.



[1] Hans Schulz, *Applied Catalysis A: General*, **1999**, 186, 3-12.

[2] Sharan Shetty, Ruriger A. van Santen, *Catalysis Today*, **2011**, 171, 168-173.

[3] Brett T. Loveless, Corneliu Buda, Matthew Neurock, Enrique Iglesia, *JACS*, **2013**, 135, 6107-6121.

Impact of defect chemistry in zeolite desilication

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The development of hierarchically-structured pore systems through the desilication in alkaline media offers one of the most effective means to enhance their performance of zeolite catalysts in diffusion-constrained reactions.¹ Intensive experimental studies have generated a wealth of knowledge over the impact of different structural and treatment variables on the amount, location, and connectivity of the resulting mesopores (Fig.1), which ultimately define the pore quality.² Yet, recent works have highlighted several gaps in understanding over why subtle changes in the treatment conditions lead to large differences in the pore connectivity, and the relative impact of internal defects on the treatment efficiency. Both synthetic and analytical challenges associated with the identification of materials differing in only a single variable need to be faced to gain insight into these factors. We are approaching this by coupling the targeted synthesis of model MFI zeolites of specific crystal size, and aluminum and defect content, exploiting both hydroxide and fluoride-mediated routes, with the detailed assessment of the metal distribution, the type and amount of defects, and the porous and acidic properties through advanced spectroscopic and visualization techniques.

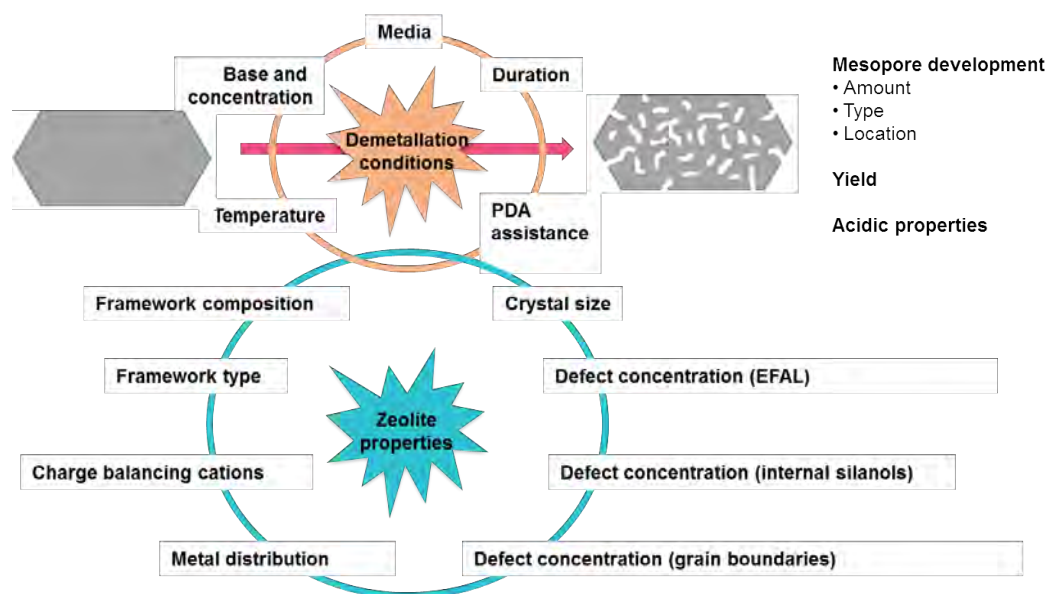


Figure 1. Parameters influencing the mesopore formation.

1. D. Verboekend, J. Pérez-Ramírez, *Catal. Sci. Technol.* **2011**, 1, 829.
2. D. Fodor, A.B. Redondo, F. Krumeich, J.A. van Bokhoven, *J. Phys. Chem. C* **2015**, 119, 5447; S. Svelle, L. Sommer, K. Barbera, P.N.R. Vennestrøm, U. Olsbye, K.P. Lillerud, S. Bordiga, Y.-H. Pan, P. Beato, *Catal. Today* **2011**, 168, 38.

Improving the Oxygen Evolution Kinetics of a Nanostructured Composite Hematite Photoanode

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In the field of solar energy conversion the storage of energy is not yet fully solved. We are pursuing an approach that uses solar light to transform its energy directly into hydrogen, which has the highest energy density per unit weight among all chemical energy carriers [1]. Photoelectrochemical water splitting allows us to circumvent the storage of electricity in batteries, capacitors etc.

Recently, we have published an in detail characterization of a composite $\text{Fe}_2\text{O}_3\text{-TiO}_2$ nanostructured photoanode composed of preformed nanoparticles which were synthesized via microwave assisted nonaqueous sol-gel route [2,3]. Dispersions of titania and iron oxide nanoparticles were mixed and then coated onto FTO substrates. Photoelectrochemical measurements of the annealed composite film revealed a ca. 20 fold increase (up to 2.1 mA/cm^2 at 1.23 V vs. RHE) in performance compared to the pure hematite photoanode. The drastic improvement is explained by the complete transformation of TiO_2 to Fe_2TiO_5 during the heat treatment. Among other contributions, the favorable band edge position of the Fe_2TiO_5 phase in comparison to the coexisting Fe_2O_3 facilitates charge transfer along the interfaces.

Within this study, we tested the influence of an amorphous water oxidation co-catalyst overlayer which was coated onto the nanostructured $\text{Fe}_2\text{O}_3\text{-TiO}_2$ photoanode. The co-catalyst consisted of a ternary amorphous metal oxide which was obtained after gentle combustion of the respective Fe(III), Cr(III) and Ni(II) 2-ethylhexanoate precursors [4,5]. After coating, a lowering of the onset potential was observed and hence the water splitting reaction took place already at lower potentials (Fig.1). Additional characterization addressing oxygen evolution measurements and physical characterization by means of charge transfer processes are under way.

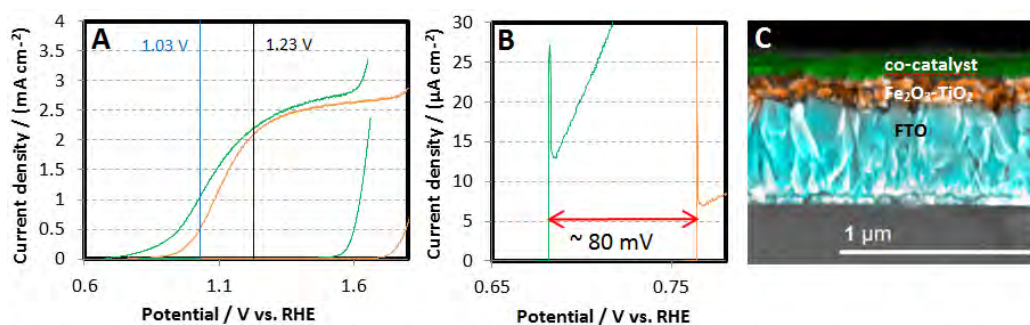


Figure 1: A: J-V curves for the composite photoanode (orange curve) and for the same photoanode containing the co-catalyst overlayer. B: The graph shows the favorable negative shift in onset potential. C: The cross-sectional SEM analysis shows a ca. 100 nm thick layer with the loaded co-catalyst.

[1] U. Maitra, S. R. Lingampalli, C. N. R. Rao, *Curr. Sci.*, **2014**, 106, 518-527

[2] D. Monllor-Satoca and M. Bärtsch et al., **2015**, submitted

[3] T. Ruoko, et al., **2015**, submitted

[4] R. D. L., M. S. Prévot, R. D. Fagan, S. Trudel and Curtis P. Berlingutte, *J. Am. Chem. Soc.*, **2013**, 35, 1158-11586

[5] J. B. Gerken, S. E. Shaner, R. C. Massé, N. J. Porubsky and S. S. Stahl, *Energy Environm. Sci.*, **2014**, 7, 2376

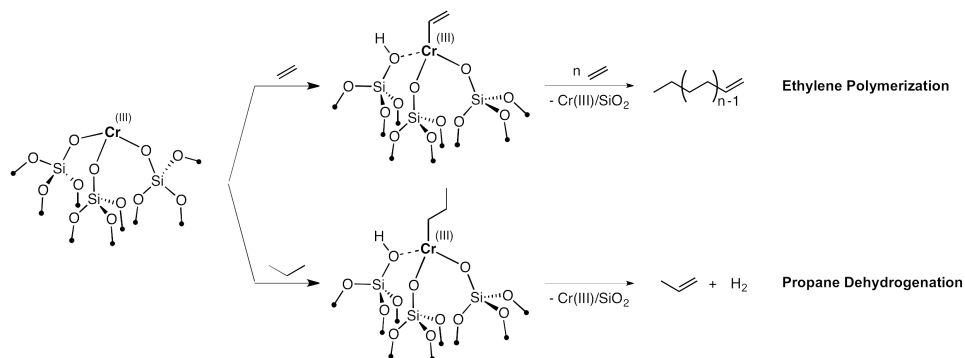
Dehydrogenation and Polymerization on Cr(III) Silicates Are Rate-Determined by an Analogous Mechanistic Step

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Chromium on oxide supports are used as catalysts for ethylene polymerization (silica supported Cr) and propane dehydrogenation (alumina supported Cr).[1] Both processes are run on industrial scales and have been the subject of extended research studies. Due to the complicated nature of the heterogeneous catalysts, i.e. the presence of multiple Cr sites, no consensus has been reached on the nature of the active site and the reaction mechanism for either propane dehydrogenation or ethylene polymerization.

Recently, we prepared well-defined Cr(III) on silica via a molecular approach, characterized by a combination of spectroscopic techniques (IR, EPR, XAS, UV/Vis, adsorption of probe molecules).[2] This material is active in ethylene polymerization and in propane dehydrogenation, which shows that mononuclear Cr(III) silicates catalyze both reactions. DFT calculations on cluster models suggest that the first step in ethylene polymerization and propane dehydrogenation is a C-H activation of the respective hydrocarbon, which is rate-determining.



[1] a) McDaniel, M. P. *Adv. Catal.* **2010**, 53, 123. b) Sattler, J. J. H. B.; Ruiz-Martinez, J.; Santillan-Jimenez, E.; Weckhuysen, B. M. *Chem. Rev.* **2014**, 114, 10613.

[2] a) Delley, M. F.; Nunez-Zarur, F.; Conley, M. P.; Comas-Vives, A.; Siddiqi, G.; Norsic, S.; Monteil, V.; Safonova, O. V.; Coperet, C. *PNAS* **2014**, 111, 11624. b) Conley, M. P.; Delley, M. F.; Nunez-Zarur, F.; Comas-Vives, A.; Coperet, C. *Inorg. Chem.* **2015**, DOI: 10.1021/ic502696n.

Improved Solution Finding in Industrial Waste Incineration Scheduling Through Implementation of Multi-Objective Strategies

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Waste management is a concern in all chemical production plants. In Switzerland, around 70 % of the chemical waste is incinerated [1]. Advantages of the incineration process are the possibilities to recover energy, the volume reduction of wastes and the conversion of toxic substances to less harmful products. The disadvantages are the high costs and technical requirements when compared to other treatment methods [2].

The main challenge for operators is to avoid holdups in the incineration process in order to keep the production steady, while respecting all governmental restrictions regarding emissions as well as technical constraints of the setup. Therefore, careful planning and scheduling of the waste incineration process is crucial [3].

In previous works it could be shown that the optimization of treatment schedules can lead to a significant reduction of the operating costs [4,5]. Due to the complexity of waste incineration systems, the number of combinatorial possibilities for waste transfer, storage, mixing and treatment are nearly infinite. Therefore, there are often many different solutions to waste incineration problems, which are optimal or at least very close to the optimum with respect to a specific objective value. To track down the most suitable solution out of many, both a-priori and a-posteriori multi-objective optimization strategies have been implemented and compared.

Weighted global criterion methods, where all objectives are grouped in one single objective function, can provide fast solutions if the weights are fixed a-priori. This requires a good knowledge of the system and is not trivial in most cases. Therefore, the weights have to be varied in different runs, leading to an optimal Pareto curve from which the most convenient solution has to be selected. In general, strategies leading to Pareto curves, such as all a-posteriori methods, come at large computational costs and require a skilled analysis of the results. Furthermore, it is difficult to handle more than two or three objectives together due to problems in the result presentation.

The most suitable method for this type of problems proved to be the lexicographic one, where an optimum solution is created by solving a sequence of single objective optimization problems according to their priority. Although different consecutive runs are needed to solve the problem, the computational effort is not increasing linearly with the number of objectives considered. This is due to the fact that in each run the system is more and more constrained and therefore the solution is found faster. Applying these strategies for improving daily routines in waste incineration is therefore not only convenient from a computational effort point of view, but it is also the only one delivering a final single schedule that can be directly implemented.

[1] BAFU. (2012). Sonderabfallstatistik: Federal Office of the Environment, Switzerland.

[2] Williams, P. T. (2005). Waste treatment and disposal (2nd ed.). Chichester. Wiley.

[3] Wassick, J. M. (2009). Enterprise-wide Optimization in an integrated chemical complex. Computers Chemical Engineering, 33(12), 1950 – 1963.

[4] Abächerli, M., Capón-García, E., Papadokonstantakis, S. and Hungerbühler, K. (2014). Natural Gas Reduction in Industrial Waste Incineration By Optimized Short-Term Scheduling, Industrial Applications in Design and Operations. Conference Proceedings of AIChE Annual Meeting, Atlanta, Georgia, USA.

[5] Steinleitner, P. (2015). Rolling-Horizon planning and scheduling for industrial waste incineration. Masterthesis, ETH Zürich.

Handling forecast uncertainty in industrial waste incineration schedulingR. Bannerman¹, M. Abächerli¹, E. Capón-García¹, K. Hungerbühler^{1*}¹ETH Zurich

In all chemical branches, waste as a byproduct of the production process is a non-negligible issue [2]. An efficient waste management can prevent holdbacks in production and guarantees unrestrained operations.

As a sustainable treatment method, waste from chemical production sites is preferably incinerated in Switzerland [3]. The incineration process detoxifies hazardous substances, reduces the waste volume and allows recovering part of the energy contained in the waste [7]. Handling all kinds of different waste streams is a complex task for the scheduler as well as the operator of the incineration site. In previous work it has been shown, that the natural gas consumption and therefore the costs of incineration can be reduced through adequate mixing and scheduling of waste streams with different energy content, thus avoiding situations with excess and shortage of energy [1].

So far the introduced mathematical tools to improve the waste incineration management in industry do not consider any uncertainty in the input data, such as in waste production forecasts.

In this work strategies are explored to approach the uncertainty of waste production forecasts, such as fuzzy programming, aggressive trade-off programming, stochastic programming and robust optimization. Fuzzy programming considers constraints as fuzzy members and some constraint violation is allowed. Aggressive trade-off programming adds the possibility of storing excess waste at a certain cost [6]. In stochastic programming the uncertainty is modeled as a scenario tree, with a finite number of decision stages [4]. Robust optimization is a conservative approach which provides only near optimal solutions by imposing tighter constraints to the system as actually needed [5].

In a simplified version of an existent mathematical model [1], random disturbances in the waste forecast are investigated first and different approaches to tackle the continuous distribution of waste amounts are included by introducing fuzzy memberships or additional possibilities for waste storage in case of excess. Standard stochastic strategies are not suitable for large-scale problems. Therefore, a sampling-based method has been implemented in order to select only a sample of all possible scenarios at once. Robust optimization provides to the scheduler a worst case scenario on which he can relay his decisions. The system can be constrained depending on the risk the scheduler is willing to take, based on his experience and historical information.

Although the computational effort increases in some cases and the solutions are not as optimal as in the case of discrete parameter input, the operator of the incineration unit receives strategies to handle unexpected short-comings or possible problems during operation.

[1] Abächerli, M., Capón-García, E., Papadokonstantakis, S. and Hungerbühler, K. (2014). Natural Gas Reduction in Industrial Waste Incineration By Optimized Short-Term Scheduling, Industrial Applications in Design and Operations. Conference Proceedings of AIChE Annual Meeting, Atlanta, Georgia, USA.

[2] Poliakoff, M., Fitzpatrick, J. M., Farren, T. R., Anastas, P. T. (2002). Green Chemistry: Science and Politics of Change. Science, 296(5582), 807 - 810.

[3] BAFU. (2012). Sonderabfallstatistik: Federal Office of the Environment, Switzerland.

[4] Sahinidis, N. V. (2004). Optimization under uncertainty: State-of-the-art and opportunities, Computers Chemical Engineering, 28, 971 - 983.

[5] Bertsimas, D., Sim, M. (2004). The Price of Robustness. Operations Research, 52(1), 35 - 53.

[6] Chakraborty, A., Linniger, A. (2003). Plant-Wide Waste Management 2. Decision Making under Uncertainty, Ind. Eng. Chem. Res, 42, 357 - 369.

[7] Williams, P. T. (2005). Waste treatment and disposal (2nd ed.). Chichester : Wiley.

Towards a general pore connectivity index in hierarchically-organized zeolites by positron annihilation spectroscopy

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Recently, we established a direct correlation between pore connectivity in hierarchically-organized ZSM-5 zeolites, quantified by positron annihilation spectroscopy (PAS), and the catalyst lifetime in the conversion of methanol to hydrocarbons.¹ The unprecedented sensitivity of PAS stems from the fact that ortho-positronium (*o*-Ps) species, formed when positrons are implanted into a solid, are long-enough lived to diffuse through the pore structure and decay in free space (*o*-Ps_{free}). The total fraction of *o*-Ps_{free} relates to the global accessibility of the pore network, which presents the prospect of defining a general pore connectivity index for zeolite catalysts. However several aspects need to be addressed to construct such an index, concerning the quantitative dependence of *o*-Ps_{free} on different sample- (e.g., zeolite framework type and composition, acidic properties) and instrument- (type of set up, energy of implantation, etc.) related variables.

To tackle these issues, a two-fold approach of experimental and theoretical studies will be undertaken in conjunction with other characterization techniques (Fig.1). Model systems with selected crystallite size and composition will be considered and will form the basis to apply the technique to more complex samples, closer to real-life applications. Theoretical calculations of Ps trapping and annihilation within materials will aid the understanding of the interactions between Ps and the open volume size, and overall connectivity. The insights gained from the application of PAS thus far are unattainable by any other technique, highlighting its potential to join the suite of methods applied for the characterization of porous materials.

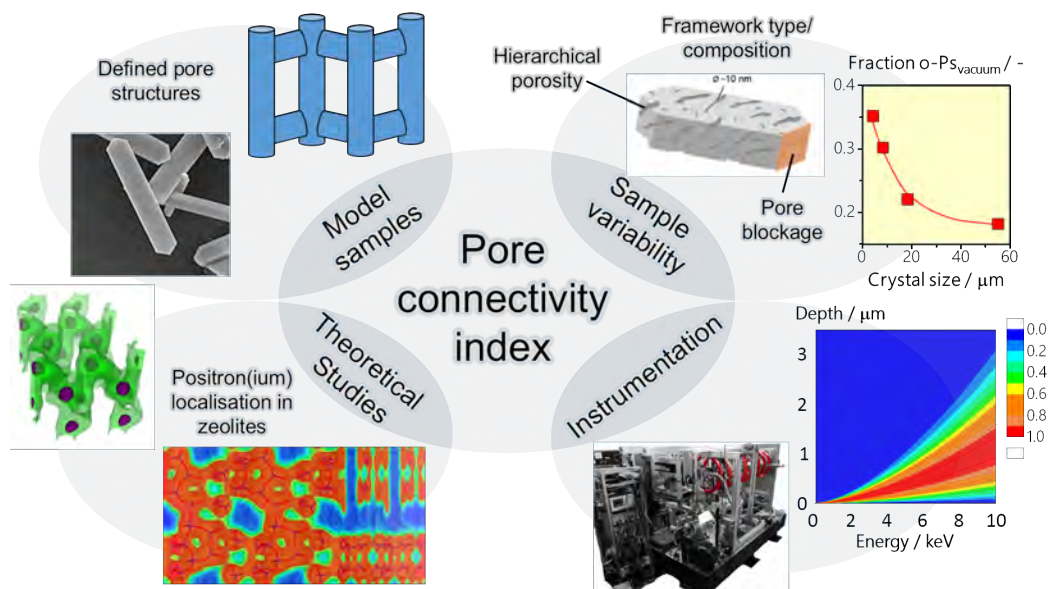


Figure 1. The combination of theory and experiments will allow to understand and develop a general pore connectivity index from PAS measurements.

[1] M. Milina, S. Mitchell, P. Crivelli, D. Cooke, J. Pérez-Ramírez, *Nat. Comm.* **2014**, 5, 3922; M. Milina, S. Mitchell, D. Cooke, P. Crivelli, J. Pérez-Ramírez, *Angew. Chem., Int. Ed.* **2015**, 54, 1591.

Integration of Hierarchical Waste Incineration Scheduling Levels for Improved Industrial Performance

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Chemical production sites provide a rich environment for the application of mathematical optimization. It has been shown that especially the planning and scheduling of operating tasks dealing with the production of chemicals and their downstream derivatives qualify for such applications in order to support decision making processes in the industry [4].

Such tasks can be e.g. the waste incineration management in industry. This is particularly interesting for companies in countries such as Switzerland, where most of the occurring industrial waste is being incinerated [2].

Previous works have shown that the performance of liquid waste incineration could be improved significantly by using mathematical optimization tools [1] and [3]. The introduced formulation allows either to schedule waste incineration at high resolution but over a very short time horizon [3] or at lower resolution considering a longer time horizon [1]. In order to efficiently support daily decision making processes in the industry, the resolution of the resulting schedules should be quite high and the horizon should be sufficiently large in order to obtain a far-sighted solution. Due to the nature of both available formulations, an expansion of the horizon in one case or the increase of the resolution in the other would come at a high computational cost. Therefore, the models have been adapted in order to combine them, such that in a first place a longer-term strategy based on waste production forecasts is defined and then a high resolution schedule based on the imposed strategy and actual waste availability data is created.

The hierarchical combination of waste incineration models for improved waste incineration scheduling has been tested in an industrial site in Switzerland. As the resulting detailed incineration schedules consider not only actual real-time information but also future forecasted events, extreme events, such as waste excesses or energy shortages, can therefore already be mitigated in advance. Even if these high resolution but also far-sighted schedules require a larger computational effort to be produced as those of each single model, the overall solution time is kept in the same order of magnitude. Therefore, the introduced hierarchical combination of different resolution and horizon levels proves to be more suitable for supporting operators in their daily decision making.

[1] Abächerli, M., Capón-García, E., Papadokonstantakis, S. and Hungerbühler, K. (2014). Natural Gas Reduction in Industrial Waste Incineration By Optimized Short-Term Scheduling, Industrial Applications in Design and Operations. Conference Proceedings of AIChE Annual Meeting, Atlanta, Georgia, USA.

[2] BAFU. (2012). Sonderabfallstatistik: Federal Office of the Environment, Switzerland.

[3] Santos, Daniel. "Mathematical optimization of real-time scheduling for industrial waste incineration." MA thesis, ETH Zürich, 2015.

[4] Wassick, J. M. (2009). Enterprise-wide optimization in an integrated chemical complex. Computers Chemical Engineering, 33(12), 1950 - 1963.

Cu Particle Size and Support Effect on CO₂ Hydrogenation to MeOH over Supported Cu Catalysts

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Methanol synthesis via direct hydrogenation of CO₂ is a key reaction, towards a future based on sustainability and responsible use of fossil materials. Numerous experimental and theoretical studies have been performed on Cu-based catalysts, especially Cu/ZnO/Al₂O₃ developed by ICI in 1960s. However the structure of active sites as well as size/morphology/oxidation state of Cu particles in Cu-based catalysts remains elusive. In this study, Cu nanoparticles on several metal oxides were prepared, and the effect of Cu particle size and support materials on CO₂ hydrogenation over Cu-based catalysts was investigated.

Using metal nitrate precursors, Cu/SiO₂, Cu/ZnO, Cu/ZrO₂, Cu/CeO₂, and Cu/TiO₂ were prepared by an incipient wetness impregnation (IWI) method. In addition, 7.8%Cu/SiO₂ was also prepared by grafting of [CuO^tBu]₄ on SiO₂, as described by Roussey et al. [1] Particle size of Cu on each catalyst was estimated from N₂O titration technique. [2] The catalytic performance for CO₂ hydrogenation was evaluated in a 9-mm I.D. tubular reactor. A mixture of 500 mg of catalyst powder and 5 g of SiC was placed in the reactor, and then reduced at 500 °C for 3 h in H₂/N₂ flow. The gaseous mixture (CO₂/H₂/N₂ = 2/6/2) was fed at a space velocity of 20 ml min⁻¹ g_{cat}⁻¹ at 25 bars. The gas composition at the reactor outlet was analyzed with a GC equipped with a TCD and a FID.

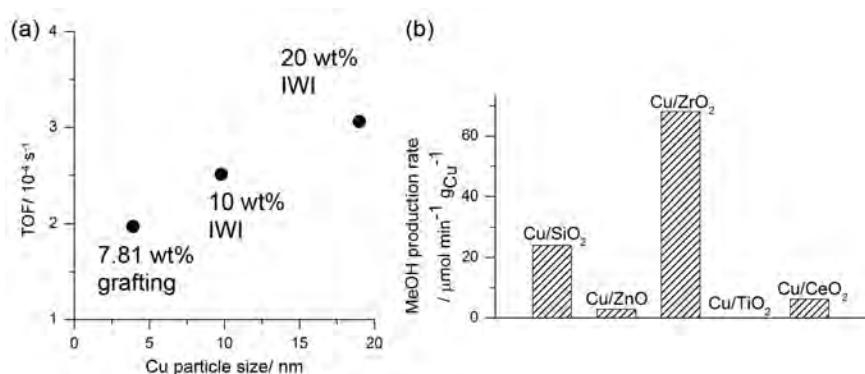


Figure 1. (a) Cu Particle size effect on TOF of MeOH production over Cu/SiO₂ catalysts prepared by IWI and grafting method. (b) Support material effect on MeOH production rate over 10wt%Cu/MO_x. Reaction temp: 230 °C.

Fig. 1 (a) shows the TOFs of MeOH production over Cu/SiO₂ increases with an increase in Cu particle size, consistent with the need of large faceted nanoparticles. Fig. (b) illustrates the MeOH production rate over 10wt%Cu/MO_x catalysts. The order of the rate was Cu/ZrO₂ > Cu/SiO₂ >> Cu/CeO₂ > Cu/ZnO > Cu/TiO₂. In addition, the yields of MeOH at 230 °C over Cu/SiO₂ and Cu/ZrO₂ were 9 and 35%, respectively. Thus, ZrO₂ is a suitable and promising support material for the title reaction.

[1] A. Roussey, P. Gentile, D. Lafond, E. Martinez, V. Jousseau, C. Thieuleux, C. Copéret, J. Mater. Chem. C 1 (2013) 1583.

[2] J.W. Evans, M.S. Wainwright, A.J. Bridgewater, D.J. Young, Appl. Catal. 7 (1983) 75.

Acknowledgements: This work was supported by SCCER Heat and Electricity Storage, Switzerland, and Japan Society for the Promotion of Science, Japan.

Why does the addition of Fe increase the activity and stability of Ni-based dry reforming catalysts: An in-situ XRD and XAS study.

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The dry reforming of methane, DRM ($\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$), is a promising process to convert two greenhouse gases into a synthesis gas (H_2/CO) that can be converted further to liquid fuels via Fischer-Tropsch synthesis [1]. Due to its comparatively low price (when compared to noble metals) and high activity, Ni-based catalysts are attractive for DRM. However, a serious drawback of monometallic Ni-based catalysts is deactivation due to sintering and coke formation. In this work, we have developed bimetallic Ni-Fe catalysts via a hydrotalcite-like precursor to embed effectively both Ni and Fe in a thermally stable and highly coke-resistant $\text{Mg}_x\text{Al}_y\text{O}_z$ -based matrix. The catalytic performance of monometallic Ni and Fe as well as Ni-Fe bimetallic catalyst was evaluated for dry reforming at 650 °C. We found that in particular, Ni_4Fe_1 (2.6 h^{-1} of TOF_{CH_4}) showed a high activity and stability, whereas deactivation and low catalytic activity was observed for monometallic Ni (1.8 h^{-1} of TOF_{CH_4}) and Fe (0.4 h^{-1} of TOF_{CH_4}) catalysts. Operando synchrotron XRD and XAS analysis supported by ex-situ characterization elucidates the effect of alloying, selective oxidation and de-alloying of Ni-Fe during reaction and allowed us to develop structure – performance relationships.

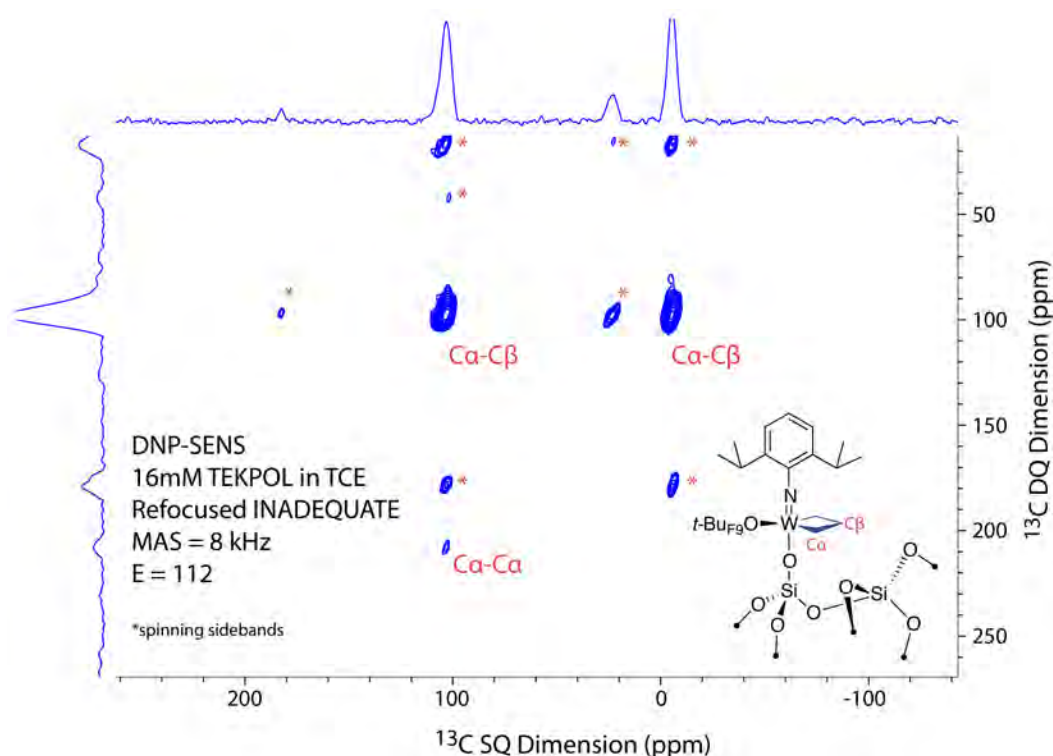
[1] S. Bhatia et al., ChemCatChem, 2009, 1, 192-208

Atomistic Description of Silica Supported (SiO)W(NAr)(=CHtBu)(OR) Catalysts Through DNP-SENS

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Metallacycle intermediates of tungsten and molybdenum based heterogeneous catalysts play a prominent role in alkene metathesis. They are however difficult to observe and characterize at a molecular level. We recently reported the solid-state NMR observation of ¹³C labeled trigonal bipyramidal (TBP) and square planar (SP) metallacycle intermediates of tungsten catalysts of the general formula (SiO)W(NAr)(=CHtBu)(X) (X = NR₂ and OR) and evaluated their catalytic activities.^{1,2} In this work, we present a detailed structural characterization of these metallacycle intermediates by dynamic nuclear polarization surface enhanced solid-state NMR (DNP-SENS). The signal enhancement gained from DNP makes feasible the acquisition of multi-dimensional NMR experiments that would otherwise be unreasonably time consuming, such as 2D dipolar or *J*-based ¹³C-¹³C correlation experiments. Notably, ¹³C-¹³C *J* couplings and chemical shift anisotropy (CSA) parameters could be measured for the two metallacycles. The results are in good agreement with density functional theory (DFT) calculations and provide new insights into the structures of these key intermediates of the metathesis catalytic cycle.



(1) Mougel, V.; Coperet, C. *Chem. Sci.* **2014**, 5, 2475.

(2) Blanc, F.; Berthoud, R.; Coperet, C.; Lesage, A.; Emsley, L.; Singh, R.; Kreickmann, T.; Schrock, R. R. *Proc. Natl. Acad. Sci. USA* **2008**, 105, 12123.

Design of mild base catalysts for the deoxygenation of bio-oil by aldol condensation

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Given the high aldehyde content of crude bio-oil, the integration of an intermediate catalytic deoxygenation *via* aldol condensation, presents a viable, cost-effective path to facilitate the sustainable production of bio-oils (Fig.1a). We have previously demonstrated the critical role of the strength of basic sites in attaining highly selective and stable catalysts.^{1,2} Herein, we report the development of MgO-based catalysts on high-silica zeolite supports in the self-condensation of propanal. Compared to bulk alkaline-earth metal oxides, it is shown that supported MgO catalysts reveal excellent stability (Fig.1b) owing to the fact that the concentration and strength of basic sites was reduced. Their deoxygenation performance is compared to previously optimized systems such as alkaline-activated zeolites and hydroxyapatites in the model reaction and under more realistic conditions with acetic acid-propanal mixtures (5-95%v/v). The supported MgO catalysts retain their stable and selective character, whereas the activity decreases by ca. 30% due to competitive adsorption of acetic acid (Fig.1c). Further catalytic insights are expected to provide representative indicators of the performance achievable with real bio-oil.

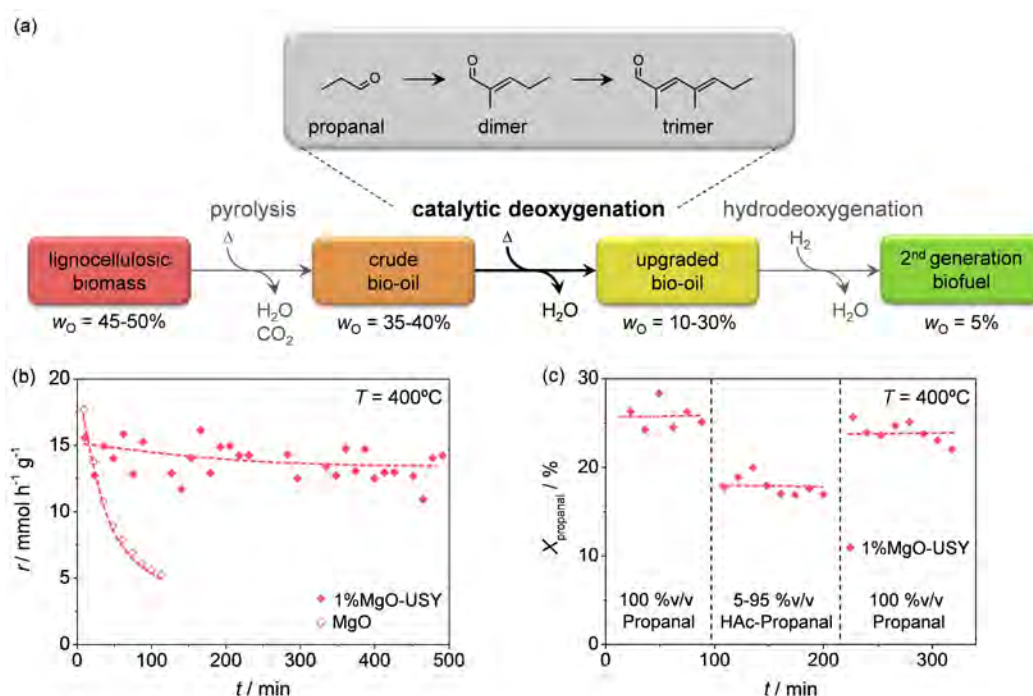


Figure 1. (a) Cascade concept for the production of second-generation biofuels. (b,c) Catalytic performance of representative catalysts.

1. T.C. Keller, E.G. Rodrigues, J. Pérez-Ramírez, *ChemSusChem* **2014**, 7, 1729.
2. E.G. Rodrigues, T.C. Keller, S. Mitchell, J. Pérez-Ramírez, *Green Chem.* **2014**, 16, 4870.br

Fast pyrolysis of lignin: Relating the Structure with Product selectivity

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Lignin pyrolysis is a simple and promising process to convert the complex and irregular structure of lignin into useful stock chemicals, while keeping some of the functionalities.¹ One drawback is the poor selectivity resulting from the high temperature and from the complex structure of lignin. Introducing a catalyst is one way to improve yield and selectivity in this process.² The other point of action is the structure of lignin: It varies by the source of biomass and also by the separation method. There are various studies comparing different lignin types³⁻⁵, but none studies exclusively the separation in correlation with pyrolysis.

This study compares lignins from the exact same bioresource (hard- and softwood) separated by the Klason-, Dioxane- and Organosolv method and commercial kraft lignin (softwood). The structural differences resulting from the chemical separation influence the pyrolysis yield and selectivity. Harsh conditions such as sulfuric acid treatment during the kraft process form many C-C bonds, which are first harder to break during pyrolysis and lead to more recombination. During milder separation conditions (Organosolv-, Klason-Process) more ether bonds stay intact, so that the temperature dependency in pyrolysis is more distinct.

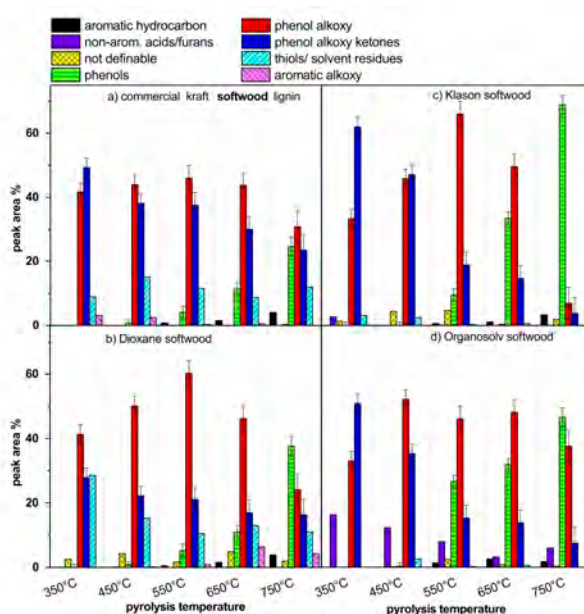


Figure 1. Product selectivity of different softwood lignin types during fast pyrolysis.

During catalytic fast pyrolysis of these lignins with USY Zeolites^{6,7} the presence of these ether bonds showed a distinct difference to the commercial lignin, as the conditions produced more phenols. These are just some of many other structural aspects, which influence the (catalytic) fast pyrolysis of lignin in terms of rate, yield and selectivity.

1. Brebu, M. Vasile, C. *Cellul. Chem. Technol.* **2010**, 44, 353
2. Ma, Z., Troussard, E. van Bokhoven, J. A. *Appl. Catal. A Gen.* **2012**, 423, 130
3. Faix, O. *Holzforschung* **1991**, 45, Suppl. 21
4. Evtuguin, D. V et al. *J. Agric. Food Chem.* **2001**, 49, 4252
5. Crestini, C., Melone, F., Sette, M. Saladino, R. *Biomacromolecules* **2011**, 12, 3928
6. Ma, Z., Custodis, V. van Bokhoven, J. A. *Catal. Sci. Technol.* **2014**, 4, 766
7. Ma, Z. van Bokhoven, J. A. *ChemCatChem* **2012**, 4, 2036

Novel catalysts for the oxybromination of methane

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The oxybromination of methane (OBM, Fig.1) is an attractive route for the selective functionalization of methane under mild conditions, which integrates the formation of methyl bromide (CH_3Br) with the regeneration of HBr stemming from the subsequent transformations of CH_3Br to chemicals.¹ We have identified a set of new metal phosphate- and oxide-based catalysts (VOPO_4 , CrPO_4 , $\text{Cu}_3(\text{PO}_4)_2$, and TiO_2) that show exceptional OBM activity. In particular, 82% selectivity to CH_3Br at 24% conversion of methane was achieved over VOPO_4 at 733K, with no detectable CO_2 formation and stable operation during 30h on-stream. Our ongoing research aims at further improving the CH_3Br yield. To this end, we study the mechanism of the complex reaction network comprising catalytic HBr oxidation, methane bromination, and CO_x formation reactions over different doped-, mixed-, and supported phosphate materials.

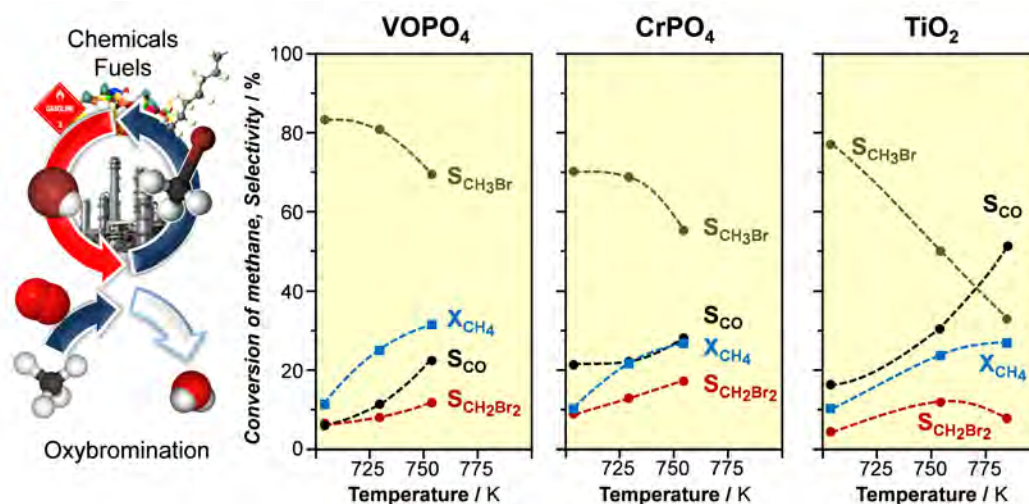


Figure1. Oxybromination of methane: General concept and catalytic performance of new materials.

[1] E. McFarland, *Science* **2012**, 338, 340; Y. Wang, J. He, T. Hu, Z. Wang, Q. Zhang, W. Deng, *Angew. Chem., Int. Ed.* **2012**, 51, 2438.

Encapsulated Polarizing Agents for Application in Dynamic Nuclear Polarization Surface Enhanced NMR Spectroscopy

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Nuclear magnetic resonance (NMR) spectroscopy is a powerful tool that provides insights to chemical structure at the molecular level. However, sensitivity has always been a weakness that limits the application of this technique, especially in solid-state chemistry. Dynamic nuclear polarization (DNP) is one promising method to enhance sensitivity in NMR experiments. To furnish a DNP NMR experiment, an exogenous single electron source, usually stable radicals, e.g. 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), is introduced in the sample of interest. [1] Nevertheless, radicals can be chemically reactive towards certain species.[2] In order to overcome this hurdle, a series of dendrimer-based encapsulated polarizing agents (PAs) were prepared. The dendrimers are constructed of apolar silicon-carbon bonds in order to decrease the interactions between the PA and polar surface, and methyl groups were avoided because of the fast electron spin relaxation they can generate.[3] The PAs were characterized by gel permeation chromatography (GPC) and electron paramagnetic resonance (EPR) spectroscopy. They showed no aggregation in solution and no significant interaction with activated solid surfaces, e.g. zinc oxide and alumina, and provide good DNP enhancement in DNP surface enhanced NMR spectroscopy (SENS) for a broad range of applications.[4]

[1] Rossini, A. J.; Zagdoun, A.; Lelli, M.; Lesage, A.; Copéret, C.; Emsley, L., *Acc. Chem. Res.* **2013**, *46*, 1942-1951.

[2] Samantaray, M. K.; Alauzun, J.; Gajan, D.; Kavitake, S.; Mehdi, A.; Veyre, L.; Lelli, M.; Lesage, A.; Emsley, L.; Copéret, C.; Thieuleux, C., *J. Am. Chem. Soc.* **2013**, *135*, 3193-3199.

[3] Zagdoun, A.; Rossini, A. J.; Conley, M. P.; Grüning, W. R.; Schwarzwälder, M.; Lelli, M.; Franks, W. T.; Oschkinat, H.; Copéret, C.; Emsley, L.; Lesage, A., *Angew. Chem. Int. Ed.* **2013**, *52*, 1222-1225.

[4] (a) Jakes, P.; Erdem, E., *Phys. Status Solidi PRL* **2011**, *5*, 56-58; (b) Wischert, R.; Laurent, P.; Copéret, C.; Delbecq, F.; Sautet, P., *J. Am. Chem. Soc.* **2012**, *134*, 14430-14449.

Opportunities of catalysis for tuning selectivity during lignin catalytic fast pyrolysis

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Lignin is the key component for biomass utilization. Conversion of lignin into renewable and value-added chemicals by thermal processes, especially pyrolysis, receives great attention. The products may serve as feedstock for chemicals and fuels and contribute to the development of a sustainable society. However, the application of this progress is limited by the low selectivity to the desired products. The opportunities of catalysis for tuning the selectivity of catalytic fast pyrolysis of lignin by using specific catalysts, such as zeolites, transition metal oxides, and supported transition metals, will be discussed. The objective is to demonstrate the possibility of controlling the selectivity to specific valuable products and to give an overview of catalytic fast pyrolysis of lignin over different catalysts, and furthermore, to gain insight into the chemistry of lignin non-catalytic/catalytic fast pyrolysis.

[1] Zhiqiang Ma, Victoria Custodis, Jeroen A. van Bokhoven, *Catalysis Science Technology*, **2014**, 4, 766-772.

[2] Zhiqiang Ma, Ekaterina Troussard, Jeroen A. van Bokhoven, *Applied Catalysis A: General*, **2012**, 423-424, 130-136.

[3] Joseph Zakzeski, Pieter Bruijnincx, Anna Jongerius, Bert Weckhuysen, *Chemical Reviews*, **2010**, 110, 3552-3559.

Electrocatalytic water oxidation with $\text{Co}_{1-x}\text{M}_x\text{NCN}$ metal carbodiimides

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Cobalt carbodiimide (CoNCN) has recently been introduced as catalyst prototype for both visible-light-driven and electrocatalytic water oxidation.^[1] The well-defined all-nitrogen coordination environment of metal carbodiimide catalysts is a highly active and stable model system that permits mechanistic insights into the complex multiparameter challenge of targeted water oxidation catalyst construction. This simple but versatile new system for fundamental electrocatalytic studies of structure-activity relationships, catalytic mechanisms and surface effects offers clear-cut tuning options through modification of the carbodiimide matrix through substitution of cobalt by transition group metals.

Binary substitution derivatives ($\text{Co}_{1-x}\text{M}_x\text{NCN}$) of this new class of non-oxidic water oxidation catalysts are currently prepared for electrochemically assessing the influence of metal composition on the electrocatalytic activity. Carbodiimide materials performances are compared to those already known for metal oxides of similar composition to evaluate the difference in the catalytic reactivity patterns.

Electrocatalytic properties, such as activity, electrochemically active surface area (EASA), long-term stability, and overpotential are investigated by cyclic and linear voltammetry, Tafel- and EASA-analysis, as well as chronoamperometry in combination with oxygen quantification by Clark-electrode, gas chromatography and fluorescence quenching. Special emphasis is directed to the normalization of obtained current densities to the active surface area of the electrodes, which varies with the method of catalyst immobilization.

[1] D. Ressnig, M. Shalom, J. Patscheider, R. Moré, F. Evangelisti, M. Antonietti and G. R. Patzke, *J. Mater. Chem. A*, **2015**, 3, 5072-5082.

Approaches towards heterogenization of Ru(II) half-sandwich catalysts for asymmetric hydrogenation

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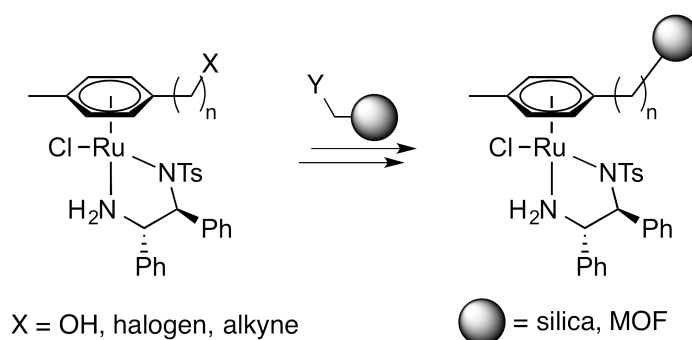
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The [Ru(II)Cl(η^6 -arene)(*N*-arylsulfonyl-DPEN)] (DPEN = 1,2-diphenylethylene-1,2-diamine) catalyst class is well established in the asymmetric hydrogenation of imines and ketones using transfer hydrogen donor.[1] These homogeneous catalysts have many advantages, such as selectivity, scope, and modularity, however, they cannot be easily recycled. It is therefore highly attractive to heterogenize them to increase their utility in the fine chemical industry.

We describe different approaches towards heterogenization of these catalysts onto solid supports. Many examples already exist, where the catalyst has been heterogenized using the DPEN ligand or its analogue.[2] This is synthetically convenient, but the main disadvantage is that the ligand is fixed to the support and hence cannot be easily replaced with another one, hampering screening structural analogues. Alternatively, the catalyst can be anchored via the η^6 -arene. This way, the ligand is freely exchangeable and screening ligand libraries becomes possible.

This project focuses on the synthesis of complexes bearing functional groups X (X = hydroxyl, halogen and terminal alkyne groups), which allow for the heterogenization by using nucleophilic substitution respectively click reactions. The selection of the functional group largely depends on the support, notably its chemical stability towards given reaction conditions. We turned our attention to mesoporous silica, which is stable, cheap, and readily available and metal-organic frameworks (MOFs), which are highly versatile, and tunable. Both materials types can be functionalized with the following groups: -NH₂, -N₃, -halogen, and -hydroxyl.

The catalysts and solid supports were prepared and fully characterized. The functionalized homogeneous catalysts were tested in asymmetric hydrogenation of a cyclic imine (6,7-dimethoxy-1-methyl-3,4-dihydroisoquinoline) and the activity and enantioselectivity were comparable with the original commercially available benchmark catalyst [RuCl(η^6 -*p*-cymene)TsDPEN]. This proves that the synthesized complexes can be used for the design and synthesis of heterogeneous catalysts by utilizing the functional group present on the η^6 -arene since the functionality does not interfere with the catalytic transformation. Testing of the heterogenization protocol is currently underway.



[1] N. Uematsu, A. Fujii, S. Hashiguchi, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1996**, *118*, 4916–4917.

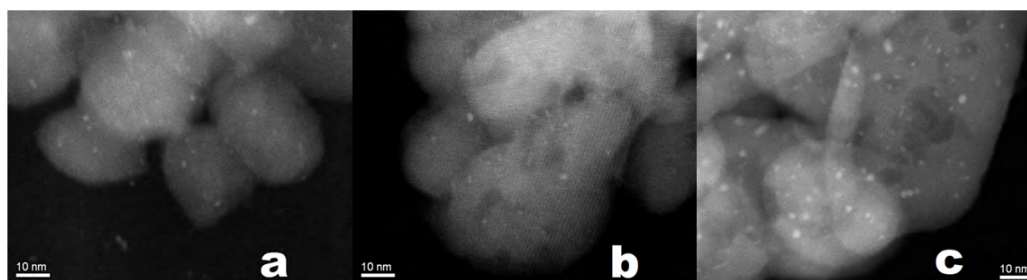
[2] J. Václavík, P. Kačer, M. Kuzma, L. Červený, *Molecules* **2011**, *16*, 5460–5495.

Hierarchical Pd/ZSM-5 catalysts for methane oxidation in the presence of steam

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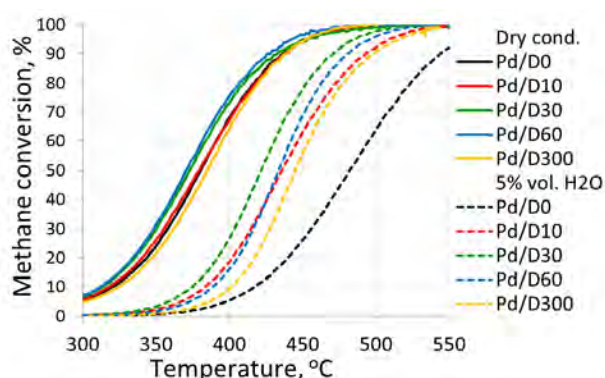
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Catalytic methane oxidation is applied in exhaust gas treatment to reduce unburnt methane emissions in stationary combustion processes as well as in natural gas vehicles to mitigate the severe greenhouse effect of methane [1]. Pd/zeolite catalysts are reported to provide higher activity than the commonly used Al_2O_3 , but suffer from rapid deactivation under reaction conditions in the presence of steam, due to sintering and formation of inactive $\text{Pd}(\text{OH})_2$ [2,3]. In this work a novel approach is proposed with the aim to inhibit sintering of Pd particles dispersed on zeolite support. Small Pd clusters are stabilized within constricted mesopores of ZSM-5 obtained by desilication with NaOH in the presence of tetrapropylammonium bromide. STEM images of Pd on conventional ZSM-5 (D0, Fig. 1a), and Pd on desilicated ZSM-5 (D30, Fig. 1b and D300, Fig. 1c) catalysts reveal constricted mesopores in D30 and D300 (dark areas in the ZSM-5 crystallite). Some Pd nanoparticles in D30 and D300 samples are located within these constricted mesopores.



As shown in Fig. 2, the catalytic activity of Pd on parent (D0) and desilicated (D10-D300) zeolites was very similar under dry conditions. However, in the presence of water vapour desilicated zeolites had 50-70°C lower light-off temperature compared to the parent zeolite.

The reason for better performance of desilicated samples compared to the parent one is the subject of further studies. Increased activity could be explained through inhibited sintering of Pd located within the constricted mesopores.



[1] P. Gelin, M. Primet, *Appl Catal B.*, **2002**, 39(1), 1-37.

[2] Y. Li, J.N. Armor, *Appl. Catal B Environmental*, **1994**, 3, 275-282.

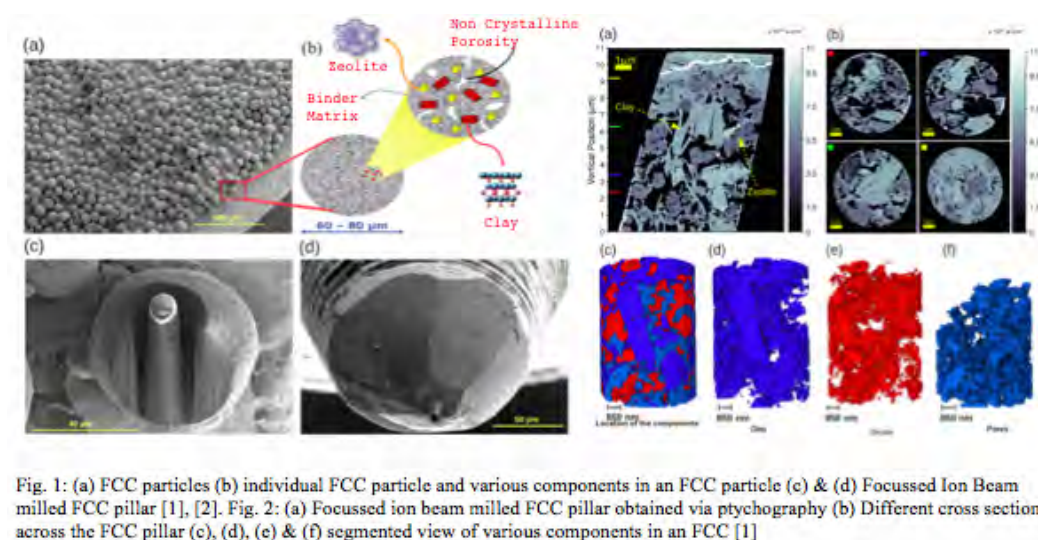
[3] C.F. Cullis, T.G. Nevell, D.L. Trimm, *J. Chem. Soc., Faraday Trans.*, **1972**, 1(1), 1406.

Structural analysis of individual Fluid Catalytic Cracking catalyst particle studied by synchrotron-based ptychographic X ray-computed tomography

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A synchrotron-based ptychographic X ray-computed tomography has been conducted to determine the structure of an individual fluid catalytic cracking (FCC) catalyst particle. FCC catalysts are composite particles containing zeolite crystals, amorphous silica alumina, clay binder as main components (Figs. 12). The interparticle porosity is essential for reactants and products to diffuse in, out, and through the FCC particle. Our ptychographic tomography enabled [1] for the first time to quantify porosity and location of zeolite and clay binder within a single FCC particle at a spatial resolution of 35 nanometer. The combination with three-dimensional analysis in the electron microscope, which is able to analyze the individual zeolite and clay particles, provides insight into the FCC particle at all relevant length scales. Changes in structure and porosity in a deactivated FCC particle are observed.



[1] J.C. da Silva et al., *ChemCatChem* **2015**, 7, 413-416.

[2] Perego and Millini *Chem. Soc. Rev.*, **2013**, 42, 3956

Exploring the self-regenerating function of perovskite-type oxides on catalytically active nickel

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Catalysts containing metallic nickel are used in many medium to high temperature industrial applications for heterogeneous catalysis. Nickel is used due to its reasonable activity and its relatively low cost. However, current catalysts with high Ni loadings may undergo microstructural changes like particle growth, as well as degradation due to carbon deposition [1] and deactivation by sulfur species [2]. All these processes seriously affect the catalyst stability. Incorporating the catalytically active Ni in a perovskite-type oxide (general formula: ABO_3) potentially allows to target these drawbacks. Upon reduction at elevated temperatures nickel is expected to reduce and segregate out of the perovskite lattice forming highly dispersed metallic Ni particles on the surface. The reversibility of this process upon re-oxidation [3, 4] and during reaction [5] has already been shown for Pd, Pt and Rh- containing perovskite-type oxides for automotive applications. This process may allow the regeneration of catalysts which have suffered from the above mentioned problems by oxidizing deposited coke and sulfur while the active metal dissolves in the perovskite matrix. Re-dispersing the active phase on the surface upon reduction is the beneficial consequence. The aim of the current study is to show similar microstructural reversibility of nickel segregation on three perovskite-type oxides ($LaFeO_3$ and $LaCoO_3$ as well as co-doped $La_{0.2}Sr_{0.7}TiO_3$) for applications in CO and CO_2 hydrogenation and water gas shift catalysis in solid oxide fuel cells, respectively. Structural and chemical information on the materials was obtained by means of XRD, XANES, TPR and SEM. Incorporated Ni can be differentiated from surface NiO species on the samples. Results indicate that nickel can be successfully incorporated in the perovskite-oxide lattice. Phase pure samples were obtained after calcination at 700°C (in the case of $LaFeO_3$ and $LaCoO_3$) and 1200°C ($La_{0.2}Sr_{0.7}TiO_3$). The principle of structural reversibility during reduction and re-oxidation cycles is demonstrated at lower temperatures.

[1] C. H. Bartholomew, Catalysis Reviews-Science and Engineering, **1982**, 24, 67-112.

[2] P. Forzatti and L. Lietti, Catalysis Today, **1999**, 52, 165-181.

[3] H. Tanaka, M. Uenishi, M. Taniguchi, I. Tan, K. Narita, M. Kimura, K. Kaneko, Y. Nishihata, and J. Mizuki, Catalysis Today, **2006**, 117, 321-328.

[4] Y. Nishihata, J. Mizuki, T. Akao, H. Tanaka, M. Uenishi, M. Kimura, T. Okamoto, and N. Hamada, Nature, **2002**, 418, 164-167.

[5] A. Eyssler, E. Kleymentov, A. Kupferschmid, M. Nachtegaal, M. S. Kumar, P. Hug, A. Weidenkaff, and D. Ferri, Journal of Physical Chemistry C, **2011**, 115, 1231-1239.

Time-resolved measurements of the terahertz conductivity in noble metal-on-TiO₂ nanoparticles for photocatalytic applications

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As the sun is the ultimate source of renewable energy, the approaches to capture and to store sunlight are manifold. Thereof, photocatalytic water splitting is particularly appealing since water as a feedstock is ubiquitous, and the produced H₂ gas may directly serve as an environmentally unproblematic fuel.

Nanoparticles of wide band-gap semiconductors, namely TiO₂, have been demonstrated to be active in water splitting under ultraviolet irradiation. The photocatalytic activity is increased when a small amount of noble metal nanoparticles is added since they promote the hydrogen half reaction, a process that requires free electrons.

Using time-resolved terahertz spectroscopy, we investigated the photoconductivity, which is a direct measure for the free carrier density, in several noble metal-on-TiO₂ nanoparticles. The photoconductivity was clearly larger than in pure TiO₂ nanoparticles; however, the differences between different metals or combination of metals are smaller than their differences in catalytic activity.

Dual-phase Zn-modified ceria nanocrystals: establishing a correlation between the structural characteristics, oxygen storage capacities and catalytic activitiesF. Lin¹, R. Delmelle², T. Vinodkumar³, B. Reddy³, A. Wokaun¹, I. Alxneit¹¹Paul Scherrer Institute, Villigen, ²EMPA, Swiss Federal Laboratories for Materials Science and Technology, ³IICT, India

Materials based on ceria (CeO_2) have been intensively studied for a wide range of applications. Notable examples include their use as efficient three-way catalysts for the abatement of harmful exhausts for automobile engines. Doping ceria with heterocations is a commonly applied strategy to alter its structural and chemical properties including its key feature oxygen storage capacity (OSC), which is very important to many catalytic reactions. First-principles calculations have shown that the enhancement of the OSC of ceria is closely related to structural modification of the ceria lattice by the dopants.^[1-3] By incorporating divalent ions such as Zn^{2+} , structural distortion to the ceria lattice is induced, creating weakly- or under-coordinated oxygen ions that are more easily removed than in pure CeO_2 .^[2] Therefore the oxygen vacancy formation energy of ceria is significantly reduced. Ahn et al. also show that lattice distortion caused by the incorporation of multivalent praseodymium increases oxygen vacancy defects and thus enhances the mobility of oxygen ions, leading to a higher OSC than pure CeO_2 .^[3] These computational studies clearly reveal a link between the structural properties of doped ceria and its chemical reactivity.

Although the structural properties and chemical reactivity of Zn-doped ceria have been reported in literature, one lacks a comprehensive investigation on the effect of zinc incorporation in the ceria lattice on its structural properties, and how it could be correlated to the changes in its chemical reactivity including OSC and catalytic activities. We will show in this poster an interesting correlation between the structural properties of dual-phase Zn-modified ceria nanocrystals, their OSCs, and their catalytic performance for the reverse water-gas shift (RWGS) reaction for CO_2 -to- CO conversion and soot oxidation, both of which are of significant environmental importance. We will show that the incorporation of zinc increases the reducibility of ceria and doubles its OSC. Moreover, this incorporation decreases the crystallinity of ceria nanocrystals, increase the oxygen vacancy concentrations, and enhances the OSC. The RWGS performance is significantly enhanced by doping with zinc, especially at 400 and 600 °C, which is attributed to its enhanced OSC. We will also present a type of composite materials based on Zn-modified ceria that is deactivation-resistant for the RWGS reaction at even higher temperatures (i.e. 800 °C). The soot oxidation activity is also enhanced marginally. In addition, the effect of the second phase, namely the un-incorporated X-ray amorphous ZnO (normally non-detectable by stand XRD),^[4] on the catalytic activity, unknown to many previous studies, will be also presented.

[1] A. Gupta, U. V. Waghmare and M. S. Hegde, Chem. Mater., **2010**, 22, 5184–5198.

[2] A. B. Kehoe, D. O. Scanlon and G. W. Watson, Chem. Mater., **2011**, 23, 4464–4468.

[3] K. Ahn, D. S. Yoo, D. H. Prasad, H.-W. Lee, Y.-C. Chung and J.-H. Lee, Chem. Mater., **2012**, 24, 4261–4267.

[4] F. Lin, I. Alxneit and A. Wokaun, CrystEngComm, **2015**, 17, 1646–1653.

From mechanism to catalyst design: Highly active formic acid decomposition catalysts under SCR-relevant conditions

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Selective catalytic reduction using ammonia is one of the most successful technologies for reducing NO_x emissions from automobile exhausts to harmless nitrogen. Despite the widespread implementation of urea as the ammonia precursor compound in automobiles, there is much interest in replacing this compound with alternative ammonia precursors, such as concentrated guanidinium formate, ammonium formate (AmFo) and methanamide solutions, which are more thermally stable, freeze at lower temperatures, have higher ammonia storage capacities, and decompose more selectively.^{1,2} In this context, AmFo is experimentally the simplest choice compound to study the catalytic activity because it contains all the main structural features, which influence the activity and selectivity with respect to ammonia release and side product formation under realistic conditions.³ Since AmFo thermolyzes into ammonia and formic acid, fast decomposition of the formate ion is needed as it can be expected that the anionic moiety is destabilized without being available to form side products like methanamide and hydrogen cyanide.

Au/TiO₂ is a highly active and uniquely selective catalyst for AmFo decomposition without ammonia oxidation.⁴ Excess ammonia in the gas phase resulted in enhanced activities.³ This work demonstrates how such an accelerated gas-phase activity can be translated into a rationally designed heterogeneous catalyst, by modifying the support with the basic additive, lanthanum. Additionally, we confirmed the validity of our concept by acid-modification with tungsten. The lanthanum-modification of titania affects both the particle-size and the support-basicity. Enhanced rates accompanied by a selective increase in carbon dioxide production were observed over the lanthanum-modified catalysts (Fig. 1). It is speculated that new sites that selectively decompose formic acid to carbon dioxide form upon base-modification. Tungsten-modification led to the lowest rates and an unfavorable increase in carbon monoxide production. These results are important for the development of catalysts for the efficient and selective decomposition of formate-based ammonia precursor compounds in the SCR process.

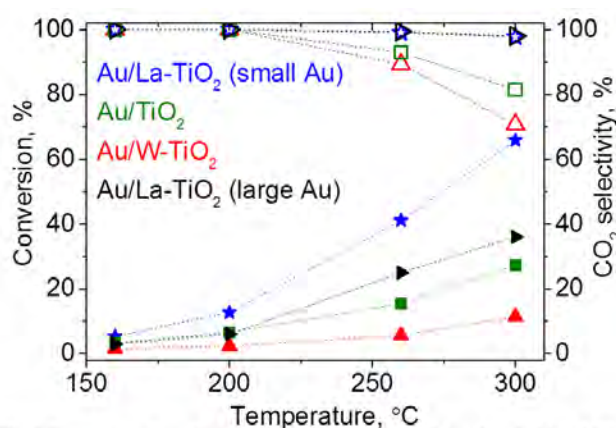


Fig. 1 Temperature dependence of formic acid conversion (closed symbols) and CO₂ selectivity (open symbols) obtained over Au/TiO₂, Au/W-TiO₂, Au/La-TiO₂ (small Au) and Au/La-TiO₂ (large Au) catalysts using formic acid at W/F = 2.4*10⁻⁵ g.s.cm⁻³.

[1] T. V Johnson, *Int. J. Engine Res.*, **2009**, 10, 275-285.

[2] O. Kröcher and D. Peitz, WO2012104205A1, **2012**.

[3] M. Sridhar, J.A. van Bokhoven, O. Kröcher, *Appl. Catal. A Gen.*, **2014**, 486, 219-229.

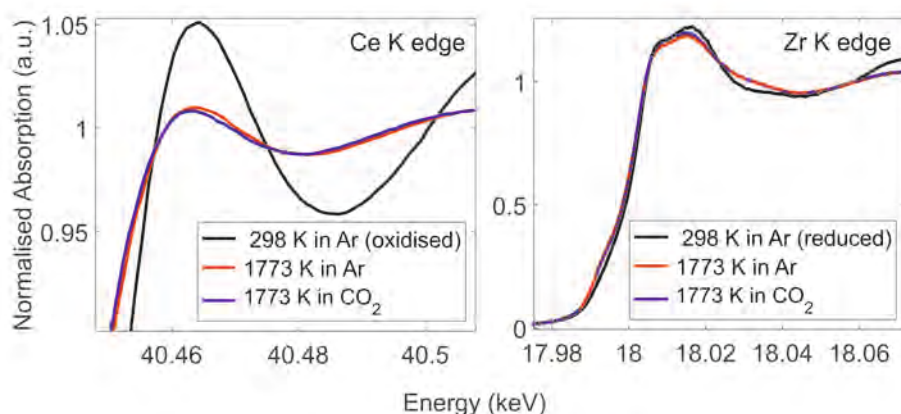
[4] M. Sridhar, D. Peitz, J. van Bokhoven, O. Kröcher, *Chem. Commun.*, **2014**, 50, 6998-7000.

In situ X-ray Absorption Spectroscopy of $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_{2-d}$ at 1773 K

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An in situ cell for XAS experiments in transmission mode was developed to determine the local electronic and geometric structure of materials at temperatures up to 1773 K in reactive environments. The cell enables to mimic the extreme conditions of a solar thermochemical looping reactor for the dissociation of water or carbon dioxide in a two-step redox cycle [1].



Absorption spectra were recorded at the Ce K and Zr K-edges at temperatures up to 1773 K. The sample was exposed to reducing and oxidizing conditions by flushing the cell with argon and carbon dioxide, respectively. While EXAFS is limited to lower temperatures, XANES analysis reveals spectral features related to temperature effects and changes in total absorption and provides clear evidence of structural changes.

[1] Abanades, S. Flamant, G. Thermochemical hydrogen production from a two-step solar-driven water-splitting cycle based on cerium oxides. *Sol. Energy* **80**, 1611–1623 (2006).

Investigating the influence of CO and ceria on CH₄ abatement on Pd-based TWC using modulation excitation spectroscopy

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Natural gas, which is mostly composed of CH₄, is receiving renewed interest as clean alternative fuel to gasoline and diesel. Despite the numerous advantages of natural gas, unburned CH₄ is a potent greenhouse gas; therefore, catalytic after-treatment of the exhaust gases is necessary to reduce its emission. Typically, Pd-based three-way catalysts (TWC) of similar composition to those used for stoichiometric gasoline engines are employed. Only few studies¹⁻² have addressed the mechanistic details of CH₄ abatement on TWC, which is CH₄ oxidation in oscillating conditions and in presence of other pollutants, such as CO and NO_x.

The aim of this study is to describe the role of CeO₂ and influence of CO on CH₄ oxidation under pulsed reaction conditions simulating the operation of a TWC. For this purpose different spectroscopic methods are combined in a single cell, specifically conceived for operando experiments³. Identical experiments were performed by X-ray absorption spectroscopy (XAS) at Pd K-edge, resonant X-ray emission spectroscopy (R-XES) at Ce L₃-edge and diffuse reflectance IR spectroscopy (DRIFTS). Modulation excitation spectroscopy (MES) and phase sensitive detection (PSD) were exploited to enhance the sensitivity towards subtle structural changes. Modulation experiments consisting of the periodic switch between 0.25 vol% CH₄/1 vol% CO (or 0.25 vol% CH₄) and 1 vol% O₂ were performed on 1.6 wt.% Pd/Al₂O₃ (PdA) and 1.6 wt.% Pd/CeO₂-ZrO₂/Al₂O₃ (PdACZ) at 320°C while synchronously collecting time-resolved spectra.

The Pd K-edge XAS results show that Pd is partially oxidized in the O₂ pulse and completely reduced in the subsequent rich pulse. Pd reduction is always faster than its re-oxidation. R-XES was used to explicitly follow the oxidation state of the O₂ storage component. During the rich pulse Ce⁴⁺ is slowly reduced while the rate of Pd reduction is decreased and the catalytic activity is sustained. Initially, CH₄ oxidation and CO₂ production are observed; when Pd is completely reduced and the threshold of Ce⁴⁺ reduction has been attained, CH₄ decomposition takes place producing H₂. While transient formate species are observed on PdA by DRIFTS, carbonate and formate species dominate in presence of ceria. CO in the feed inhibits CH₄ oxidation likely by the instantaneous CO adsorption and Pd reduction. Consequently, CH₄ decomposition is accompanied by the water gas shift reaction in the rich pulse. Despite its rapid reduction by CO, ceria is still able to mitigate the Pd reduction simultaneously ensuring higher CH₄ conversion than on PdA. On PdACZ, the extent of Pd oxidation is clearly enhanced by Ce while CO₂ production protracts into the O₂ pulse.

The present study should contribute shading light on the elementary steps of the complex reaction network involved in the three-way catalysis of CH₄ abatement in order to support ongoing catalyst development.

[1] Fouladvand, S., Skoglundh, M., Carlsson, P.A., *Catal. Scie. Tech.*, **2014**, 4, 3463. Becker, E., Carlsson, P. A., Khyllhammar, L., Newton, M. A., Skoglundh, M., *JPCA*, **2011**, 115, 944.

[2] Bounechada, D., Groppi, G., Forzatti, P., Kallinen, K., Kinnunen, T., *Appl. Catal. B*, **2012**, 119, 91.

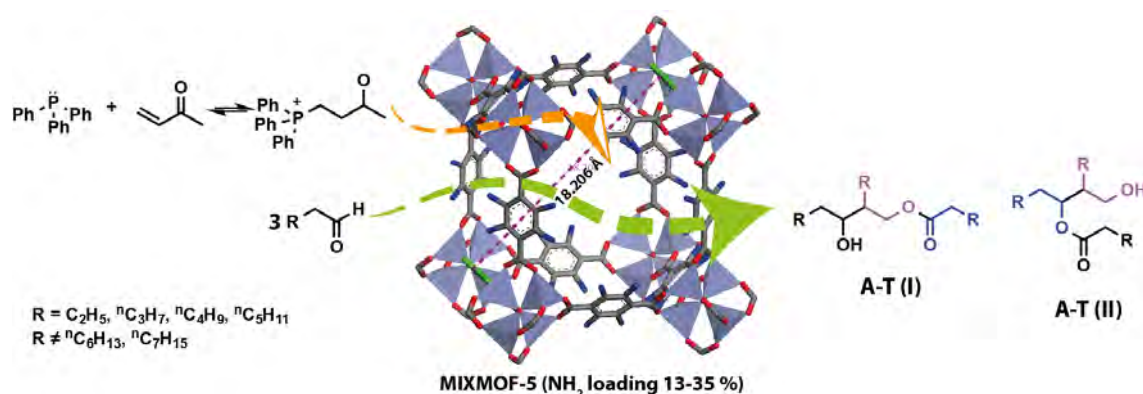
[3] G. L. Chiarello, M. Nachtegaal, V. Marchionni, L. Quaroni, and D. Ferri. *Rev. Sci. Instr.*, **2014**, 85, 074102.

Tuning reactant selectivity in the direct aldol-Tishchenko reaction using space constraints in multifunctional MOFs

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Metal-organic frameworks (MOFs) possess high surface area, relatively good thermal stability and large pores, which make them good materials for catalysis.^[1] Aldol-Tishchenko (**A-T**) is an over 100-years-old organic reaction, which has been widely used for the synthesis of 1,3-diol monoester from enolizable aldehydes and ketones.^[2] Triphenylphosphine (PPh₃) is a Lewis-base organocatalyst, which is widely used for organic synthesis such as [3+2] and [4+2] cycloaddition, coumarin synthesis, Umpolung addition, and Marita-Baylis-Hillman reaction.^[3] We describe herein the first successful catalysis of PPh₃ together with amino-containing MIXMOFs for the reaction of linear aldehydes to give the **A-T** product (Figure). Neither PPh₃ nor amino MOF catalyzes the **A-T** reaction.



The catalytic systems of PPh₃ and MIXMOFs-NH₂ (feature topology of MOF-5, UMCM-1) were added in the **A-T** reaction, which is the self-trimerization of linear aldehydes. The reaction yielded 62 % conversion and 86 % selectivity when pentanal was the starting reactant in the presence of MIXMOF-5-NH₂ (13 %). The **A-T** reaction only occurs when amino density in MIXMOFs is in the range between 13 and 35 % for MOF-5 topology and 34 and 100 % for UMCM-1 topology. The amino group likely plays a role as hydrogen donor for the intermediates and only a specific distance between two non-adjacent amino groups within a pore or cage enables chelating the intermediates. The confined space in the cages of the MOFs and unique topology that behave like an enzymatic catalyst allow this unique catalytic behavior to occur.

This finding encourages research towards designing highly selective and effective catalysis via introducing known structured heterogeneous solid porous frameworks to tune the reactivity and selectivity of catalysis via functional groups and confined space.

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

[2] R. Mahrwald, *The Aldol - Tishchenko Reaction*, Wiley, **2004**, 327-344.

[3] J. L. Methot, W.R. Roush, *Adv. Synth. Catal.* **2004**, 346, 1035-1050.

Synthesis of hollow ZSM-5 nano-reactors containing copper-metal oxide nanoparticles

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Metal nanoparticles are the catalytic work horses in industrial fuels and chemicals production and in environmental applications due to their superior activity compared to bulk materials. Nanoparticles often suffer from agglomeration, which results in the drop of catalytic activity.[1] The design of stable and highly active catalysts has thus become a topic of great interests. Nano-reactors, where active catalytic centers are confined within a nano-cage, are promising candidates for such purposes.[2] Here we present the zeolite nano-reactor composed of hollow ZSM-5 nano-cage and CuM alloy nano-particles (M=Zn, Zr, Ce etc.) deposited inside the cavity (Figure 1).[3] Copper and reducible metal oxide alloys are predominantly introduced in the hollow cavity of zeolite by conventional wet impregnation. The materials maintain high surface area and porosity. The separation of highly dispersed nano-particles will likely to excellent activity and durability toward further catalytic applications of nano-materials.

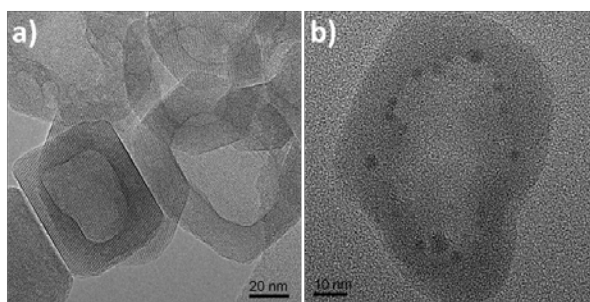


Figure 1. Transmission electron microscope images of a) hollow ZSM-5, and b) hollow ZSM-5 containing copper nano-particles inside its cavity.

[1] a) T. W. Hansen, A. T. DeLaRiva, S. R. Challa, A. K. Datye, *Acc. Chem. Res.* **2013**, *46*, 1720; b) Q. Xu, K. C. Kharas, B. J. Croley, A. K. Datye, *ChemCatChem* **2011**, *3*, 1014.

[2] a) J. Lee, J. C. Park, H. Song, *Adv. Mater.* **2008**, *20*, 1523; b) Y. Yin, R. M. Rioux, C. K. Erdonmez, S. Hughes, G. A. Somorjai, A. P. Alivisatos, *Science* **2004**, *304*, 711.

[3] a) D. Fodor, L. Pacosova, F. Krumeich and J. A. van Bokhoven, *Chem. Commun.* **2014**, *50*, 76; b) D. Fodor, T. Ishikawa, F. Krumeich and J. A. van Bokhoven, *Adv. Mater.* **2015**, *27*, 1919; c) D., Fodor, F. Krumeich, R. Hauert, J. A. van Bokhoven, *Chem. Eur. J.* **2015**, *21*, 6272.

Engineering Streptavidin as Scaffold for the Design of Artificial Metalloenzymes

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To combine the advantages of enzymes and of homogeneous catalysts artificial metalloenzymes (ArMs) have gained attention in the last decade.^[1] Artificial metalloenzymes result from anchoring an organometallic cofactor within a host protein. In this context, the biotin-streptavidin technology has proven extremely versatile, thanks to the high affinity of biotinylated moieties for either avidin or streptavidin (Sav hereafter).^[2,3] Chemo-genetic optimization strategies have allowed to optimize both the first- and the second coordination sphere around the metal cofactor. This has led to significant rate and selectivity improvements for a variety of ArMs-catalyzed transformations. One main bottleneck to screen large Sav libraries has been the necessary purification of each mutant prior to catalysis. Herein we present a general ArMs screening protocol in 24 deep well plates using optimized autoinduction media. Twenty-eight positions were selected around the biotin binding pocket and 12 amino acids were introduced at each position yielding 336 Sav mutants. Two rapid screening strategies will be presented, alleviating the need to purify the libraries prior to screening.

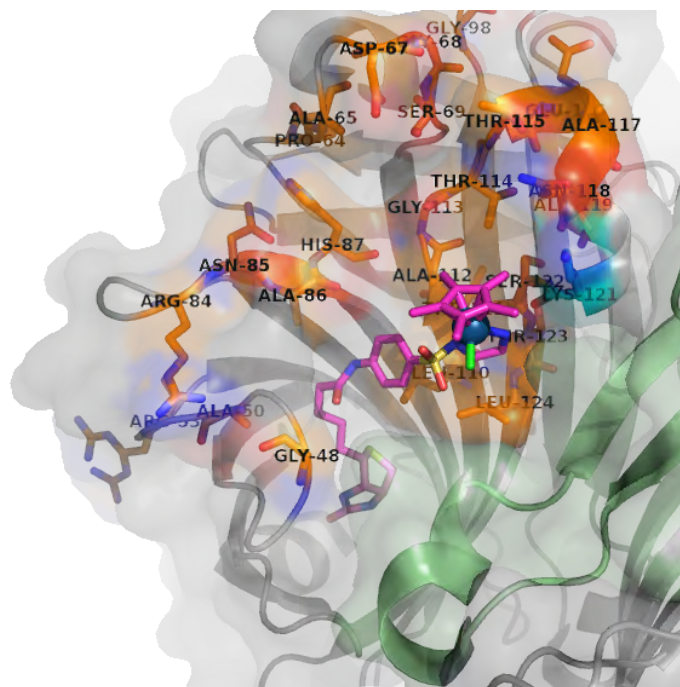


Figure 1: X-ray structure of an artificial transfer hydrogenase based on the biotin-streptavidin technology (pdb: 3PK2)^[3] The biotinylated Ir-Cp* cofactors bound are displayed as stick and Sav is displayed as surface representation. Positions selected for mutagenesis are highlighted.

[1] Yu, F.; Cangelosi, V. M.; Zastrow, M. L.; Tegoni, M.; Plegaria, J. S.; Tebo, A. G.; Mocny, C. S.; Ruckthong, L.; Qayyum, H.; Pecoraro, V. L., *Chem. Rev.* 2014, 114, 3495.

[2] Ward, T. R., *Acc. Chem. Res.* 2011, 44, 47.

[3] Dürrenberger, M.; Heinisch, T.; Wilson, Y. M.; Rossel, T.; Nogueira, E.; Knörr, L.; Mutschler, A.; Kersten, K.; Zimbron, M. J.; Pierron, J.; Schirmer, T.; Ward, T. R., *Angew. Chem. Int. Ed.* 2011, 50, 3026. 4.b

Towards cheap and sustainable energy sources by exploiting self-organized catalyst micro- and nano structures

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Energy in forms of fossil fuels and electricity are essential to maintain the quality of modern life. During the last decades global energy consumption increased almost exponentially [1]. But our natural resources are shrinking, while the pollution is increasing. For this reasons, cheap, green and sustainable energy production has become one of the greatest wishes of our time. A sustainable alternative, which can possibly allay our needs, can be found in the use of Sun`s energy. In terms of energy storage and transport, direct conversion of solar energy into fuels is of interest. The production of hydrogen fuel by solar induced photocatalytic water splitting in photo-electrochemical cells (PECs) represents a promising way to reach this aim [2]. In order to facilitate decomposition of water into oxygen and hydrogen, catalyst materials are needed, showing both corrosion stability and high absorbance in the visible and near-visible region of the sun`s spectrum. In the past it was shown that micro and nano-structured catalyst materials show enhanced efficiencies compared to bulk materials. One part of our research is therefore focused on techniques and systems which can possibly be used to produce very cheap, easily reproducible and highly catalytically active micro and nano structured catalyst surfaces, by combining the WET-stamping techniques and Liesegang phenomena [3]. Together with our research collaboration we used this lithographic free technique for the production of highly periodic micro and nano structures (Fig. 1) made out of hematite / rust ($\alpha\text{-Fe}_2\text{O}_3$) (Fig. 2) or metal coordination compounds (Fig. 3, 4).

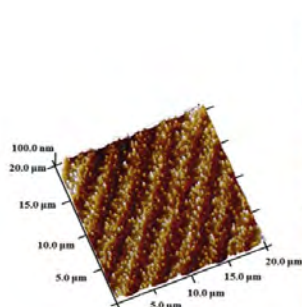


Figure 1: AFM surface profile

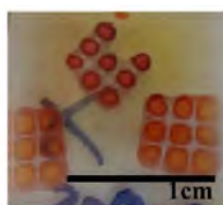


Figure 2: Hematite pattern



Figure 3: Fe(II) coordination compound

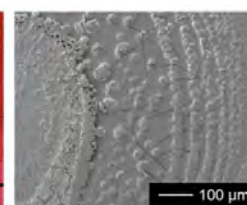
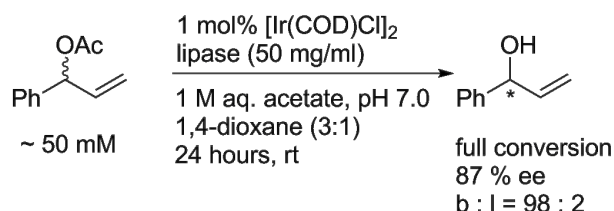


Figure 4: Ru(II) coordination compound

- [1] International Energy Agency. Annual Energy Outlook 2014 with projections to 2040; **2014**.
 [2] D. K. Bora, A. Braun, E. C. Constable, Energy Environ. Sci. **2013**, 6, 407.
 [3] R. M. Walliser, F. Boudoire, E. Orosz, R. Tóth, A. Braun, E.C. Constable, Z. Rácz, I. Lagzi, Langmuir **2015**, 31, 1828.b

Dynamic kinetic resolution of allylic acetatesV. Köhler¹¹University of Basel

The dynamic kinetic resolution of secondary alcohols by a combined transition metal catalyzed racemisation process with *in-situ* stereoselective enzymatic acylation has received widespread attention and has been probed for industrial application,^[1] whereby a number of studies have been concerned with the DKR of allylic alcohols.^[2] Typically processes proceed in the synthesis direction in regard to the hydrolase, namely from racemic alcohol to enantioenriched ester, whereas Ir-catalyzed allylic substitution enables the reaction scheme in the reverse direction: from the racemic allylic acetate to the enantioenriched allylic alcohol. Ir-mediated allylic substitution displays a favorable branched to linear ratio of the products and racemisation of the acetate can be achieved in partly aqueous solution with acetate as a dummy nucleophile. Concurrent stereoselective hydrolysis of the allylic acetate by bacterial lipase leads to the enantioenriched alcohol.

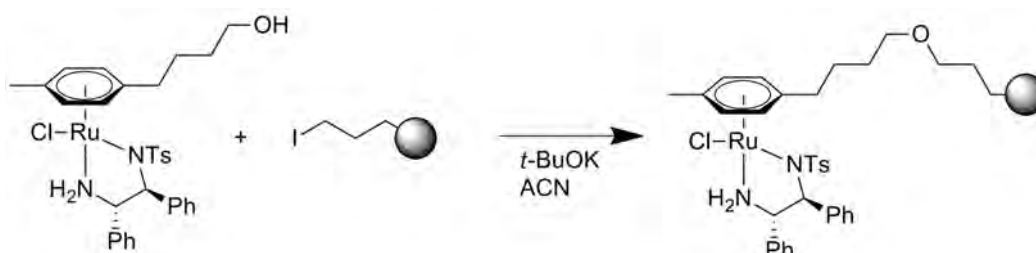


[1] B. Martín-Matute, J.-E. Bäckvall, *Curr. Opin. Chem. Biol.* **2007**, *11*, 226-232.

[2] S. Akai, *Chem. Lett.* **2014**, *43*, 746-754.

Heterogenization of chiral Ru(II) catalysts on mesoporous silica via the arene ligandJ. Aubrecht¹, B. Vilhanová¹, M. Kuzma², P. Kačer^{1*}¹University of Chemistry and Technology, Prague, Czech Republic, ²Institute of Microbiology, Academy of Sciences of the Czech Republic

The anchoring of homogeneous catalysts on a solid support is one of the main aims in the industry since it allows for facile separation from the reaction mixture and recycling. Catalysts [Ru(η^6 -arene)(*N*-R-sulfonyl-diamine)] (R = alkyl, aryl) are often used for enantioselective hydrogenation of ketones and imines.[1] Typically, the heterogenization of such catalysts is based on a connection with the diamine ligand.[2] However, this approach limits the catalyst to one particular modified ligand and the modular principle of catalyst tunability is thus hindered. Here we demonstrate a new method for immobilization through the η^6 -arene, where the diamine ligand is unmodified, therefore easily accessible and replaceable. The connection is made between a nucleophilic group present at the catalyst and a suitable electrophilic group on the support. For this idea, a new catalyst has been developed, bearing a 4-hydroxybutyl group as the nucleophilic synthon. SBA-15 was chosen as the solid support due to its properties (namely mesoporosity, stability and cost) that are appropriate for this purpose. This material was grafted with 3-iodopropyl groups and the remaining silanol groups were protected with chlorotrimethylsilane. Finally, the catalyst was directly immobilized via an S_N2 reaction (Scheme 1). The resulting heterogeneous catalyst was characterized and tested in asymmetric hydrogenation of cyclic imines (1-alkyl-3,4-dihydroisoquinolines) because the motif of optically pure 1-alkyl-1,2,3,4-tetrahydroisoquinolines is present in the structures of many biologically active compounds.

**Scheme 1:** Heterogenization of the chiral catalyst on 3-iodopropyl-SBA-15

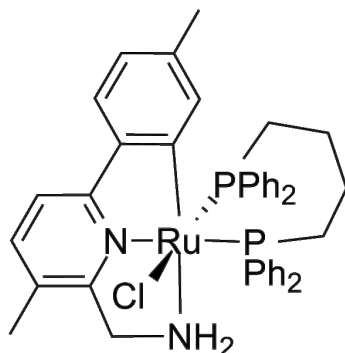
This project was financially supported by the Grant Agency of the Czech Republic (Grants GACR P106/12/1276 and 15-08992S) and by financial support from specific university research (MSMT No 20/2015).

[1] Shohei Hashiguchi, Ryoji Noyori, *Accounts of Chemical Research*, **1997**, 30, 97-102

[2] Jiří Václavík, Petr Kačer, Marek Kuzma, Libor Červený, *Molecules*, **2011**, 16, 5460-5495

Synthesis of highly active ruthenium catalyst for transfer hydrogenation of ketonesL. Kořený¹, J. Pechacek¹, M. Kuzma², P. Kačer^{1*}¹University of Chemistry and Technology, Prague, ²Academy of Sciences of the Czech Republic, Prague

The reduction of a carbonyl group is often a crucial step in the synthesis of chemical specialties. Transfer hydrogenation is a safer alternative to classical pressure hydrogenation. This method is currently not preferred by the industry due the reasons such as the price of the catalysts and their relatively low activity. The new generation of the ruthenium based [1] complexes bearing CNN ligands appear to be very promising within the category of catalytic transfer hydrogenation of ketones. Their very high activity (TOF reaching 10^6 h^{-1}) [2] enables them to be used in a very low catalytic loading (0.001 mol. %). [2] The high reactivity of these catalysts comes at the cost of lower stability, as the complexes are air- and moisture-sensitive. The aim of this study was to synthesize a ruthenium based catalyst, analogical to those found in the literature, with modifications leading to a complex with an increased stability. The prepared complex was thoroughly tested in the transfer hydrogenation of acetophenone. It was found to be very active even when very low catalytic loading (0.002 mol. %) was applied. Compared to the previous generation of the catalysts this new complex provided the quantitative yield when the substrate-to-catalyst (S/C) ratios of 10,000 and even 50,000 were used. These facts indicated a significant increase of the produced complex stability compared to the previous generation of the catalysts.



Acknowledgements : This work has been financially supported by the Grant Agency of the Czech Republic (Grant GACR 106/12/1276 and GACR 15-089925). Financial support from specific university research (MSMT No 20/2015).

[1] Walter Baratta, Marco. Bosco, Giorgio Chelucci, Alessandro Del Zotto, Katia Siega, Micaela Toniutti, Ennio Zangrando, Pierluigi Rigo, *Organometallics* **2006**, 25, 4611-4620.

[2] Walter Baratta, Giorgio Chelucci, Serafino Gladiali, Katia Siega, Micaela Toniutti, Matteo Zanette, Ennio Zangrando, Pierluigi Rigo, *Angewandte Chemie* **2005**, 117, 6370-6375.

TiO₂ and Ag-doped TiO₂ nanocontainers as photocatalysts for CO₂ reduction

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CO₂ gas is one of the major factors of the climate imbalance. Some solutions are proposed to convert CO₂ gas into more valuable molecules (such as CH₄, CH₃OH etc.). The reduction of CO₂ by photocatalysis pathway is interesting to scientists since the energy requirement of CO₂ reduction in the photocatalysis process is lower than in other processes and may be activated by solar light [1]. For this process, titanium dioxide-based materials with various structures are commonly used as photocatalysts [2], [3]. Moreover, TiO₂ can be doped with small metal islands (such as Pt, Ag, Au [1], [4]) used as electron traps to increase its efficiency (Fig. 1).

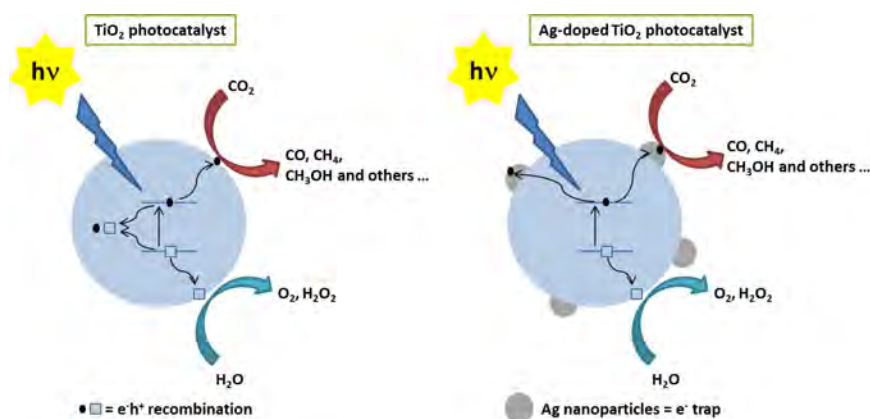


Fig.1. Schemes of basic mechanism of the TiO₂ and Ag-doped TiO₂ photocatalytic process

In this project, TiO₂ nanocontainers (NCs) were synthesized to evaluate the structural and the morphologic effects on their photocatalytic properties. Then TiO₂ NCs were doped with silver nanoparticles (NPs) to separate e⁻ h⁺ pairs formed under light exposure and to enhance their lifetime. The synthesis principle is based on the TiO₂ coating on the surface of template beads containing Ag NPs (illustration given in Fig. 2).

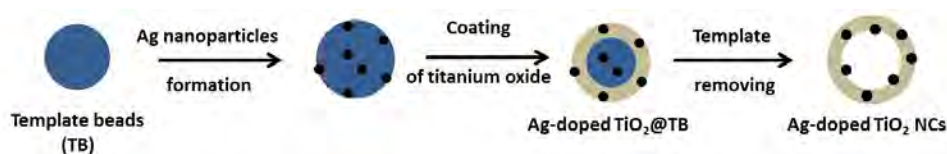


Fig. 2. Schematic illustration of the Ag-doped TiO₂ nanocontainers synthesis

[1] P. Usubharatana, D. McMartin, A. Veawab, P. Tontiwachwuthikul, *Ind. Eng. Chem. Res.* **2006**, 45, 2558-2568.

[2] T. Wanga, X. Menga, P. Lia, S. Ouyangb, K. Changa, G. Liua, Z. Meia, J. Ye, *Nano Energy*, **2014**, 9, 50-60.

[3] P-Q. Wang, Y. Bai, J-Y Liu, Z. Fan, Y-Q. Hu, *Catal. Commun.* **2012**, 29, 185-188.

[4] W-N. Wang, W-J. An, B. Ramalingam, S. Mukherjee, D.M. Niedzwiedzki, S.Gangopadhyay, P. Biswas, *J. Am. Chem. Soc.* **2012**, 134, 11276-11281.

Metal Center Tuning of Layered Double Hydroxides for Electrochemical Water Oxidation

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Development of an artificial and functional photocatalytic water splitting system remains a major challenge on the way to conversion of solar light into chemical fuels [1]. Heterogeneous water oxidation catalysts with low-cost metals and high operational stability are essential to master the most difficult step of artificial photosynthesis.

We explored the potential of well-defined layered double hydroxide (LDH) structures for electrocatalytic water oxidation. LDHs consist of stacked and ordered sheets of edge sharing $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{q+}$ octahedra [2]. Numerous combinations of di- and trivalent cations in LDHs have been tested for their photo- and electrochemical WOC performance with multiple and diversified experimental setups. Further chemical approaches are also used to overcome the reduced electrical conductivity of the LDH-matrix [3]. These diverse protocols render an objective evaluation of the WOC performance based on the cation combinations rather difficult. We thus decided to investigate metal combinations of di- and tri-valent cations in the LDH matrix $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{q+}$ with the main focus of on divalent $M^{2+} = Co^{2+}, Ni^{2+}$ and trivalent $M^{3+} = Al^{3+}, Co^{3+}, Mn^{3+}, Fe^{3+}$ supported with a standardized carbon paste (CP) setup. The electrochemical water oxidation performance of the LDH-matrixes is evaluated and the WOC-activity is furthermore analyzed by impedance spectroscopy (EIS).

These results are expected to optimize cation combinations in LDH-based WOC design in order to transfer this knowledge on different oxide/non-oxide based WOC systems.

[1] M. D. Kärkäs, O. Verho, E. V. Johnston, B. Åkerman, *Chem. Rev.* **114** (2014) 11863.

[2] G. Fan, F. Li, D. G. Evans, X. Duan, *Chem. Soc. Rev.* **43** (2014) 7040.

[3] F. Song, X., Hu, *Nature Comm.* **5** (2014), 4477.

Doped Manganese Oxides as Water Oxidation Catalysts

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Inspired by nature's photosystem II, manganese oxides have been intensely investigated as heterogeneous water oxidation catalysts (WOCs) in the past. Compared to other metal oxides, manganese oxides have the advantage that they are relatively cheap, abundant and can be found in many different structural motifs. In a recent study^[1], the activity of different manganese oxides such as α -/ β - MnO_2 , Mn_2O_3 and Mn_3O_4 was compared, of which the latter two showed the best catalytic performance. Furthermore, Fe has been shown^[3] to play a critical role in enhancing the activity of the electrocatalytic oxygen evolution of $\text{Ni}_{1-x}\text{Fe}_x(\text{OH})_2/\text{Ni}_{1-x}\text{Fe}_x\text{OOH}$ thin films and of Co_3O_4 .^[2,3]

Inspired by these results, we started investigating the effects of doping Fe and other metal ions into different manganese oxides on the water oxidation activity. We have used different methods (hydrothermal, microwave-assisted, solid-state) to synthesize doped manganese oxides. The obtained materials were tested as photocatalytic WOCs using $[\text{Ru}(\text{bpy})_3]^{2+}$ as photosensitizer and $\text{Na}_2\text{S}_2\text{O}_8$ as sacrificial electron acceptor at different catalytic conditions. We found that the phase-purity of the samples is crucial, because very low impurity concentrations can have a notable effect on the activity. Moreover, we could not observe any activity for pure β - MnO_2 , which has been reported^[4] to be catalytically active.

[1] D. M. Robinson, Y. B. Go, M. Mui, G. Gardner, Z. Zhang, D. Mastrogiovanni, E. Garfunkel, J. Li, M. Greenblatt, G. C. Dimukes, *J. Am. Chem. Soc.* **2013**, 135, 3494.

[2] T. Grewe, X. Deng, H. Tüysüz, *Chem. Mater.* **2014**, 26, 3162.

[3] L. Trotochaud, S. L. Young, J. K. Ranney, S. W. Boettcher, *J. Am. Chem. Soc.* **2014**, 136, 6744.

[4] V. Bharat, R. Boppana, F. Jiao, *Chem. Commun.* **2011**, 47, 8973.

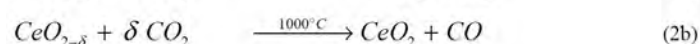
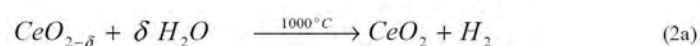
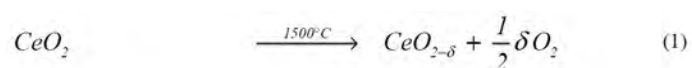
Optimization of Ceria-Based Materials for Solar Thermochemical Two-Step CO₂-Splitting

R. Jacot¹, R. Michalsky², A. Steinfeld^{2*}, G. R. Patzke^{1*}

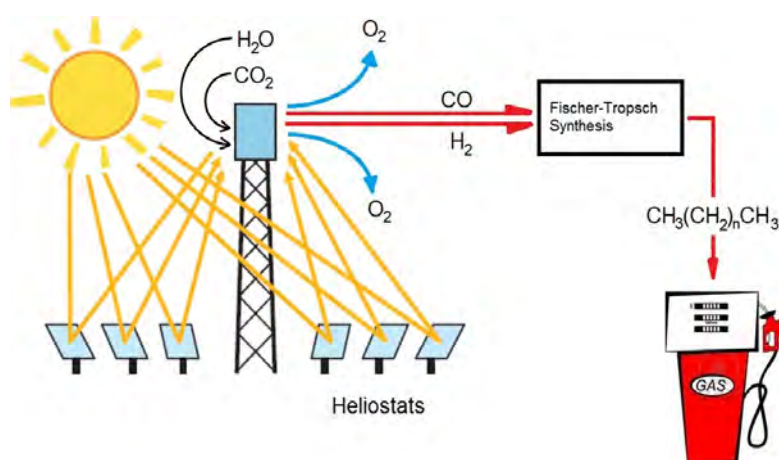
¹University of Zurich, ²ETH Zurich

To satisfy the increasing need of energy and fuels, producers reach for more difficult-to-tap sources of mineral oil. Therefore the price for mineral oil is continuously increasing. On the other hand, renewable solar energy sources become more and more interesting due to improving efficiencies. Also the demand for renewable fuels grows with the progressively visible influence of the increasing CO₂ content in the atmosphere (e.g. melting of the glaciers, arctic ice etc.). It is only a question of time until renewable fuels will dominate the energy market.

One of the most promising pathways to gain renewable fuels is the thermo-solar two-step water-splitting technology. This technology uses concentrated thermal solar energy which is focused on a solar reactor. This solar reactor contains a metal-oxide (ceria or perovskite), which is able to split water and CO₂ into syngas (H₂ and CO) in two steps.^[1] In a first step, ceria (CeO₂) is reduced at 1500 °C by releasing oxygen (Eq. 1). In a second step the reduced ceria reacts with H₂O and/or CO₂ at 1000 °C to afford H₂ and/or CO, respectively (Eq. 2a, 2b). CO and H₂ (syngas) can further be converted into fuels (gasoline, diesel and alcohols) by the Fischer-Tropsch process. However, the efficiency is still too low to produce CO₂ neutral fuels economically.



Herein we report the improvement of the solar-to-fuel-conversion-efficiency by doping ceria with tetravalent dopants. Dopants with the same valency as Ce^{+IV}, but with a different effective ionic radius than ceria, introduce strain forces in the ceria lattice which facilitates O₂ release (in step 1).^[2] To determine the best dopant for ceria, we screened all 27 possible tetravalent, eight-fold coordinated cations (chosen from Ref. 3) on the thermal stability of the doped ceria and by thermogravimetric analysis (TGA).



[1] W. C. Chueh, C. Falter, M. Abbott, D. Scipio, P. Furler, S. M. Haile, A. Steinfeld, *Science*, **2010**, 330, 1797.

[2] J. R. Scheffe, R. Jacot, G. R. Patzke, A. Steinfeld, *J. Phys. Chem. C*, **2013**, 117, 24104.

[3] R. D. Shannon, *Acta Cryst. A*, **1976**, 32, 751.

Screening of Lewis Acidic Chlorometallate Ionic Liquids Combined with Nanoparticle Catalysts for Aromatic Hydrogenation Activity

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Ionic liquids (ILs) are excellent media for immobilizing nanoparticle catalysts, providing rotational freedom and access to the entire surface of a nanoparticle. Imidazolium-based ILs display a high degree of 3D structural organization compared to other ionic liquids favoring their application as liquid supports for nanoparticles. Besides, functionalized ILs can work cooperatively with metal nanoparticles in various catalytic reactions [1,2]. These features of imidazolium-based ILs allow to develop NP-IL based catalytic systems imitating and surpassing supported heterogeneous catalysts.

Herein we present a novel catalytic system composed of metal nanoparticles dispersed in BMimBF₄ ionic liquid and Lewis acidic chlorometallate IL. Lewis acidity was quantified using a method based on IR spectroscopy with a nitrile-functionalized IL probe (Fig. 1). The metal incorporated in an ionic liquid and the ratio of metal chloride:organic salt used for its synthesis determine anionic speciation of the ionic liquid and, thus, Lewis acidity. Subsequent addition of strongly acidic chlorometallate ILs to the metal nanoparticle catalyst produced highly effective system for the hydrogenation of aromatic substrates. The conversion was considerably enhanced with the addition of the Lewis acidic ILs and activities were correlated to the acidity of the ILs.

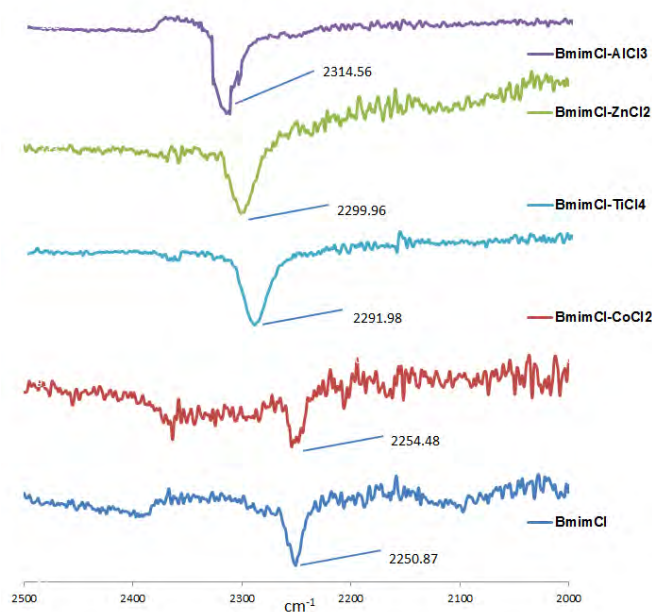


Fig. 1

[1] N. Yan, Y. Yuan, R. Dykeman, Y. Kou, P. J. Dyson. *Angew. Chem. Int. Ed.*, **2010**, 49, 5549-5553.

[2] X. Yuan, G. Sun, H. Asakura, T. Tanaka, X. Chen, Y. Yuan, G. Laurenczy, Y. Kou, P. J. Dyson, N. Yang. *Chem. Eur. J.*, **2013**, 19, 1227 – 1234.

Continuous flow synthesis of metal-organic frameworks utilizing microwave irradiation

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Metal-organic frameworks (MOFs) are porous crystalline materials with high scientific and industrial impact exhibiting high surface areas and chemical and structural versatility. Besides potentially industrial applications in gas storage, adsorption and separation, metal-organic frameworks are widely studied as catalysts. [1] Synthesis from inorganic precursors and organic linkers occurs slowly within hours or days following conventional solvothermal routes. [2] The reaction times can be drastically reduced by employing microwave irradiation, but the batch sizes are limited due to the low penetration depth of the microwaves into the polar reaction mixtures. [3]

We developed a continuous flow synthesis setup utilizing microwave irradiation that allowed the production of a number of benchmark MOFs, such as HKUST-1, MIL-53(Al), UiO-66, MIL-101(Al)-NH₂ and ZIF-8, with remarkable space-time yield, mass efficiency, crystallinity, and purity. It combines the advantages of the continuous flow and the internal volumetric heating effect of the microwave irradiation, giving the prospect of large-scale production of MOFs.

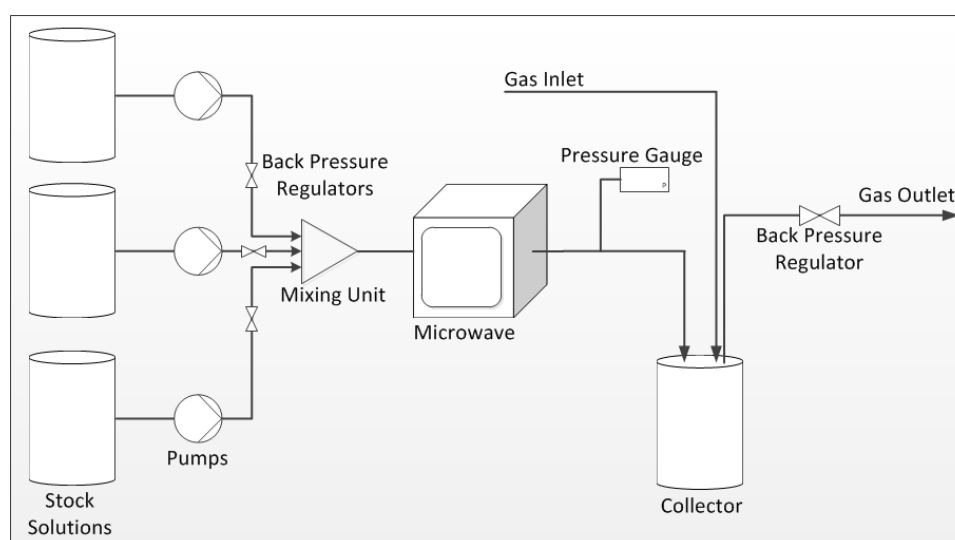


Figure 1 Schematical setup for the continuous flow synthesis of metal-organic frameworks utilizing microwave irradiation.

[1] Marco Ranocchiari, Jeroen A. van Bokhoven, *Phys. Chem. Chem. Phys.*, **2011**, 13, 6388-6396.

[2] Flavien Morel, Marco Ranocchiari, Jeroen A. van Bokhoven, *Ind. Eng. Chem. Res.*, **2014**, 53, 9120-9127.

[3] C. Oliver Kappe, Alexander Stadler, Doris Dallinger, *Microwaves in Organic and Medicinal Chemistry*, Second Edition, Wiley-VCH Verlag Co. KGaA, Weinheim (2012).

Cationic co-doped TiO₂ nanoparticles as efficient visible-light active photocatalyst: experimental and theoretical study

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In the field of solar energy conversion and environmental cleanup, TiO₂ based materials have been widely studied due to their photocatalytical activity, non-toxic nature and abundance. The efficient photocatalytic activity relies on the ability of solar energy photons absorption, effective charge transfer to the active surface sites and their utilization in oxidation/reduction processes. TiO₂ based materials possess promising physical and chemical properties, however, the intrinsic wide band gap limits its absorption to only UV region of the solar spectrum. It has been shown that mono-doping as well as anion-cation co-doping in TiO₂ lattice can enhance the visible light absorption and in some cases boost the photoelectrochemical performance. While latter was extensively studied both in terms of experiment and theory, scarce studies can be found on successful cationic pair co-doping.

In this contribution combined experimental and theoretical study of transition metal cationic co-doping in anatase TiO₂ nanoparticles will be presented. Large varieties in size, morphology observed and differences in optical, photocatalytical (PC) and photoelectrochemical performance (PEC) of various different cationic dopant-pairs tested, will be presented and in addition discussed by means of theoretical calculations. Apart from the doping influence on the core electronic structure also the surface states will be considered, with emphasis on doping effect on the stability of high-energy facets in PC and oxygen evolution kinetics in PEC water splitting.

Design and technical development of iron zeolite catalysts for the gas phase oxidation of glycerol to dihydroxyacetone

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Dihydroxyacetone (DHA) is an intermediate of growing importance for the manufacture of lactic acid and specialty polymers. Herein, we introduce the design of highly active and selective iron zeolites for its production through the gas-phase oxidation of glycerol¹ and their development to technical shapes. An optimized catalyst, characterized by mild acidity and oligonuclear iron oxide species, was obtained by steaming hydrothermally-prepared iron silicalite at mild temperature (Fig.1a). After successfully accomplishing the synthesis of the ferrosilicate at the pilot scale, we studied the impact of variables such as the binder type and sequence of preparative steps on the performance, acid properties, and morphology of the iron species, of shaped bodies (Fig.1b). Technical catalysts displaying equivalent selectivity to the best material in powder form were obtained using an inert binder and the template-containing zeolite and shaping the zeolite-binder mixture under water-free conditions (Fig.1b). Finally, the DHA production process based on iron zeolites was assessed by life cycle analysis and compared to the established enzymatic technology. Preliminary results point to substantially reduced energy demand, global warming potential, and operating costs, endowing the alternative chemocatalytic strategy with bright perspective for a future industrial implementation.

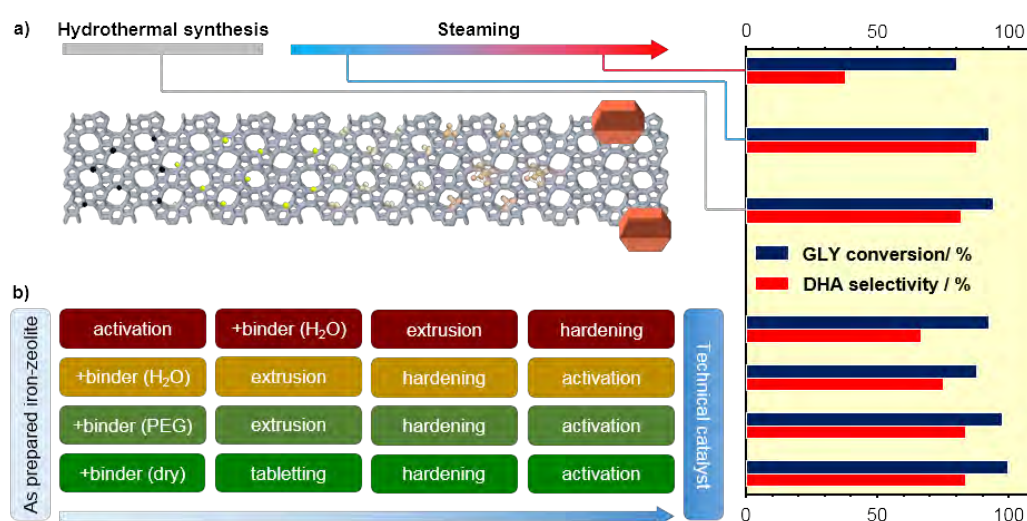


Figure 1. a) Catalytic performance and iron morphology of as-prepared and steamed Fe-MFI zeolites and of b) iron silicalite-based technical catalysts attained *via* different synthetic strategies.

[1] G. M. Lari, C. Mondelli, J. Pérez-Ramírez, *ACS Catal.* **2015**, 5, 1453.b

Zinc-rich copper catalysts promoted by gold for methanol synthesis

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In this study, we gathered further understanding of the function of the components in the commercial Cu-ZnO-Al₂O₃ catalyst for methanol synthesis from mixed syngas feeds (CO/CO₂/H₂) to rationally develop systems displaying superior performance (Fig. 1). In order to unravel the role of ZnO¹ in the hydrogenation of the preferred methanol source, CO₂,² and in the reverse water-gas shift (RWGS) reaction, we tested coprecipitated materials with variable surface zinc content under industrially-relevant conditions (5.0 MPa, 503–543 K). We found that a surface enrichment in zinc leads to higher activity and selectivity due to (i) the enhancement of the unique synergistic Cu-ZnO interactions boosting CO₂ hydrogenation, (ii) the inhibition of the RWGS reaction which produces the undesired CO, and (iii) the electronic stabilization of the Cu sites against re-oxidation by CO₂ or H₂O. Thus, a catalyst with a surface Zn/(Cu+Zn) ratio of 0.8 displayed superior catalytic properties than a commercial benchmark sample, which featured only half of the ratio. The retention of the metallic state of copper was greatly favored by the deposition of an electron-withdrawing metal, such as gold, which favors the electronic flux from ZnO to Cu. The Cu-based activity in the hydrogenation of mixed syngas and CO₂ over the zinc-rich gold-promoted catalyst was ca. 2 and 4 times higher, respectively, than that exhibited by the commercial system.

b

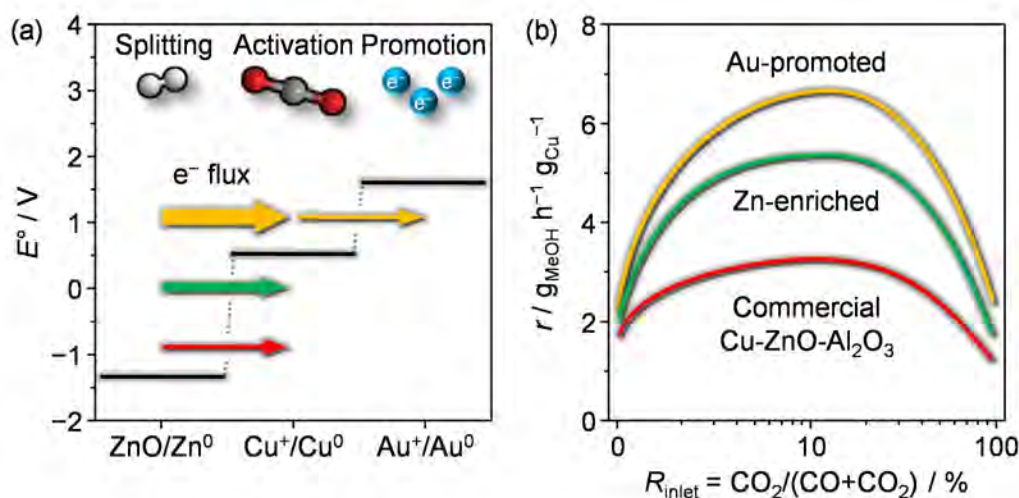


Figure 1. (a) Schematic representation of the promotional effect of gold in Cu-Au-ZnO-Al₂O₃ on the basis of the standard reduction potentials E° of the individual catalyst components. (b) Rate of methanol formation as a function of the CO₂ concentration in the feed.

[1] O. Martin, J. Pérez-Ramírez, *Catal. Sci. Technol.* **2013**, 3, 3343.

[2] J. Schumann, M. Eichelbaum, T. Lunkenbein, N. Thomas, M. C. Álvarez-Galván, R. Schlögl, M. Behrens, *ACS Catal.* **2015**, DOI:10.1021/acscatal.5b00188.br /

Evidence on the direct formation of methane from H₂O and CO₂ by thermochemical cycles using Ni- and Rh-doped ceria

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In 1971, 86% of the world's total primary energy supply came from fossil sources, according to a very recent publication by the International Energy Agency.^[1] More than four decades later, due to increased demand of energy, this value dropped by a mere 4% to 82% in 2012 despite the significant growth of non-fossil energies such as nuclear and hydropower. The heavy reliance on fossil fuels has been contributing to the rapidly increasing anthropogenic CO₂ emission that is often regarded as the main cause of global warming. In light of projected increase of energy consumption, depleting supply of fossil fuels and the need to cut CO₂ emission, solar energy, by far the largest exploitable source of renewables, will need to play a pivotal role in the world's energy and environmental security in the 21st century. However, scientific and technological innovations and advancements will be required for wide-spread utilization of solar energy. In particular, due to the intermittency of the insolation, the storage of solar irradiation in various forms, long- or short-term, is absolutely necessary if solar energy is to become our primary energy supply. One attractive approach is to store solar energy in the form of chemical bonds by producing the so-called solar fuels, carbon-zero (i.e. H₂) or carbon-neutral, from the vastly available H₂O and the "un-desired and harmful" greenhouse gas CO₂. An interesting example is the solar-driven high temperature ceria-based thermochemical cycles for the dissociation of H₂O and CO₂ to produce synthesis gas (a mixture of H₂ and CO).^[2] The energy-intensive Fischer-Tropsch (FT) process is required to convert synthesis gas to higher grade fuels including methane and liquid hydrocarbons.

Based on these, in this presentation we will firstly introduce the concept of incorporating the FT process into thermochemical cycles in order to synthesize higher grade fuels (i.e. methane) directly from H₂O and CO₂ by utilizing concentrated solar radiation. The strategy that will be discussed is to incorporate the cations of a FT catalyst into the lattice of ceria (CeO₂), the state-of-the-art materials for thermochemical cycles. Ideally, the FT cations should serve two purposes in this concept. One is to improve the oxygen storage capacity (OSC) of ceria so that a higher degree of reduction can be achieved, thus increasing the fuel production per cycle. The other is to catalyze the quasi-direct or direct formation of simple organic molecules (i.e. methane) in the reoxidation step, with or without the formation of intermediate synthesis gas. The requirements from the materials' perspective for this concept will be discussed. Two examples will be given, with Ni-doped ceria and Rh-doped ceria. We will show the full incorporation of the cationic Ni and Rh in the ceria lattice by X-ray diffraction and Raman spectroscopy. The enhancement of the OSC of ceria will be presented. We will present the evidence showing the direct formation of methane at ~500 °C when a mixture of H₂O and CO₂ is introduced to the doped ceria that is firstly chemically reduced. Promise of Rh-doped ceria will be discussed. Further steps and an outlook will be discussed. Combined with a previous study,^[3] we strive to demonstrate the feasibility of this innovative concept and would like to bring it to a wider audience.

[1] IEA, *CO₂ Emissions from Fuel Combustion 2014*, International Energy Agency, 2014.

[2] W. C. Chueh, C. Falter, M. Abbott, D. Scipio, P. Furler, S. M. Haile and A. Steinfeld, High-Flux Solar-Driven Thermochemical Dissociation of CO₂ and H₂O Using Nonstoichiometric Ceria, *Science*, 2010, **330**, 1797-1801.

[3] F. Lin, A. Wokaun and I. Alxneit, Rh-doped Ceria: Solar Organics From H₂O, CO₂ and Sunlight?, *Energy Procedia*, 2015, **69**, 1790-1799.

Towards stabilization of active methanation catalysts: Effect of boron promotion

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The conversion of biomass to energy carriers like CH₄ through CO methanation reaction is a desirable route towards development of efficient energy production/conversion systems. Carbon deposition during this process is a significant challenge in terms of catalyst lifetime. It results from the severe reaction conditions imposed by the presence of unsaturated hydrocarbons (e.g. ethylene) in the gasified feedstock. This work investigated the structure of boron-modified Ni/Al₂O₃ catalysts exhibiting enhanced resistance to carbon deposition. The catalysts were synthesized by impregnating B and Ni precursors on commercial γ -Al₂O₃. Stability tests were conducted in a fixed-bed reactor using 25 vol% H₂-5 vol% CO in N₂ in the presence of 2000 ppm C₂H₄. The amount/type of carbon deposits was estimated by temperature programmed oxidation. All catalysts were characterized using transmission electron microscopy and Raman spectroscopy. The operando XAS-XRD-Raman-MS supplied unique information about the kinetic of pre-treatment process to produce an active and carbon resistant material for CO methanation, the evolution of the local environment of nickel in the presence and absence of modifier and interactions during the process. As a consequence of B promoting the growth of Ni crystallites during calcination, the structure of the B-modified catalyst was demonstrated to be different at the nanoscale (Fig.1). The modified catalyst possesses larger Ni particles with porous regions where B is present. The absence of carbidic and amorphous carbon species, which are considered critical for catalyst deactivation in low temperature processes, confirms that B effectively prevents carbon diffusion into Ni, thus enhancing the durability for CO methanation (Fig.2). These results may reveal a strategy of wider significance for developing catalysts with improved stability.

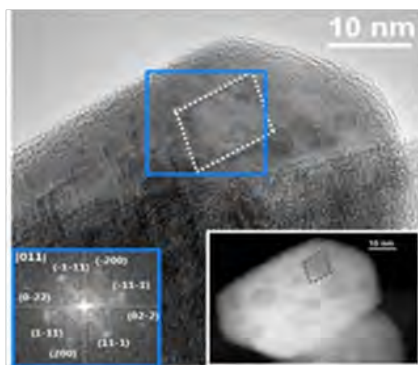


Fig.1: HRTEM image of a NiO particle on NiB(coWI)Al.

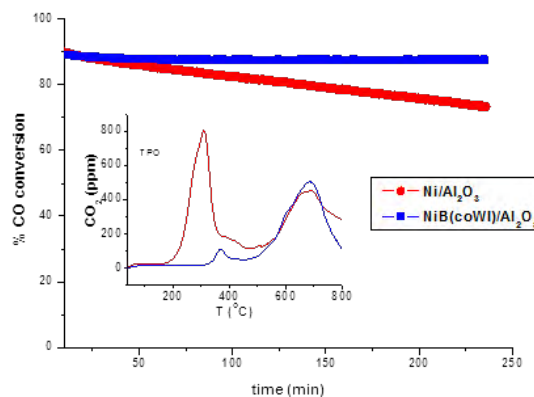


Fig.2: Stability test at 320°C in the presence of C₂H₄ and TPO (inset graph).

[1] A. Kambolis, D. Ferri, Y. Lu, S.N. Yannopoulos, S. Pokrant, D. Rentsch, O. Kröcher, submitted

Superior durability of flame-made $\text{WO}_3/\text{CeO}_x\text{-TiO}_2$ DeNO_x catalystsK. A. Michalow-Mauke¹, D. Ferri¹, K. Kowalski², T. Graule³, O. Kröcher^{1,4*}¹Paul Scherrer Institute, Villigen, ²AGH University of Science & Technology, Krakow, Poland, ³EMPA Dübendorf, ⁴EPF Lausanne

The most efficient technology for NO_x abatement (DeNO_x) in stationary and mobile applications is the selective catalytic reduction (SCR) by NH₃. However, the most commonly used V₂O₅-WO₃/TiO₂ catalyst possesses low thermal and hydrothermal stability resulting in its deactivation with simultaneous release of tungsten and vanadium species to the environment at high temperatures.¹ The optimum operating window for this catalyst type is between 300°C and 450°C. Above this temperature range, it loses N₂ selectivity in favor of N₂O production.² Thus, the design of a thermally stable catalyst is highly desirable. CeO₂-based SCR catalysts have been recently intensively studied. Due to its redox properties and better thermal durability, ceria has a high potential to replace vanadia improving the overall catalyst performance and stability.

In our previous work, we have demonstrated that flame-made WO₃/CeO_x-TiO₂ shows comparable DeNO_x performance as the state-of-the-art V₂O₅-WO₃/TiO₂ catalyst. The exceptional catalytic activity of WO₃/CeO_x-TiO₂ is related to its unique morphology: cubic CeO₂:Ti particles grow out of rutile TiO₂:Ce particles, TiO₂:Ce rutile and anatase particles and CeTi₂O₆ brannerite are present as individual particles, all crystalline phases are homogeneously coated by amorphous WO₃ clusters. Such a morphology, phase composition and defect structure ensures close interaction of each catalyst component and a high Ce³⁺ concentration, which is the DeNO_x active site.^{3,4}

Here, we show that after hydrothermal and thermal ageing at 700°C this catalyst type remains superior to V₂O₅-WO₃/TiO₂. After thermal aging, the NO_x conversion at 350°C dropped from 100% to 41% for V₂O₅-WO₃/TiO₂, whereas WO₃/CeO_x-TiO₂ and CeO_x-TiO₂ showed 100% and 90% NO_x conversion, respectively. The structure of WO₃/CeO_x-TiO₂ was only marginally affected by ageing. Especially, no crystalline WO₃ phase was observed in contrast to V₂O₅-WO₃/TiO₂ and Ce did not segregate in contrast to CeO_x-TiO₂. Both effects, increased WO₃ crystallinity and CeO₂ particles growth, are at the origin of the decreased performance of Ce-W-Ti-based SCR catalysts, when synthesized by another methods.

Hence, flame-made catalysts exhibit superior thermal and hydrothermal stability, which is related to their composition and morphology. Moreover, stable and amorphous WO₃ seems to be a key factor for thermal and hydrothermal durability.

[1] Busca, G., Larrubia, M. A., Arrighi, L., Ramis, G., *Catal. Today* **2005**, 107-108, 139

[2] Madia, G., Elsener, M., Koebel, M., Raimondi, F., Wokaun, A., *Appl. Catal. B-Environ* **2002**, 39, 181

[3] Michalow-Mauke, K. A., Lu, Y., Ferri, D., Kowalski, K., Graule, T., Elsener, M., T., Kröcher, O., *CHIMIA* **2015**, 69, 220

[4] Michalow-Mauke, K. A., Lu, Y., Ferri, D., Kowalski, K., Graule, T., Kröcher, O., submitted to *ACS Catalysis*

Photo-catalytic evolution of dihydrogen from water by Ni@MOF: a nickel catalyst encapsulated inside MIL-125-NH₂ (Ti)

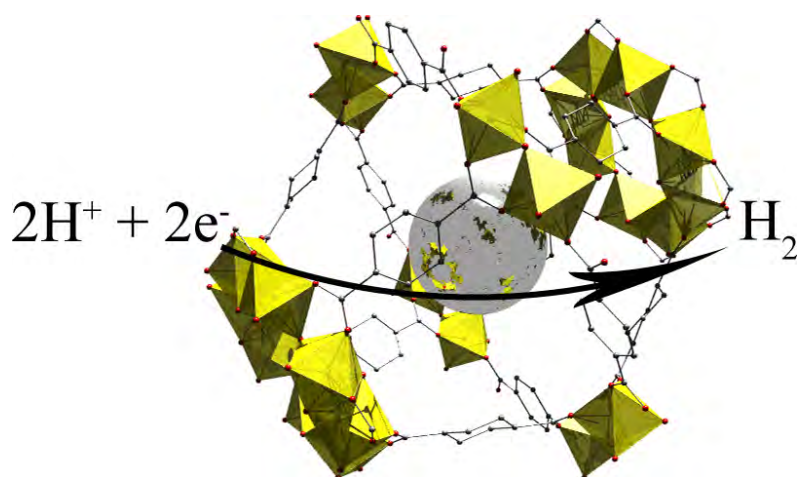
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Photo-catalysed water splitting provides a direct route to the fuel carrier dihydrogen from the abundant renewable resources sunlight and water. But this deceptively simple solution to the global energy crisis is framed by non-trivial requirements, among them; absorption of catalytic materials within the energetically lucrative portions of the solar spectrum, the thermodynamically demanding water oxidation half-reaction, and efficient harnessing of energy at sites or inter-faces for water splitting.¹

Certain metal organic frameworks (MOFs) are able to use the energy of light to drive catalytic processes via their photo-receptive organic linkers and metal-oxide secondary building units.² In a compelling parallel with metal-oxide based semiconductors, experimental evidence suggests that photo-excited electrons and holes in some MOFs may be used to carry out water splitting.³

We have assembled a homogeneous dihydrogen evolving catalyst inside photo-sensitized MIL-125-NH₂ (Ti).⁴ Under UV light the new composite material, Ni@MOF, is three orders of magnitude more active for dihydrogen evolution than the MOF alone, and five times more active than the homogeneous complex, under comparable conditions. We describe the preparation, characteristics and catalytic activity of Ni@MOF, and elaborate on the underlying mechanisms believed to be at play during photo-catalysed water splitting.



[1] M. G. Walter, E. L. Warren, N. S. Lewis *et al.*, *Chem. Rev.* **2010**, 110, 6446–6473.

[2] T. Zhang, W. Lin, *Chem. Soc. Rev.* **2014**, 43, 5982.

[3] K. Meyer, M. Ranocchiari, Jeroen A. Van Bokhoven, *Energy Environ. Sci.* **2015**, submitted.

[4] Y. Horiuchi, T. Toyao, M. Matsuoka *et al.*, *J. Phys. Chem. C* **2012**, 116, 20848.

Metal-support interaction of platinum nanoparticles supported on yttria stabilized zirconia catalysts for environmentally important reaction systems

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Yttria-stabilized zirconia (YSZ) has attracted significant attention in the last decades due to its interesting chemical and physical properties such as the relatively high ionic conductivity in the temperature range of 300 - 1000°C due to the presence of oxygen vacancies in its crystallographic structure [1].

Recently [2], we demonstrated that Pt nanoparticles (2.5 ± 0.5 nm) deposited on YSZ, ceria (CeO_2) and samarium doped-ceria (SDC) show a strong metal-support interaction (SMSI) resulting in O^{2-} transfer towards Pt through the triple phase boundary (tpb) and electron transfer from Pt to the ceramic support. This charge transfer leads to a remarkable catalytic activity of Pt nanoparticles for carbon monoxide and ethylene oxidation in the absence of oxygen in the gas feed.

In this work, we investigate further the catalytic activity of these catalysts for the electrooxidation of volatile organic compounds as well as for carbon monoxide methanation for the purification of hydrogen gas rich stream used in fuel cell applications. Detailed STEM and XPS analysis are used to shed light on Pt/YSZ interface and interaction.

Table 1: List of supported catalysts prepared

Catalyst	Pt size from ADF-STEM (nm)	Pt Loading (wt. %) ^a	Pt Dispersion (%) ^b
Pt/YSZ-1	6.7 ± 1.0	1.0	9.5
Pt/YSZ-2	4.4 ± 0.3	1.1	30.1
Pt/YSZ-3	3.0 ± 0.8	1.1	39.5
Pt/YSZ-4	1.9 ± 0.4	0.9	51.8

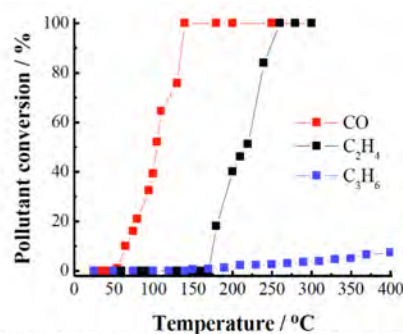


Figure 1: The catalytic activity of Pt/YSZ-3 (3 nm) for the electrooxidation of CO, C₂H₄ and C₃H₆ in oxygen-free gas environment.

Results and Discussion

Figure 1 shows high catalytic activity of Pt nanoparticles for the electrooxidation of CO, C₂H₄ and C₃H₆ in the absence of oxygen in the gas feed. Complete conversion of 909 ppm CO and 909 ppm C₂H₄ is achieved at 110 and 240°C, respectively, while low activity is observed for propylene electrooxidation. It is proposed that Pt nanoparticles and YSZ form local nanogalvanic cells, where the anodic reaction is CO or VOCs oxidation by O^{2-} at the tpb and the cathodic reaction is the partial reduction of zirconia. Each CO and C₂H₄ molecule consumes one O^{2-} and 6O^{2-} anions from YSZ, respectively while each C₃H₆ molecule requires 9O^{2-} for complete conversion. This explains the low activity of the catalyst towards C₃H₆ electrooxidation which depletes O^{2-} from YSZ surface faster in this case compared with CO and C₂H₄ electrooxidations.

Acknowledgement: Financial support from the Natural Science and Engineering Research Council (NSERC) and Ontario Graduate Scholarship (OGS)

[1] J.H. Shim, C. Chao, H. Huang, F.B. Prinz, Chemistry of Materials 19 (2007) 3850.

[2] C. Zhang, C. -J. Li, G. Zhang, X. -J. Ning, C. -X. Li, H. Liao, C. Coddet, Mater. Sci. Eng. B.137 (2007) 24-30.

Stabilisation of gas species via incorporation in porous solids

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Catalysis and energy conversion processes often involve the formation of thermodynamically unstable, transient and rapidly evolving species. Their detection and characterization are fundamental to understanding and controlling the underlying physical and chemical phenomena. The difficulties in storing and structurally characterizing these species limit their evaluation and exploitation for applications.

In our recent work, the stabilization of a gaseous, thermodynamically unstable species is achieved by incorporation in the nanocavities of a robust metal-organic framework. While the gas-phase molecules decompose rapidly after formation in inert atmosphere at ambient conditions [1], the adsorbed species are stable for months in the same conditions and even up to 350 K in vacuum. This novel approach opens new possibilities for the preparation, characterization and storage of metastable compounds.

[1] E. Callini, et al., JPCC 118 (1), 77 (2014)

Hydrogen Sorption in Metal Intercalated Fullerides

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Alkali or alkali earth metals can be intercalated in fullerenes (C_{60}) forming charge transfer salts, so called fullerides, where charge from the metal is transferred to the fullerenes.

The hydrogen sorption properties of Li and Na intercalated fullerides were investigated by a volumetric method. Up to 3.5 mass% hydrogen can reversibly be absorbed in $Na_{10}C_{60}$ at 200 °C and a hydrogen pressure of 200 bar.¹ $Li_{12}C_{60}$ shows an uptake of up to 5 mass % hydrogen.² Additionally to the formation of hydrofullerides the hydrogen ab/desorption is accompanied by a partial de/reintercalation of metal atoms and appearance/disappearance of the corresponding metal hydride. By metal intercalation the stability of the hydrogenation reaction can be changed and the activation energy for the hydrogen desorption is a function of the extend of conversion.³

[1] Ph. Mauron et al., Int. J. Hydrogen Energ. 37 (2012) 14307.

[2] Ph. Mauron et al., J. Phys. Chem. C 117, (2013) 22598.

[3] Ph. Mauron, J. Phys. Chem. C 119, (2015) 1714.