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Aging of Model Diesel Oxidation Catalysts: Hydrothermal vs Chemical Effects

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An increased concern about air pollution is leading to stringent regulations to reduce gas emissions in all energy-consuming activities, including the automotive sector. Diesel engines are widely spread in both heavy-duty and passenger vehicles due to their high efficiency, durability and low operating cost. For mitigating Diesel emissions (comprising of CO, NO and hydrocarbons), Diesel oxidation catalysts (DOC) are used [1]. An important task of DOC is to oxidize NO to NO_2 to assist the downstream selective catalytic reduction (SCR) process converting NO_x into N_2. In order to develop efficient DOC, it is crucial to understand catalyst deactivation over time. Thermal sintering and chemical poisoning (especially due to accumulation of S and P compounds present in fuel and lube oils) are two important aspects that contribute to the aging of the DOC [2]. This research aims at investigating the combined effects of thermal as well as S and P aging on a model 1 wt% Pt/Al_2O_3 catalyst prepared by incipient wetness impregnation. For this purpose, NO oxidation activity and physico-chemical properties were evaluated for catalysts with and without P (added by incipient wetness impregnation of ammonium phosphate), as well as after subsequent hydrothermal aging (750 °C, 16 h) and SO_2 exposure (30 ppm, 250 °C, 16 h). While hydrothermal aging of the fresh catalyst resulted in a significant increase of NO conversion (Figure 1), a gradual catalyst deactivation was observed for P and particularly S poisoned catalysts. Sample characterization allowed to understand the catalyst properties after each treatment. It was concluded that hydrothermal aging promoted the severe sintering of Pt nanoparticles (from 1 to 50 nm). Besides chemical poisoning, the treatments with P and S had an effect on the Pt nanoparticle morphology: P prevented severe thermal sintering while SO_2 is known to promote the Pt nanoparticle growth [2, 3].

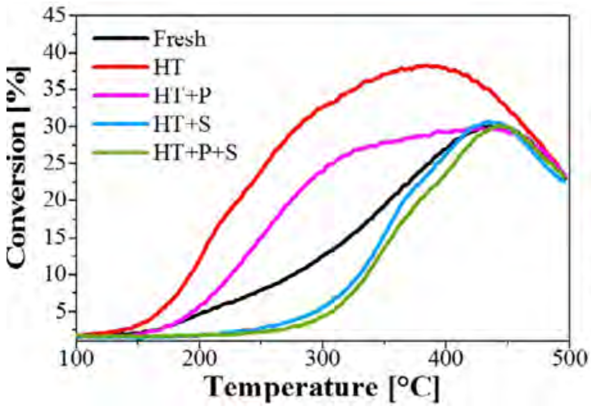

Figure 1. NO oxidation conversion for 1 wt% Pt/Al_2O_3 in the fresh state and after hydrothermal (HT) treatment at 750 °C 16 h, after addition of 2.3 wt% phosphorous (P) and after exposure to 30 ppm of SO_2 (S).

[1] A. Russell, W.S. Epling. *Catal. Rev.*, **2011**, 53, 337-423; [2] A. Winkler, D. Ferri, R. Hauert. *Catal. Today*, **2010,** 155, I 140-146; [3] X.P. Auvray, L. Olsson. *Ind. Eng. Chem. Res.,* **2013,** 52, 14556-14566.

Exsolution of Metallic Ru Nanoparticles to Impart Stability on Catalysts for the Dry Reforming of Methane

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The dry reforming of methane (DRM) converts two major greenhouse gases (CH_4 and CO_2) into a useful chemical feedstock (synthesis gas).[1] Owing to the elevated operating temperatures of the DRM reaction (800-1000 °C), catalysts typically undergo severe deactivation, mainly due to sintering, coke deposition, and the oxidation of the active M(0) phase.[2] Here, we report on the formation of metallic Ru nanoparticles (NPs) via the in situ exsolusion of Ru from a defective, fluorite-type, $Sm_2Ru_xCe_{2-x}O_7$ (x = 0.1, 0.2, 0.4) solid solutions. The method described here leads to highly dispersed, supported Ru(0) NPs (~ 1 nm) that are highly active for the DRM and, at the same time, show excellent thermal stability. The incorporation of ruthenium into the $Sm_2Ce_2O_7$ lattice was confirmed by X-ray absorption spectroscopy (XAS at Ru, Sm and Ce K-edges), X-ray diffraction (XRD), Raman spectroscopy and transmission electron microscopy. The exsolution of Ru nanoparticles was studied by time-resolved, combined XAS and XRD under temperature programmed reduction. Using XRD analysis, we observe that the exsolution of Ru(0) NPs is accompanied by a rearrangement of oxygen vacancies within the crystal lattice. Importantly, this transformation process is reversible. The original structure of the solid solution can be restored by the re-dissolution of the exsolved Ru NPs via air oxidation. The materials were tested for DRM and show only ≤ 1 % deactivation after ca. 100 h time on stream at 700 °C. Further underlining this performance, benchmark catalysts prepared by wetness impregnation and sodium borohydride reduction methods display inferior stability, losing ca. 8 and 12 % of the initial activity after only 48 h on stream, respectively.

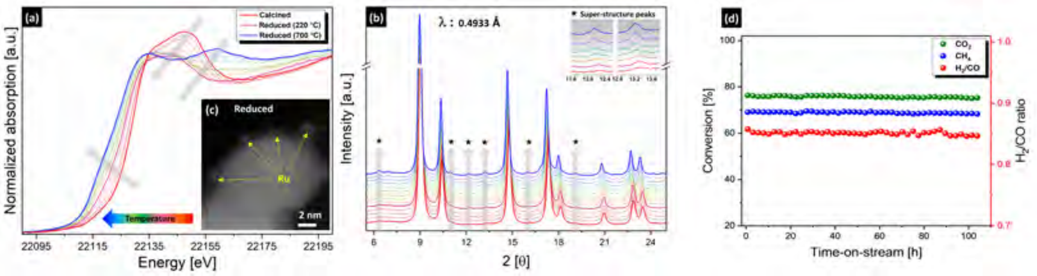

Figure 1. (a) In situ XANES, (b) XRD profile (λ=0.4933 Å) of $Sm_2Ru_{0.2}Ce_{1.8}O_7$ under reducing and DRM conditions. (c) STEM image of the reduced catalyst. (d) Conversion of CH_4 and CO_2 and H_2/CO ratio with TOS under DRM conditions at 700 °C.

[1] Devendra Pakhare and James Spivey, *Chemical Society Reviews*, **2014,** 43, 7813–7837.
[2] Sibudjing Kawi, Yasotha Kathiraser, Jun Ni, Usman Oemar, Ziwei Li, Eng Toon Saw, *ChemSusChem*, **2015,** 8, 3556 –3575.

In-situ formed highly stable Cu-Al catalyst for the Reverse Water Gas Shift reaction

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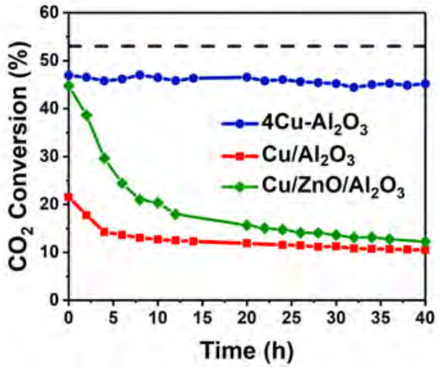
Excessive emission of CO_2 and other greenhouse gases has caused critical issues such as sever changes in climate and ecosystem. Since this issue has been noted, the catalysis society has tackled it through introduction of various catalysts to convert the greenhouse gases and CO_2 specifically to value-added chemicals such as methanol [1]. Conversion of CO_2 to CO, also known as the Reverse Water Gas Shift (RWGS) reaction has recently gained more attention to produce syngas. RWGS reaction, however, requires high temperature since it is thermodynamically limited at lower temperatures. Copper-based catalysts which are highly active and selective but suffer from sintering at high temperatures. Here in this study, a coprecipitated Cu-Al catalyst is introduced which is not only highly active towards formation of CO from CO_2 through the RWGS reaction (47% CO_2 conversion at WHSV = 300,000 mL g^{-1} h^{-1}), but also highly stable at 600 °C (no sign of deactivation after 40 h). This activity, so far is the highest achieved using a copper-based catalyst for this reaction. This catalyst was compared to a conventional Cu/Al_2O_3 catalyst which served as a reference material. A commercial $Cu/ZnO/Al_2O_3$ also was tested for this reaction for comparison. Ambient pressure XPS (APXPS), CO-DRIFTS, H_2-TPR, N_2 physisorption, ICP-OES, XRD, EPR, etc. were used to characterize the catalysts and to verify the reasons for different activity and stability of the catalysts. The results of the catalytic test are shown in Figure 1. It can be seen that $4Cu-Al_2O_3$ outperformed both $Cu/ZnO/Al_2O_3$ and Cu/Al_2O_3 in terms of both activity and stability. Through catalysts characterization methods such as H_2-TPR and EPR, it was concluded that higher concentration of isolated Cu^{2+} ions were found on $4Cu-Al_2O_3$ catalyst which could form strong metal-support interactions (SMSI). Based on the literature, it is known that isolated Cu^{2+} ions in the presence of steam (which in this case could be formed through H_2 treatment) can react with alumina to form a surface spinel [2], the existence of which was confirmed through APXPS and CO-DRIFTS. Therefore, it was confirmed that the active surface participating in the reaction was Cu-Al surface spinel which was formed in-situ during the H_2 treatment before the reaction. Based on DFT studies, it was concluded that doubly folded Cu ions as well as threefold surface oxygen atoms constitute the active sites of this catalyst participating in this reaction.



[1] Niall MacDowell, Nick Florin, Antoine Buchard, Jason Hallett, Amparo Galindo, George Jackson, Claire Adjiman, Charlotte Williams, Nilay Shah, Paul Fennell, *Energy & Environmental Science,* **2010**, 3, 1645-1669.

[2] Jiyang Yan, Guandao Lei, Wolfgang Sachtler, Harold Kung, *Journal of Catalysis,* **1996**, 161, 43-54.

Electrochemical stability and mechanistic studies of mixed oxides upon water oxidation investigated by in situ electrochemical XAS

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Efficient and durable electrocatalysts are necessary for oxygen evolution reaction (OER) which is an essential reaction in rechargeable metal-air, metal-O_2 batteries and water splitting devices.[1] Despite promising researches on application of mixed oxides in OER, their stability during long-term water splitting reactions is still widely unexplored. On the contrary, it has to be noticed that the number of mixed oxide materials with OER activity does not cease to grow, making the topic even more promising. The almost infinite possible compositions of mixed oxides make it a great challenge to find the stable and true active species of them during OER. Herein, we study the stability and conversion behavior of $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ mixed oxide as a well-known mixed oxide in OER. The transition mechanism of this compound, as well as the true active sites during the OER are studies by applying in-situ electrochemical X-ray absorption spectroscopy such as X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) methods. Furthermore, this conversion process has reinvestigated by several ex-situ methods such as X-ray photoelectron spectroscopy (XPS), powder X-ray diffraction (PXRD), Raman spectroscopy, transmission electron microscopy, (TEM), scanning electron microscopy (SEM), cyclic voltammetry (CV), linear sweep voltammetry (LSV) and Electrochemical impedance spectroscopy (EIS).

[1] W. T. Hong, M. Risch, K. A. Stoerzinger, A. Grimaud, J. Suntivich, Y. Shao-Horn, *Energy Environ. Sci.* **2015**, *8*, 1404.

In situ spatial resolution in catalysis

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The phenomenon of strong metal-support interactions (SMSI) in catalytic systems was discovered 40 years ago [1]. SMSI was observed in metal catalysts supported upon reducible oxides such as TiO_2 and manifests as a profound loss of chemisorption capability after high-temperature reduction. The absorption strength of molecules on catalytic surfaces is the key factor for its activity. Thus, this phenomenon is of uttermost importance and is heavily debated. In the 90s, the coverage of the metal by support species after reduction was detected [2]. Ever since, the opinion solidified that partially reduced oxide species creep over the metal surface and thereby cause the encapsulation. The process is believed to be reversible by a high temperature oxygen treatment. However, on real catalytic systems little proof for these assumptions exists as these effects have almost ubiquitously been studied in an *ex situ* manner. It is high time to investigate strong metal-support interactions with state-of-the-art characterization tools to clarify and settle a scientific argument existing for decades. We present a combined investigation of *operando* transmission electron microscopy (TEM), ambient pressure X-ray photo emission spectroscopy (XPS) and *in situ* powder X-ray diffraction (PXRD). Our ongoing studies on the prototypical Pt-TiO_2 system (Fig.) revealed that the system actually behaves diametrically opposite to the former understanding: At high temperatures in O_2 a mostly crystalline TiO_2 overlayer on Pt nanoparticles is stable and H_2 reduction reduces the thickness of this layer. We therefore suggest that speculations in the original work on alloy formation as first step could lead to a real understanding of the dynamic behaviour of this system. This would have severe consequences on the understanding of important class of oxide supported metal catalysts. TEM videos of the TiO_2 encapsulation growth and decrease under realistic conditions supported with *in situ* XPS will be presented.

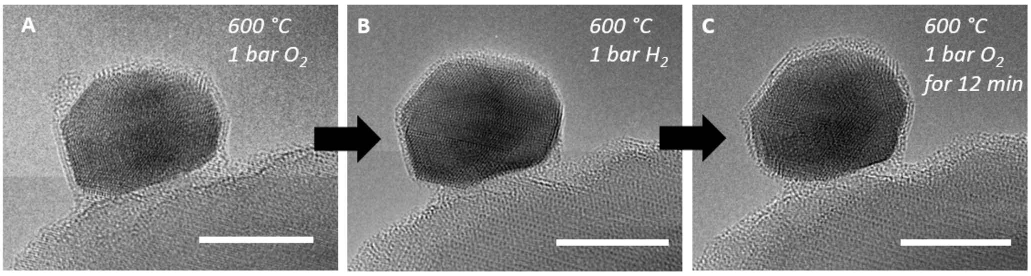

Figure: The formation of a crystalline TiO_2 overgrowth under O_2 and the decrease to an amorphous single layer in H_2 by *operando* TEM.

[1] S. J. Tauster, F. C. Fung, R.L. Garten, *J Am Chem Soc.* **1978**;100(1):170-175.
[2] A. D. Logan, E. J. Braunschweig, A. K. Datye, D. J. Smith, *Langmuir*, **1988**, 4, 827.

Hydrogen on Cu/ZnO catalysts

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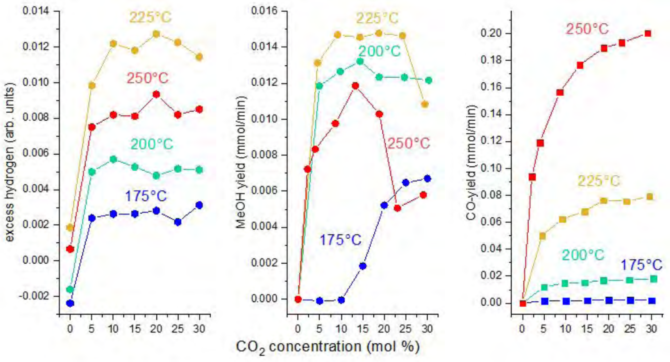
[1]Advanced Analytical Technologies, [2]Advanced Analaytical Technologies, [3]Laboratory for Neutron Scattering and Imaging (LNS), [4]UZH

Recently, the careful structural analysis of established industrial methanol catalysts triggered the hypothesis that zinc oxide has the ideal reducibility to catalyse methanol synthesis, which was found to be a consequence of the stability of the Cu/ZnO nano-composite with the right bulk defects, and peculiar interface and surface structures. The authors concluded that the functioning of the methanol catalyst "could be further evaluated if a method of quantitatively relating the reducibility to the catalytic properties could be found." [1] Our approach is based on the interaction of neutrons with matter, which is isotope selective. The method allows for the quantification of the absolute amount of hydrogen containing compounds on a catalyst over the course of the reaction, and by relating to the surface area, the number of occupied sites is estimated. The simplicity of the method makes it ideal to apply it to different catalyst systems, in particular, we are able to measure the conceptual parameter "reducibility" by hydrogen deuterium exchange probed by neutrons. In addition, we mimic the neutron experiments by hydrogen deuterium exchange in laboratory experiments, i.e., the measurement of weight changes upon H/D exchange and diffusive reflectance infrared spectroscopy.



Left graph: "excess hydrogen" on a Cu/ZnO catalyst as determined by Neutron imaging under operating conditions at 12 bar hydrogen as a function of the CO_2 concentration and temperature. Simultaneously, the MeOH-yield (middle graph) and CO yield (right graph) is measured.

The main outcome is that hydrogen reduction of Cu/ZnO nano-composites modifies the catalyst in way that at operating temperature hydrogen is dynamically absorbed and thereby the extraordinary good catalysis of copper if supported by ZnO is its ability to act as a hydrogen reservoir supplying hydrogen to the surface covered by CO_2, intermediates, and products during catalysis. This form of hydrogen attachment related to the reducibility of catalysts is to be distinguished from common hydrogen ad- or absorption. This is manifested by its temperature dependence: the amount of hydrogen in Cu/ZnO catalysts peaks at a temperature, which coincides with the optimum reaction temperature, in contrast to the adsorption of hydrogen.

[1] Jeffrey Greeley, Active Site of an Industrial Catalyst. *Science*, **2012**, *336*, 810.

Selectivity Descriptors for Nickel Catalysts based on Tailored Carbons in the Electroreduction of CO_2

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The direct electrochemical reduction of CO_2 to valuable products receives considerable interest as a possible strategy for managing the global carbon balance.[1] Single-atom catalysts (SACs) based on nickel and iron are reported to be highly selective for this reaction, reaching high Faradaic efficiency towards CO.[2] Despite the promising results, understanding of the structure-function relationships governing the performance of SACs remains limited. Furthermore, recent work indicated that surface-modified nickel nanoparticles on carbon-based supports could also display high selectivity leading to uncertainty over the nature of the optimal active site.[3] Here, we prepare a series of nickel catalysts comprising single atoms and nanoparticles supported on carbon nanotubes and nitrogen-doped analogues[4] (**Figure 1**). The metal speciation is controlled by varying the nitrogen content in the host, the amount of metal introduced, and the temperature of thermal activation. The deposition of colloidal nanoparticles ensures the absence of single atoms, while nanoparticle-free systems are derived by selective acid leaching. Detailed characterization of the metal speciation and electronic properties distinguishes the contribution of the distinct nickel species, identifying performance descriptors.

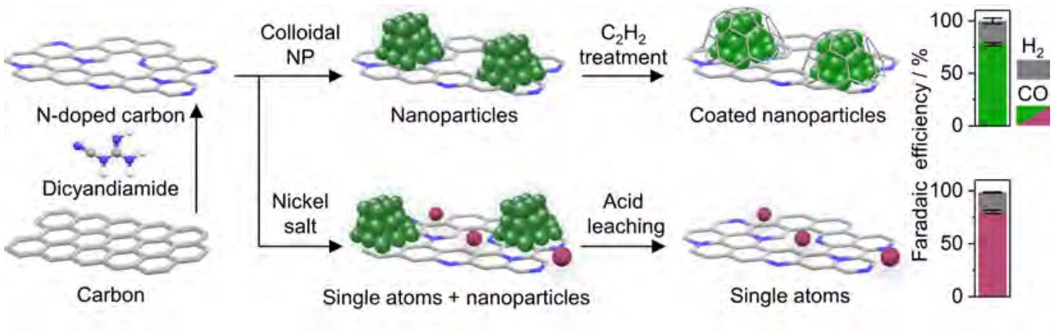

Figure 1 Synthesis of distinct nickel species on nitrogen-doped carbons and corresponding Faradaic efficiencies in the electrochemical CO_2 reduction reaction.

[1] O. Larrazábal, A. J. Martín, J. Pérez-Ramírez, *J. Phys. Chem. Lett.*, **2017**, 8, 3933.
[2] W. Ju, A. Bagger, G.-P. Hao, A. S. Varela, I. Sinev, V. Bon, B. R. Cuenya, S. Kaskel, J. Rossmeisl, P. Strasser, *Nat. Commun.*, **2017**, 8, 944.
[3] M. Jia, C. Choi, T.-S. Wu, C. Ma, P. Kang, H. Tao, Q. Fang, S. Hong, S. Liu, Y.-L. Soo, Y. Jung, J. Qiu, Z.Sun, *Chem. Sci.*, **2018**, 3, 59.
[4] S. Büchele, Z. Chen, S. Mitchell, R. Hauert, F. Krumeich, J. Pérez-Ramírez, *ChemCatChem*, **2019**, doi:10.1002/cctc.201900547R1.

Metal-Organic Frameworks for Catalysis: a systematic study of their stability

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Metal-Organic Frameworks are promising materials for heterogeneous catalysis.[1] Their high surface area and chemical versatility has shown potential in catalytic applications aimed at the synthesis of organic molecules.[2] The structure of these materials allows a rational design of their structure and synthesis with chemical control at the atomic level.[3] Despite these properties, they are not generally accepted as potential catalysts, at least partially based on concern about their stability. MOFs do not show high thermal and hydrothermal stability compared to other inorganic materials.[4] However, such conditions are not relevant for organic reactions. Since there is a general consensus about the potentiality in catalyzing complex organic transformations,[5] data about their stability in organic solvents is needed. We systematically studied the behavior of widely used MOFs with topologies such as MIL-101, MOF-74, UiO-66, MOF-5 and ZIF-8, after treatment with organic solvents and inorganic and organic acids and bases. Their stability was assessed via X-ray diffraction and nitrogen physisorption. We explored the effect of the solvent used, of the excess and the strength of the acid or base and of the metal ion in the nodes of the framework. There is a complicated dependence on many parameters, since the solvent affects both the stability of the framework and the strength and solubility of the acid or base. The MOFs studied proved to be partially compatible with bases or acids in organic solvents and can be used to catalyze organic transformations. The stability is strongly dependent on the system and on the conditions used.

[1] H. Furukawa, K. E. Cordova, M. O'Keeffe, O. M. Yaghi, *Science* **2013**, *341*.
[2] M. Ranocchiari, J. A. v. Bokhoven, *PCCP* **2011**, *13*, 6388-6396.
[3] C.-D. Wu, A. Hu, L. Zhang, W. Lin, *J. Am. Chem. Soc.* **2005**, *127*, 8940-8941.
[4] A. J. Howarth, Y. Liu, P. Li, Z. Li, T. C. Wang, J. T. Hupp, O. K. Farha, *Nature Reviews Materials* **2016**, *1*, 15018.
[5] A. Corma, H. García, F. X. Llabrés i Xamena, *Chem. Rev.* **2010**, *110*, 4606-4655.

N-heterocycles for Hydrogen Storage and Delivery using Homogeneous Ruthenium(II) Phosphine Catalysts

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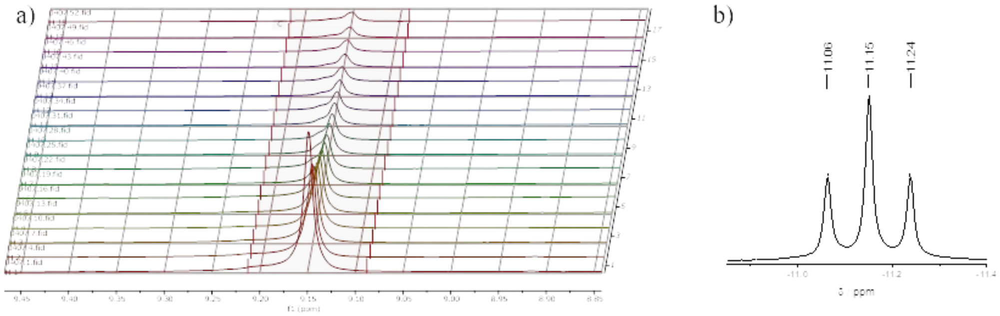
Hydrogen could become a major energy carrier if safe and suitable ways to store and deliver hydrogen are developed. Liquid Organic Hydrogen Carrier (LOHC) compounds represent an attractive way to provide hydrogen for mobile applications as they have similar energy storage densities and manageability as fossil fuels.[1] Compared to cycloalkanes, N-heterocycles have lower enthalpy changes ΔH^0 in dehydrogenation and hydrogenation reactions, thus N-heterocycles could be suitable candidates as LOHCs.[2–4]

In the present work, we investigated the hydrogenation and dehydrogenation of a series of N-heterocycles catalyzed by homogeneous Ru(II) phosphine complexes, i.e. with meta-trisulfonated triphenylphosphine (*m*TPPTS), meta-disulfonated triphenylphosphine (*m*TPPDS), meta-monosulfonated triphenylphosphine (*m*TPPMS) and triphenylphosphine (PPh_3). With Ru/*m*TPPTS in 10%H_2O/DMF, the yield for the dehydrogenation of 1,2,3,4-tetrahydroquinoaline at 100 ℃ is 93%, and the yield for the hydrogenation of quinoxaline at 70 ℃ and 10 bar H_2 is 95%. These reactions were monitored by NMR spectroscopy to obtain mechanistic insights (Fig. 1).



Acknowledgements

The authors are grateful to the Swiss National Science Foundation and EPFL for financial support.

[1] Andrew Dalebrook, Weijia Gan, *Chemical Communication,* **2013**, *49* (78), 8735–8751.
[2] Masahiro Nagao, Kazuyo Kobayashi, *Journal of the Electrochemical Society,* **2015**, *162* (4), 410–418.
[3] Daniel Teichmann, Wolfgang Arlt, *Energy & Environmental Science,* **2011**, 2767–2773.
[4] Philippe Makowski, Arne Thomas, *Energy & Environmental Science,* **2009**, 480–490.

Screening Alkaline Earth Metal Catalysts for Hydrogenation of Alkenes using Molecular Volcano Plots

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Hydrogenation of unsaturated bonds is one of the most fundamental transformations in chemistry and finds broad applications in all scales of chemical production. With the conventional hydrogenation catalysts utilizing rare, expensive and often toxic transition metals, there exists a great incentive for chemists to find cheaper and environment-friendly alternatives. In this context, particularly significant is the recent development of the alkaline earth metal amides (AeN''2: Ae=Mg, Ca, Sr, Ba, N''= N(SiMe3)2) as effective hydrogenation catalysts for various alkenes and imines [1]. Although combined experimental-computational studies by Bauer *et al.* demonstrated the ability of the AeN''2 complexes to effect hydrogenation, a comprehensive understanding on how to tailor the activity of these catalysts currently does not exist. Here, we use linear scaling relationships and molecular volcano plots to determine the potential of the alkaline earth metal-based catalysts for hydrogenation of alkenes. The crucial role of the central metal ions, as well as the associated ligands on the energetics of the catalytic hydrogenation cycle, is also revealed. Our findings highlight how molecular volcano plots [2,3] can be utilized for the rapid screening of prospective alkaline earth metal-based catalysts to establish a guideline to achieve a maximum activity in facilitating the hydrogenation process.

[1] Heiko Bauer, Mercedes Alonso, Christian Fischer, Bastian Rosch, Holger Elsen, and Sjoerd Harder, *Angewandte Chemie International Edition*, **2018,** 57(46), 15177-15182
[2] Michael Busch, Matthew D. Wodrich, and Clemence Corminboeuf, *Chemical Science*, **2015**, 6(12), 6754-6761
[3] Matthew D. Wodrich, Boodsarin Sawatlon, Ephrath Solel, Sebastian Kozuch, and Clemence Corminboeuf, *ACS Catalysis,* **2019**, Just Accepted

Noncovalent Interactions Drive the Efficiency of Mo Imido Alkylidene Catalysts for Olefin Metathesis

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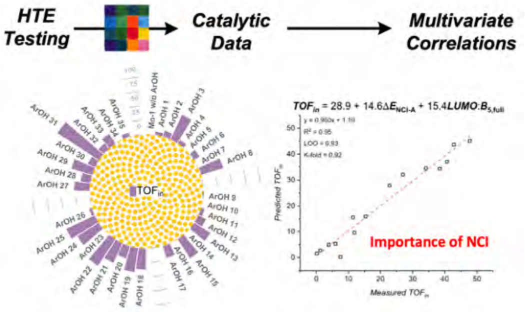
The widespread application of olefin metathesis in various fields of chemical synthesis has fueled the continuous search for catalysts with enhanced activity.[1] Well-defined tungsten and molybdenum imido alkylidene complexes bearing alkoxy ligands are classical Schrock-type catalysts for olefin metathesis.[2] In addition to the development of more active catalysts, the search for catalysts with enhanced selectivity (Z/E) or stability against deactivation remains a major challenge in the olefin metathesis field.[3]

Herein, we describe a high-throughput experimental (HTE) approach to identify active, in-situ-generated molybdenum alkylidene complexes tested for a prototypical metathesis reaction, the homodimerization of 1-nonene. The HTE methodology is integrated with multivariate statistical modelling strategies that guide the search for highly efficient catalysts.



High-throughput experimentation for identification of active catalysts in homodimerization of 1-nonene.

[1] Higman, C. S.; Lummiss, J. A. M.; Fogg, D. E. *Chem., Int. Ed.* **2016**, 55, 3552.
[2] Grubbs, R. H., Ed.; Handbook of Metathesis; Wiley-VCH: Weinheim, Germany, **2015**.
[3] (a) Mougel, V.; Santiago, C. B.; Zhizhko, P. A.; Bess, E. N.; Varga, J.; Frater, G.; Sigman, M. S.; Copéret, C. *J. Am. Chem. Soc.* **2015**, 137, 6699. (b) Santiago, C. B.; Guo, J.-Y.; Sigman, M. S. *Chem. Sci.*, **2018**, 9, 2398.

Exploring the role of secondary metals in the selective hydrogenation of CO_2 at supported palladium nanoparticles - an SOMC approach

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The mitigation/utilisation of anthropogenic CO_2 emissions represents a huge challenge in the modern world.[1] Efficient conversion of CO_2 to fuels and feedstock chemicals provides an appealing potential solution to this problem.[2] To this end, we have chosen to exploit the unique reactivity of supported palladium-containing nanoparticles, which are reported to be proficient in both CO_2-to-methanol ($PdIn@SiO_2$, $PdZn@SiO_2$),[3,4] and the conversion of CO_2-to-C_{2+} alcohols ($PdCu@MO_2$).[5] However, the characterisation of complex bimetallic systems (information regarding molecular-level structure of nanoparticle, metal segregation, core-shell structure etc), alongside the behaviour of the material in dynamic systems, and the role of specific components in catalysis makes them difficult to understand/improve in a rational manner. Our current work highlights the unique role of mixed metal nanoparticles, and the divergent reactivity when compared to their monometallic counterparts.

Using a surface organometallic chemistry (SOMC) approach, we are able to generate well-defined, uniform materials as model systems.[6] The use of tailored organometallic precursors confers control of composition and metal distribution, and sequential grafting of metal ions offers unique insight into the role of each component in mono-, bi- and trimetallic systems. This methodology can be applied to a range of composite systems ($Pd@MO_2$, $PdM'@MO_2$ etc), allowing direct comparison of different secondary metals, and providing opportunity to probe the role of alloying in the reactivity of these systems. The versatility of this approach also allows us to delineate bulk and surface support effects by comparing tailored supports to bulk oxides (e.g. $Pd/M@SiO_2$ and $Pd@MO_2$), aiding the development of tailored catalytic systems and offering insight into the role of each material component (oxygen vacancies, Lewis acid sites, bulk → surface migration of metal ions in reducible supports etc). The material properties of these systems can then be probed using various techniques (*in situ* and *ex situ* spectroscopies, materials characterisation techniques, imaging and catalytic tests) and correlations can be made – further aiding rational catalyst design.

[1] A. Goeppert, M. Czaun, J.-P. Jones, G. K. Surya Prakash, G. A. Olah, *Chem. Soc. Rev.* **2014**, *43*, 7995–8048.
[2] A. Álvarez, A. Bansode, A. Urakawa, A. V Bavykina, T. A. Wezendonk, M. Makkee, J. Gascon, F. Kapteijn, *Chem. Rev.* **2017**, *117*, 9804–9838.
[3] A. García-Trenco, A. Regoutz, E. R. White, D. J. Payne, M. S. P. Shaffer, C. K. Williams, *Appl. Catal. B Environ.* **2018**, *220*, 9–18.
[4] J. Araña, N. Homs, J. Sales, J. L. G. Fierro, P. de la Piscina, *Catal. Letters* **2001**, *72*, 183–189.
[5] S. Bai, Q. Shao, P. Wang, Q. Dai, X. Wang, X. Huang, *J. Am. Chem. Soc.* **2017**, *139*, 6827–6830.
[6] C. Copéret, A. Comas-Vives, M. P. Conley, D. P. Estes, A. Fedorov, V. Mougel, H. Nagae, F. Núñez-Zarur, P. A. Zhizhko, *Chem. Rev.* **2016**, *116*, 323–421.

Atomic-Scale Engineering of Indium Oxide Promotion by Palladium for Maximized and Stable Methanol Production via CO_2 Hydrogenation

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The conversion of CO_2 into energy carriers is regarded as an essential measure to combat global warming in the short term. In_2O_3 has been discovered as a breakthrough system for green methanol synthesis due to its high selectivity and stability.[1] Aiming at enhancing its activity, promotion with the H_2-splitter palladium led to partial success since palladium nanoparticles mediate the parasitic reverse water-gas shift (RWGS) reaction, reducing selectivity, and sinter or alloy with indium, limiting metal utilization and robustness. Here, we show that low-nuclearity palladium clusters bound to the active ensembles curtail these drawbacks. We successfully produced In_2O_3 featuring palladium atomically dispersed in the oxide matrix by coprecipitation, which shows a stable activity enhancement compared to bulk In_2O_3 exclusively directed to methanol production (**Figure 1**, left). This contrasts the decaying improvement of both methanol and CO formation over a benchmark system comprising palladium nanoparticles attained by dry impregnation. In-depth characterization by a battery of techniques, including solid-state ^{115}In NMR, introduced as a novel method to elucidate vacancy formation and short-range crystallinity in (Pd-promoted) In_2O_3 catalysts, and extensive theoretical modeling uncovered that embedding one Pd atom in the oxide matrix enables a controlled growth of the extra-lattice atoms, leading to the stabilization of low-nuclearity palladium clusters that improve H_2 dissociation and water desorption. Their small size is crucial to avoid the onset of the RWGS reaction on palladium sites, which is relevant already for clusters of 3 extra-lattice promoter atoms (**Figure 1**, right). The easy water removal avoids sintering of the In_2O_3 crystals, due to coalescence of surface hydroxide groups. Our atomic engineering of promotion unlocks a record sustained methanol productivity ($0.96\ g_{MeOH}\ g_{cat}^{-1}\ h^{-1}$) at high selectivity and conversion and impressively short residence times, implying strong economic and ecological benefits for a prospective process and holding potential for tailoring new or existing promoted systems in other applications.

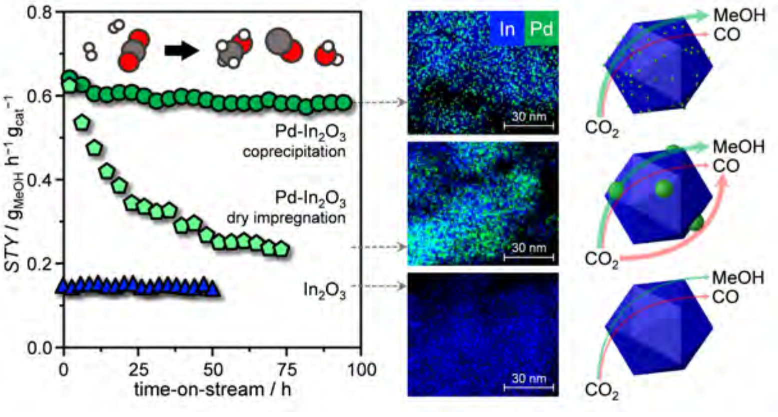

Figure 1 Methanol space time yield (*STY*) versus time-on-stream over Pd(0.75 wt.%)-In_2O_3 catalysts and pure In_2O_3 during CO_2 hydrogenation at 553 K, 5 MPa, and H_2:CO_2 = 4. EDX maps of In and Pd and representation of the distinct promotional effect of palladium for the same catalysts after equilibration.

[1] O. Martin, A. J. Martín, C. Mondelli, S. Mitchell, T. F. Segawa, R. Hauert, C. Drouilly, D. Curulla-Ferré, J. Pérez-Ramírez, *Angew. Chem. Int. Ed.* **2016**, 55, 6261.

Superior performances of Fe-FER compare to Fe-ZSM5 in NO_x and N_2O abatements

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Nitric acid is one of the most produced commodity worldwide. It is mainly used as a strategical chemical for the synthesis of fertilizers and in 2013 the production reached 78 million tons[1] [2]. In recent years, the higher awareness in the greenhouse effect and in the environmental pollution, have highlighted the importance of a new development in the nitric acid tail gas treatment, especially concerning the N_2O and NO_x species [1]. Many metal oxide and zeolite catalysts have been developed for N_2O and NO_x abetment, each one with benefits and drawbacks. The state of the art materials are based on Fe-zeolites which both show NO_x and N_2O abatement with the same catalyst. Many Fe zeolites have been explored, such as Ferrierite (FER), ZSM5 and BEA [3]. In this paper, the comparison of fresh and laboratory aged Fe-FER and Fe-ZSM5 industrial catalysts, both supplied by ALSYS, has been carried out. Fe-FER catalyst is a proprietary catalyst of CASALE and ALSYS and is used in nitric acid plants [4]. The results from field and laboratory showed that Fe-FER will allow customers to benefit from a higher catalytic activity and greater stability compare to the current commercial solution with Fe-ZSM5. The extruded catalysts tested were prepared at industrial scale, from process production to quantity scale, by ALSYS. The catalytic tests were carried out in an Inconel reactor under industrial nitric acid plant conditions. The feed compositions are reported in figure 1 caption. The GHSV used was 25,000 h^{-1}. Very high space velocity was chosen with the purpose to highlight the differences in catalytic activity among the catalysts tested. The detector used was FT-IR coupled with a lambda probe for oxygen measurement.

In this work, representative industrial catalysts were investigated in industrial conditions before and after severe aging treatments. Results showed that Fe-FER is the most stable catalyst and high performance that can be used for tail gas treatment in nitric acid plants. Moreover Fe-FER is extremely selective in N_2 even after severe aging while the Fe-ZSM5 exhibited a larger undesired N_2O formation. The Fe-FER catalyst for DeN_2O and $DeNO_x$ applications has superior performances compared to the Fe-ZSM5.

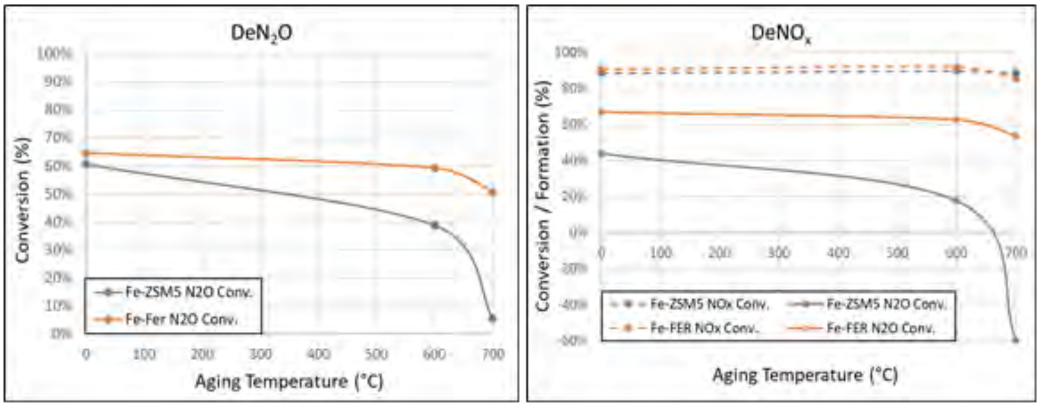

Figure 1. (Left) deN_2O condition: NO 70 ppm, NO_2 30 ppm, N_2O 900 ppm, O_2 3.0%, H_2O 0.3% and N_2 balance. (Right) $deNO_x$ condition: NO 325 ppm, NO_2 325 ppm N_2O 40 ppm NH_3 650 ppm, O_2 3.0%, H_2O 0.3% and N_2 balance.

[1.] Thiemann, E. et al., *Ullmann's Encycl. Ind. Chem.* Vol. 24, vol. **2003**, Vol 24. 177-223.
[2.] A. Grande et al., *Ind. Eng. Chem. Res.*, vol. 57, no. 31, pp.**2018**, 10180–10186.
[3.] Skalska, J. S. Miller, S. Ledakowicz, *Sci. Total Environ.*, vol. 408, no. 19, **2010,** pp. 3976–3989.
[4.] Hamon, D. Le Guern, O. Le Lamer, L. Navascues, EP1918016B1, **2006**.

Fabrication and in situ heating TEM studies of a recyclable manganese oxide based anode for water oxidation

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Electrochemical water splitting to H_2 and O_2 is a promising method to replace petroleum fuels with hydrogen gas, as a clean fuel for a sustainable energy future. According to its high thermodynamic and kinetic barriers, water oxidation half-reaction is the bottleneck of this process. Therefore, an efficient catalyst is needed to lower these barriers and rise the water-splitting rate. In nature, a $CaMn_4O_5$ in photosystem II is responsible for oxidation of water.[1] Hence, this cluster has attracted grate attention as a blueprint to design and synthesize of efficient water oxidizing molecules or metal oxides especially manganese-based catalysts.[2,3] Earth abundancy, environmentally friendly and low-cost of manganese oxides make them well-suited materials for water oxidation. In this work, we have developed an inexpensive and recyclable manganese oxide-based anode for water oxidation at pH=7. The fabricated electrodes were calcined at different temperatures and the differences in water oxidation ability among these catalysts were probed using X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS). Formation path of manganese oxide film and effect of calcination on its structural properties have been studied with an in-situ heating TEM. The most active catalyst showed a stable current density of 1.0 $mA.cm^{-2}$ at an over potential of 480 mV for more than 4 days. Even greater current densities of 9 and 13 $mA.cm^{-2}$ have been achieved at 1.4 and 1.5 V (vs. Ag|AgCl), respectively.

[1] Yasufumi Umena, Keisuke Kawakami, Jian-Ren Shen, Nobuo Kamiya, *Nature,* **2011,** 473, 55-60.
[2] Fangyuan Song, René Moré, Mauro Schilling, Grigory Smolentsev, Nicolo Azzaroli, Thomas Fox, Sandra Luber, Greta R. Patzke, *J. Am. Chem. Soc.* ***2017.*** 139, 14198–14208.
[3] Mohammad Mahdi Najafpour, Gernot Renger, Małgorzata Hołyńska, Atefeh Nemati Moghaddam, Eva-Mari Aro, Robert Carpentier, Hiroshi Nishihara, Julian J. Eaton-Rye, Jian-Ren Shen, and Suleyman I. Allakhverdiev, *Chem. rev*. **2016.** 116, 2886–2936.

Biogas from microbial electrolysis

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Domestic wastewater and remaining sludges from the sewage treatment contains valuable chemical energy, which can be harvested as electricity or biogas by bioelectrochemical systems (BES) [1]. In these systems, electrogenic microorganisms are key-players as they catalyze the oxidation of organic compounds and release free electrons to the system. Among BES, microbial electrolysis cell (MEC) system boosts methane or hydrogen formation by the application of external potential between anode(s) and cathode(s) [2]. In the renewable energy era, surplus in electrical wind and solar energy could therefore be invested through this system in the production of easily stored biogas [3].

In our study, two MEC reactors with a capacity of 50 L were built to produce biogas at room temperature from waste sludge (wastewater treatment plant from Châteauneuf, VS). Several applied voltages (0 to 4.0 V) were tested in order to optimize biogas formation in term of production rates and methane concentration. In all set-ups, the energy recovered as methane overcame the supplied electrical energy. Moreover, the biogas formed in the MEC reactors had higher methane concentrations compared with the biogas formed in our reference WWTP anaerobic digester, heated at 37°C. Increasing the applied voltage increased the rates of biogas production, but had a negative impact on the overall methane concentration. Novel microbial electrolysis cell systems can contribute to save energy in wastewater treatment processes, reduce carbon dioxide emission and act as intermediate storage for surplus electricity.

[1] Hubertus V. M. Hamelers, Annemiek Ter Heijne, Tom H. J. A. Sleutels, Adriaan W. Jeremiasse, David P. B. T. B. Strik and Cees J. N. Buisman, *Applied Microbiology and Biotechnology*, **2010**, 85, 1673-1685.
[2] Marc Sugnaux, Manuel Happe, Christian P. Cachelin, Andrea Gasperini, Maxime Blatter and Fabian Fischer, *Chemical Engineering Journal*, **2017**, 324, 228-236.
[3] Adriàn Escapa, Raul Mateos, Elia J. Martínez and Jorge Blanes, *Renewable and Sustainable Energy Reviews*, **2016**, 55, 942-956.

Efficient reductive amination of HMF with well-dispersed Pd nanoparticles immobilized in a porous MOF/polymer composite

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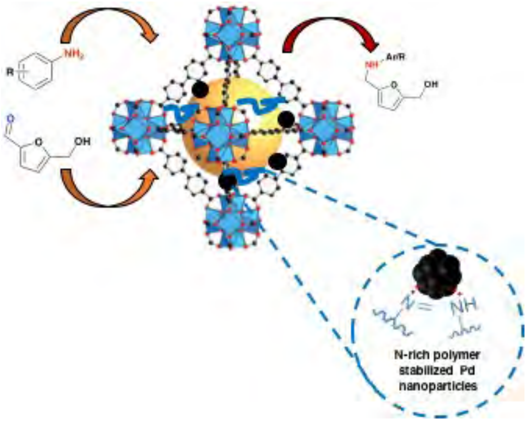
Aminated derivatives of 5-hydroxymethylfurfural (HMF) and furfural are envisioned to be critical intermediates for the pharmaceutical industry. The state-of-the-art catalysts currently used for the conversion of HMF and furfural are mostly homogeneous in nature, motivating the design of recyclable, heterogeneous catalytic systems. In this work, we report a palladium functionalized MOF/polymer composite catalyst [Figure 1] for the reductive amination of HMF under mild conditions. The catalyst shows excellent conversion (>99%) and selectivity (>99%), which is maintained over a significant number of reaction cycles. It is thought that the origin of the catalyst recyclability lies in preventing the aggregation and leaching of the palladium nanoparticles. This is achieved through the development of a novel method to introduce poly-para-phenylenediamine (PpPDA) into a MOF structure via in-situpolymerization. In order to understand the true stability of the catalyst, the kinetics of the HMF conversion is also probed over 15 cycles. To the best of our knowledge, this is the first report of a MOF based catalyst that illustrates a significant kinetic and thermodynamic recyclability coupled with a high activity and selectivity for the reductive amination of 5- HMF under mild reaction conditions.



Vikram V. Karve et. al., submitted, **2019**.

Sorption-enhanced steam methane reforming over Ru/$Ca_3Al_2O_6$-CaO bi-functional catalyst-CO_2 sorbent for the production of high purity hydrogen

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The sorption-enhanced steam methane reforming (SE-SMR) allows to produce high purity hydrogen by combining the steam methane reforming (SMR), water-gas shift reaction (WGS) and a CO_2 abstraction reaction ($CH_4 + 2H_2O + CaO \leftrightarrows 4H_2 + CaCO_3$, $\Delta H = -13$ kJ/mol).[1] The SE-SMR process operates with alternating SE-SMR/sorbent regeneration cycles, requiring a CO_2 sorbent with high and stable CO_2 uptake in the temperature range of interest (500–900 °C), and highly active catalysts for SMR.[2] To this end, we developed a bifunctional catalyst-sorbent, via a citrate sol-gel route, that contains CaO as the solid CO_2 sorbent, a structural stabilizer ($Ca_3Al_2O_6$) and Ru nanoparticles (~5 nm, 3 wt. %), formed upon reduction in H_2 from a $CaRuO_3$ phase. The developed material, Ru/$Ca_3Al_2O_6$-CaO, was found to outperform significantly the benchmarks Ni-CaO and Ru/limestone in terms of yield of high-purity hydrogen, coke resistance and cyclic stability. The highly active Ru nanoparticles for the SMR allowed to maximize the weight fraction of the CO_2 sorbent, CaO, with respect to Ni-CaO. In addition, we demonstrate that the material Ru/$Ca_3Al_2O_6$-CaO developed was very stable over multiple SE-SMR/regeneration cycles. The $Ca_3Al_2O_6$ stabilized effectively the material against sintering leading to the improved cyclic stability with respect to Ru/CaO.

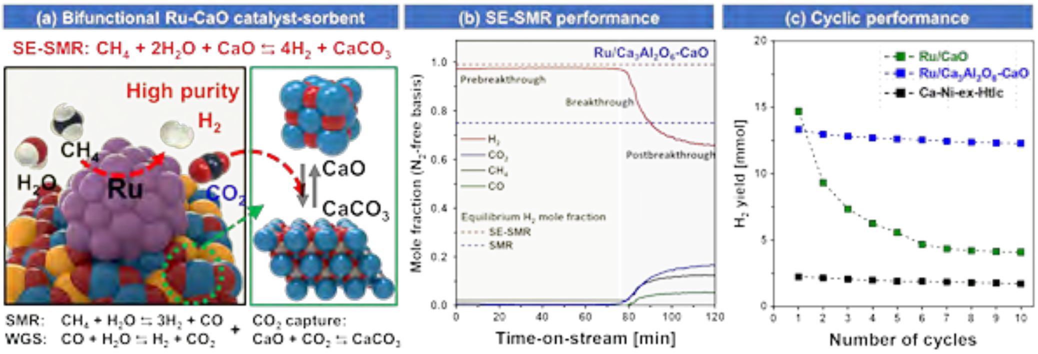

Figure 1. (a) Schematic representation of the SE-SMR over bifunctional Ru-CaO catalyst-sorbent. (b) Off-gas composition on SE-SMR test on Ru/$Ca_3Al_2O_6$-CaO in the 1st cycle. (c) The H_2 yield in the prebreakthrough as a function of number of repeated SE-SMR-regeneration cycles

[1] A. Lopez Ortiz and D. P. Harrison, *Ind. Eng. Chem. Res.* **2001,** 40, 5102-5109.
[2] A. Iulianelli, S. Liguori, J. Wilcox, A. Basile, *Catal. Rev.* **2016,** 58, 1-35.

Copper-exchanged omega (MAZ) zeolite: morphology dependent conversion of methane to methanol

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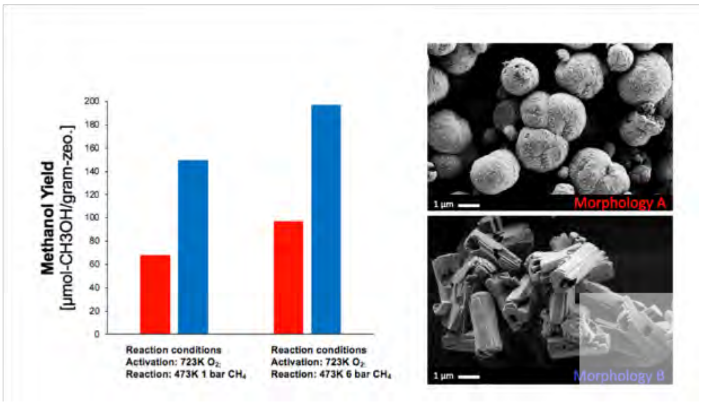
[1]ETH Zürich, [2]Paul Scherrer Institut

During petroleum extraction, methane often accompanies crude oil as it is carried to the surface. Utilizing this methane is not always economically feasible due to the high costs of transportation. Depending on local environmental regulations and economics of transportation, this methane is released into the atmosphere, combusted (flared), or reinjected. One proposed alternative is to utilize this methane by converting it to more easily transportable products like methanol.[1]

Direct conversion of methane to methanol has been observed when a stepwise process is applied over copper-exchanged zeolites.[1] Over the course of the past 15 years of research on this topic, the methanol yield has steadily increased.[1-5] However, certain inconsistencies remain: there are a wide range of methanol yields, proposed active sites,[1,2] and observed differences in the oxidation and reduction of the copper.[3] Here we have explored one of the most promising zeolites for this important conversion, copper-exchanged omega zeolite (**MAZ**).[4] By taking a zeolite synthesis approach, we observe that different synthesized morphologies result in large differences in the methanol yield despite having similar Si/Al, aluminum T-site occupancy, copper speciation (FTIR and EXAFS), and XRD.[5]



Since most groups tackling the methane to methanol problem work on differently sourced zeolites, the wide range of methanol yields and observations may be at least partially explained by differences in the parent zeolite. This work shows that care should be taken when selecting a parent zeolite for such studies, but more importantly it highlights the opportunity that the zeolite itself has for optimizing this process.

[1] Groothaert, M. H., Smeets, P. J., Sels, B. F., Jacobs, P. A., Schoonheydt, R. A. *Am. Chem. Soc.,* **2005**, 127, 1394.
[2] Grundner, S., Markovits, A. C., Li, G., Tromp, M., Pidko, E. A., Hensen, E. J. M., Jentys, Sanchez-Sanchez, A. M., Lercher, J. A. *Nat. Commun.,* **2015,** 6, 7546.
[3] Knorpp, A. J., Newton, M. A., Pinar, A. B., van Bokhoven, J. A. Ind, Eng. Chem. Res., **2018**, 57, 12036.
[4] Knorpp, A. J., Pinar, A. B., Newton, M., Sushkevich, V. L., van Bokhoven, J. A., *ChemCatChem,* **2018**, 10, 5593.
[5] Knorpp, A, J., Newton, M. A., Sushkevich, V. L., Zimmermann, P. P., van Bokhoven, J. A., Catal. *Sci. Technol.,* **2019**, Accepted.

Ru-modified zeolite catalyzed indirect CO_2 methanation: Hydrogenolysis of cyclic carbonates

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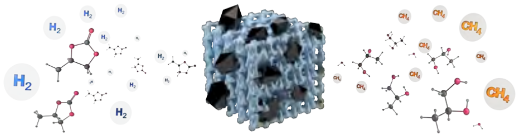
Efficient methane and propylene glycol production are achieved through hydrogenolysis of propylene carbonate with the employment of ruthenium-modified zeolite under solvent-free conditions.[1] High product selectivity together with the heterogeneous Ru catalyst minimizes post-treatments prior to the use of resulting liquid- and gas-products (water-containing glycol as an anti-freeze solution and hydrogen-enriched methane as an energy carrier).[2] Additionally, investigations on catalytic performance after multiple cycles showed no significant aging effects. This hydrogenolysis process of carbonates (CO_2 fixation chemicals) binds energy storage section and chemical synthesis domain sustainably.[3]



[1] Lee, W. T.; van Muyden, A. P.; Bobbink, F. D.; Huang, Z.; Dyson, P. J.,*Angew. Chemie - Int. Ed.* **2019**, *58* (2), 557–560.
[2] Jones, D. R.; Al-Masry, W. A.; Dunnill, C. W., *Sustain. Energy Fuels* **2018**, *2*, 710–723.
[3] Milligen, Han van ;VanderWilp, Brian; Wells, G. J., *Shell Glob. Solut.* **2016**, 1–12.

The activity of single atoms and particles in steam-treated Pt/CeO_2 catalyst studied with in situ ambient X-ray photoelectron spectroscopy

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[1]Laboratory for Catalysis and Sustainable Chemistry

In situ ambient X-ray photoelectron spectroscopy (AP-XPS) was used to elucidate the active sites and mechanistic steps associated with the CO oxidation reaction over high-temperature steam-treated Pt/CeO_2 catalysts.[i] Our results suggest that cationic Pt^{2+} is the exclusive active site on the “as synthesized” Pt/CeO_2 catalyst while metallic Pt^0 sites, which are the likely active species for the higher CO oxidation activity, are detected after steam treatment. The ceria support has an active role in the reaction, displaying reversible reduction-oxidation behavior under different reaction conditions. We introduced in situ time-resolved[ii] measurements to quantitatively follow the fraction of Ce^{3+} and Ce^{4+} as a function of the reaction temperature and gas environment. The kinetic rates of ceria oxidation and determine the ceria reduction degree under reaction conditions and their role in the reaction mechanism are established.

[1] Nie, L.et al, *Science,* **2017,** *358* (6369), 1419-1423.
[2] Artiglia L, et al, *The Journal of Physical Chemistry Letters*, **2017,** 8(1):102-8.

Dynamic role of molecular cocatalysts on hematite photoanodes for water oxidation

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Loading of cocatalysts is one of the most efficient way to promote the performance of photoelectrodes, while the understanding of their functionality is rather limited. We employed the well-defined cobalt-based molecular cocatalysts on hematite surfaces as the model system, systematic photoelectrochemical analysis revealed an interesting dynamic function of these loaded cocatalysts. Basically, their role changed from hole collectors at lower bias to catalytic centers at higher bias. Kinetic analysis indicated that the function transition originated from the dynamic equilibria of surface charge carriers. The functional transition of the cocatalysts and the related kinetic properties could be reproduced by many other cobalt based molecular and heterogeneous catalysts, indicating the wide applicability of the observed phenomenon. Our conclusions here could help to clarify the long-debating 'cocatalysts function', and inspire the design of efficient photoelectrode for a wide range of applications.

Laskowski, F. A. L.; Nellist, M. R.; Qiu, J.; Boettcher, S. W. *J. Am. Chem. Soc.* **2019**, *141*, 1394–1405

Uncovering the interfacial carrier dynamics in emerging photoelectrodes for solar fuel production – an operando spectroelectrochemical study

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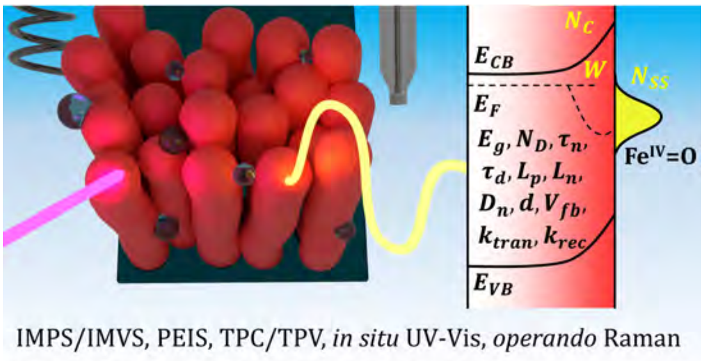
Storing solar energy in chemical form (*e.g.* hydrogen from water splitting), represents a promising route to enable a carbon-neutral society. Photoelectrochemical (PEC) water splitting holds the key to perform this process with simplicity and at high theoretical conversion efficiency. However, the realization of PEC H_2 production at a global scale is limited by the current performance of semiconductor materials suitable for PEC. To advance the field, an improved fundamental understanding of the semiconductor-liquid junction (SCLJ), wherein the photoelectrosynthetic reaction is occurring, is urgently needed to identify the parameters limiting the performance and direct actions for their improvement.



Here, we show how a toolbox of *operando* and *in situ* characterization techniques, namely, intensity-modulated photocurrent/photovoltage spectroscopy (IMPS/IMVS), transient photocurrent/photovoltage spectroscopy (TPC/TPV), photoelectrochemical impedance spectroscopy (PEIS), *in situ* UV-Vis spectroscopy, and *operando* Raman spectroscopy can be used to gain deep insight of the competing processes at the SCLJ. We highlight our recent studies with emerging semiconducting photoelectrodes ($CuIn_{0.3}Ga_{0.7}S_2$, $CuFe_2O_4$,[1] $ZnFe_2O_4$,[2] SnS_2,[3] and $LaFeO_3$), which have provided insights into the interfacial carrier behavior, *i.e.*, energetic across the interface, kinetics of charge transfer and recombination, nature of the surface states, and chemical identity of intermediate species. In particular, we implement light modulation techniques (IMPS/IMVS) on $CuFe_2O_4$ to reveal an unfavourable kinetic competition which significantly hampers the charge transfer efficiency. Likewise, by fitting the impedance response with equivalent circuits, a clear map of the density of surface states is shown. Overall, these findings provide a better understanding on the electrochemical phenomena at the SCLJ, establishing a precise roadmap to engineer the interface and optimize the performance of solar fuel devices.

[1] Yongpeng Liu, Florian Le Formal, Florent Boudoire, Liang Yao, Kevin Sivula, Néstor Guijarro, *Journal of Materials Chemistry A*, **2019**, 7, 1669-1677.
[2] Xiaodi Zhu, Néstor Guijarro, Yongpeng Liu, Pascal Schouwink, Rebekah A. Wells, Florian Le Formal, Song Sun, Chen Gao, Kevin Sivula, *Advanced Materials*, **2018**, 30, 1801612.
[3] Yong Zuo, Yongpeng Liu, Junshan Li, Ruifeng Du, Xiaoting Yu, Congcong Xing, Ting Zhang, Liang Yao, Jordi Arbiol, Jordi Llorca, Kevin Sivula, Néstor Guijarro, Andreu Cabot, *ACS Applied Materials & Interfaces,* **2019**, 11, 6918-6926.

Impact of Carrier Acidity on the Conversion of Syngas to Higher Alcohols over Zeolite-Supported Copper-Iron Catalysts

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The development of catalysts showing satisfactory performance to realize a large-scale synthesis of higher alcohols (HA) *via* CO hydrogenation, which promises higher sustainability compared to current industrial routes, is hindered by limited fundamental understanding.[1] In this contribution, the impact of acidity of MFI-type zeolite carriers on the properties of CuFe catalysts was elucidated. Introducing Brønsted acidity into the support, while mostly retaining metals structure and morphology, dramatically altered activity and selectivity, inducing a strong shift in the HA composition from primary to secondary alcohols. Individual feeding of methanol, mixtures of selected primary and secondary alcohols, and hydrocarbons over an acidic zeolite unravelled the intricate network of reactions occurring in parallel and consecutively (**Figure 1**). Secondary HA originated from the hydration of olefins, formed through the parasitic Fischer-Tropsch synthesis, as well as from dehydration of primary HA generated followed by rehydration. Still, olefins also underwent coupling reactions with subsequent hydrogenation and cracking to paraffins. K as a promoter was incorporated by ion exchange, deposition, or their combination, whereby the second was superior and increased the HA selectivity over CuFe/silicalite to 43%. The CO_2 selectivity was outstandingly minimized to 2%. Finally, the HA productivity was boosted by operating a zeolite with tuned acidity in series to a catalyst producing a high fraction of olefins.[2] The combination of the two systems favored the hydration of the latter and dominated over other parallel reactions, leading to a state-of-the-art space-time yield of HA of 0.61 $g_{HA}\ h^{-1}\ g_{cat}^{-1}$ at a HA selectivity of 45%.

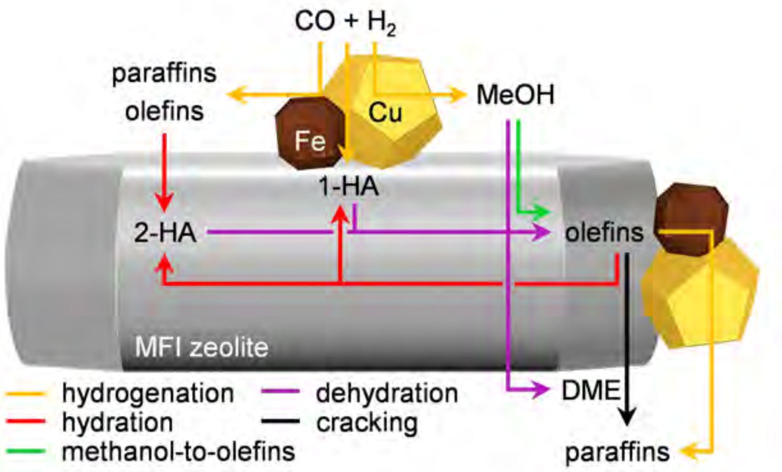

Figure 1 Reaction network for higher alcohols synthesis over copper-iron catalysts supported on acidic MFI zeolites.

H. T. Luk, C. Mondelli, D. Curulla Ferré, J. A. Stewart, J. Pérez-Ramírez, *Chem. Soc. Rev*. **2017**, 46, 1358.
H. T. Luk, C. Mondelli, S. Mitchell, D. Curulla Ferré, J. A. Stewart, J. Pérez-Ramírez, *J. Catal.* **2019**, 371, 116.

Revising the mechanism of the catalytic ethanol oxidation

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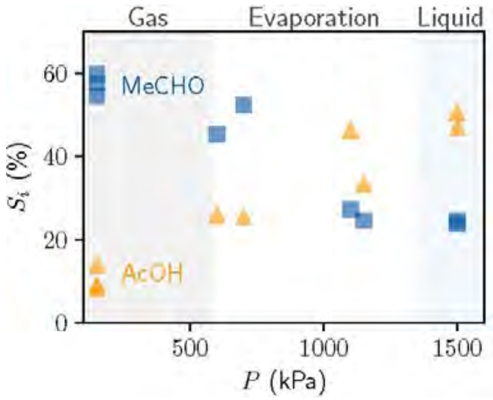
The aerobic oxidation of aqueous bioethanol is an environmentally-friendly route for the production of acetic acid at large scale, reducing our dependency on fossil feedstocks. Au/TiO_2 is relatively selective to acetic acid but also produces large quantities of by-products. High selectivity could be achieved by improved catalyst designs, which requires a deeper understanding of the reaction mechanism.[1-3] Ethanol to acetic acid consists of two key steps: dehydrogenation of ethanol to acetaldehyde and oxidation of acetaldehyde to acetic acid.[2] Experimentally, the second step was observed primarily in the liquid-phase of aqueous ethanol. The phenomenon was attributed to the presence of water and a mechanism where the gold sites become more active when covered by hydroxides.[4] However, the above mechanism was determined under strongly alkaline solution, which makes it unrelatable to the typical ethanol-to-acetic acid reaction conditions, i.e. pH-neutral ethanol solutions.[1-3] Hence, the research field still necessitates a more universally applied reaction mechanism. Herein, we studied the criteria for acetaldehyde oxidation as part of the overall mechanism of the oxidation of ethanol and its effect of the product selectivity.



The study of the acetaldehyde oxidation, under the same reaction conditions as typical ethanol oxidation, revealed that the reaction proceeds independently of the presence of the catalyst. The reaction mechanism was experimentally attributed to the formation of radicals, similarly to the non-catalytic oxidation of aromatic aldehydes.[5] Further studies revealed the criteria for the non-catalytic acetaldehyde oxidation: operation in liquid-phase and the presence of both water and oxygen. We further established the relation between the catalytic oxidation of ethanol and the radical-driven, non-catalytic oxidation of acetaldehyde by altering the criteria required for the later. When operating in gas-phase, even in excess of water and oxygen, Au/TiO_2 did not oxidise the intermediate acetaldehyde to acetic acid (figure). Hence, in the overall catalytic oxidation of aqueous ethanol, supported gold catalysed only the oxidative dehydrogenation of ethanol to acetaldehyde, which is subsequently oxidised in the liquid phase to acetic acid.
These findings challenge the established catalytic ethanol oxidation mechanism, which could also have implications on the oxidation of other primary alcohols. Our study provides a deeper understanding of the interplay between catalytic and non-catalytic reaction steps and outlines guiding principles for the design of new and more selective alcohol oxidation catalysts.

[1] C. H. Christensen, et al., *Angew. Chem. Int. Ed.* **2006**, *45*, 4648–4651.
[2] B. Jørgensen, S. Egholm Christiansen, M. L. Dahl Thomsen, C. H. Christensen, *J. Catal.* **2007**, *251*, 332–337.
[3] S. Mostrou, T. Sipcz, A. Nagl, B. Fodi, F. Darvas, K. Föttinger, J. A. Van Bokhoven, *React. Chem.*

Eng. **2018**, *3*, 781–789.
[4] B. N. Zope, D. D. Hibbitts, M. Neurock, R. J. Davis, *Science* **2010**, *330*, 74–78.
[5] K. J. Liu, et al., *ACS Sustain. Chem. Eng.* **2018**, *6*, 4916–4921.

Defect-induced enhanced activity in Ce-substituted $La_{0.6}Sr_{0.4}MnO_{3\pm\delta}$, a promising perovskite redox material class for solar thermochemical CO_2 splitting

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Solar thermochemical CO_2/H_2O splitting has the potential to generate industrial-scale quantities of synthetic liquid fuels while simultaneously curbing greenhouse gas emissions. Thermochemical pathway utilize concentrated solar radiation as a source of high-temperature process heat to split CO_2 and H_2O into CO and H_2 (*syngas*), a precursor for synthetic liquid hydrocarbon fuels. The two-step thermochemical temperature-swing cycle involves an endothermic reduction step of a redox metal oxide at high temperatures (1773 K), generating oxygen vacancies, followed by an exothermic re-oxidation step with CO_2 and H_2O at low temperatures (1273 K). Particularly, non-stoichiometric ceria ($CeO_{2-\delta}$), is considered as the state of the art redox material because of its phase stability, variable Ce^{3+}/Ce^{4+} valence, and rapid kinetics.[**1**] Unfortunately, ceria suffers from low reducibility and demands high-temperatures (>1773 K) to achieve even moderate oxygen non-stoichiometry ($\Delta\delta$).[**2,3**] However, material innovations that can overcome the thermodynamic limitations of the current class of redox material are required to increase efficiencies. Perovskites oxide materials are currently emerging as an alternate class of redox materials, mainly because of its thermodynamic and structural tuning derived through engineered composition. Here, we have identified a novel class of Ce substituted (at A-and B-sites) perovskite redox materials $La_{0.6}Sr_{0.4}MnO_{3\pm\delta}$ (LSM), which can overcome the individual limitations of ceria and perovskites. Amongst them, 25% Ce-substituted $La_{0.6}Sr_{0.4}MnO_3$ displayed 3 times higher reduction extent than pure ceria and 2 times faster reoxidation kinetics than pure LSM perovskite during TGA redox cycling experiments at lower reduction temperatures (1673 K). In addition, comparison of analytical characterizations of redox active materials before and after TGA cycling experiments by XRD, Raman, FT-IR & SEM-EDX elucidate the role of induced defect-states in enhancing the thermochemical CO_2 splitting ability.

[1] C. Chueh, C. Falter, M. Abbott, D. Scipio, P. Furler, S. M. Haile, A. Steinfeld, *Science*, **2010**, 330, 1797–1801.
[2] D. Marxer, P. Furler, M. Takacs, A. Steinfeld, *Energy Environ. Sci.*, **2017**, 10, 1142–1149.
[3] R.Jacot**,** J. Madhusudhan Naik, R. Moré, R. Michalsky, A. Steinfeld, G. R. Patzke, *J. Mater. Chem. A,* **2018**, 6, 5807–5816.

Generation and understanding of low-valent Molybdenum sites towards olefin metathesis

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[1]ETH Zürich

Recent studies have shown more concise evidence of the presence of a Mo(IV) species acting as the pre-catalyst in Olefin metathesis.[1,2] Concurrently, we are investigating the synthetic generation of such species to simultaneously provide further prove of the proposed mechanism and to better understand the underlying redox processes.

To interrogate the redox processes, we have applied both preparative methodologies incorporating chemical reducing agents, as well as electrochemical methodology.

[1] Yamamoto, K.; Chan, K. W.; Mougel, V.; Nagae, H.; Tsurugi, H.; Safonova, O. V.; Mashima, K.; Copéret, C., *Chem. Commun.,* **2018,** 54, 3989-3992
[2] Chakrabarti A.; Wachs I.E., *J. Phys. Chem. C,* **2019,** Article ASAP

Modulated-Excitation Spectroscopy of Cu/SSZ-13: Unraveling the Mechanism of Selective Catalytic Reduction (SCR)

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Cu/SSZ-13 has emerged as a commercial solution for the selective catalytic reduction (SCR) of NO_x in automotive vehicles. Not only does it possess superior activity at low temperature, but it can also resist significant deactivation in the presence of water and hydrocarbons. The scientific literature abounds with spectroscopic investigations of Cu/SSZ-13, but transient response studies have not been utilized fully to extract key mechanistic insights. As a result, many catalytic features of the Cu/SSZ-13 system still remain unresolved. Perhaps one of the most debated ones is the involvement of nitrate species in the catalytic cycle. IR spectroscopy could potentially provide an answer, but this is not straightforward: under SCR conditions, the spectra are dominated by the strong signals of the interaction between NH_3 molecules and the catalyst thus precluding unequivocal identification of other adsorbed species.

To solve this difficulty, we have applied the technique of modulated excitation (ME) and phase-sensitive detection by repeatedly pulsing NO in a gas feed of $NH_3/H_2O/O_2/Ar$ while continuously recording IR spectra. The time-resolved spectra of Cu/SSZ-13 at 200 °C and 300 °C revealed the presence of only adsorbed water and NH_3. In contrast, the phase-resolved spectra provided a much detailed view of the molecular species on the catalyst surface. At 200 °C, adsorbed NH_3, NO^+, and nitrate species were found to be present. A control experiment at this temperature with the metal-free zeolite did not display any change in the nitrate region of the spectra. NO pulses in $H_2O/O_2/Ar$ (i.e., without NH_3) showed no phase-resolved nitrate signal as well. These data suggest that at 200 °C, nitrate can be formed on the catalyst surface and may be important as reaction intermediates. A very different set of phase-resolved spectra was obtained at 300 °C: NH_3 was the only significantly adsorbed species. At this temperature, nitrates are no longer stable and NO probably reacts with NH_3 in a different mechanism.

The depth of this molecular information exceeds what can be provided by conventional IR experiments under steady-state conditions. Therefore, transient-response and ME studies could potentially advance our fundamental understanding of SCR.

Halogen-Mediated Valorization of Methane over Zeolites:Interaction of Halogenated Compounds with MFI

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Catalytic halogenation of methane into halomethanes (CH_3X, X = Cl, Br) followed by their coupling into value-added chemicals and liquid fuels over zeolite catalysts constitutes a 'dream technology' that could transfigure the valorization of abundant natural gas by avoiding the costly and energy-intensive syngas generation.[1] Herein, we performed the first comprehensive evaluation of a large library of carriers, noble metals, metal oxides, chlorides, and oxyflourides supported over different carriers, sulfated systems, and zeolites in chlorination and bromination of methane under practically-relevant conditions. While the bromination rate was almost unaffected by the solids in the whole temperature range (643-723 K), the chlorination activity of different catalyst beds at low temperatures (473-523 K) was 2-5.5 higher compared to the non-catalytic reaction. Zeolites displayed the highest promoting effect in chlorination, which followed a volcano-like dependence on their micropore size. Strikingly, the maximum was achieved for the ZSM-5 micropores, the size of which coincides with the sum of kinetic diameters of methane and chlorine radical (**Figure 1a**) that participate in the rate-limiting step. This along with the marginal impact of Si:Al ratio, counter-ions, and extraframework aluminium species on its catalytic behavior, as well as more prominent performance differences induced by intracrystalline mesoporosity and reduction of crystallite size, indicate that confinement effects are relevant in this reaction. In addition, in-depth characterization of the ZSM-5 catalysts equilibrated in methane halogenation, as well as in pure halogens, hydrogen halides, or CH_3X feeds by a broad set of complementary characterization techniques revealed subtle changes in the speciation of Al sites associated with the coordination of halogenated compounds, which do not affect the long-range crystalline order and are reversible in nature (**Figure 1b,c**). The findings provide fundamental insights into halogen activation by zeolites and pave the way for the practical implementation of halogen-mediated natural gas valorization.

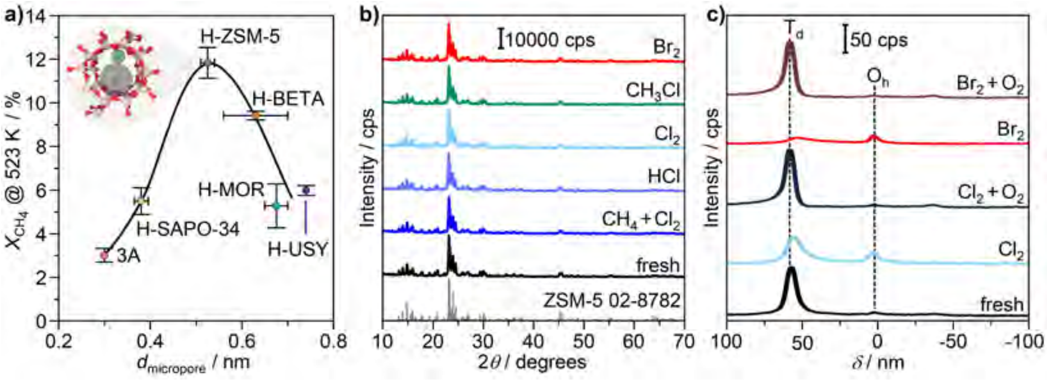

Figure 1 a) Conversion of methane over different zeolites at 523 K as a function of their micropore size. b) X-ray diffraction pattern of ZSM-5 catalysts in fresh form and after equilibration in streams containing different halogen compounds. c) ^{27}Al magic angle spinning nuclear magnetic resonance spectra of ZSM-5 catalysts in fresh form, after equilibration in streams containing molecular halogens (Cl_2, Br_2), and subsequent calcination in air ($Cl_2 + O_2$, $Br_2 + O_2$).

[1] R. Lin, A. P. Amrute, J. Pérez-Ramírez, *Chem. Rev.*, **2017**, 117:4182.

Heterogeneous Olefin Metathesis Catalysts prepared via SOMC: which metal, which ligand for which olefins

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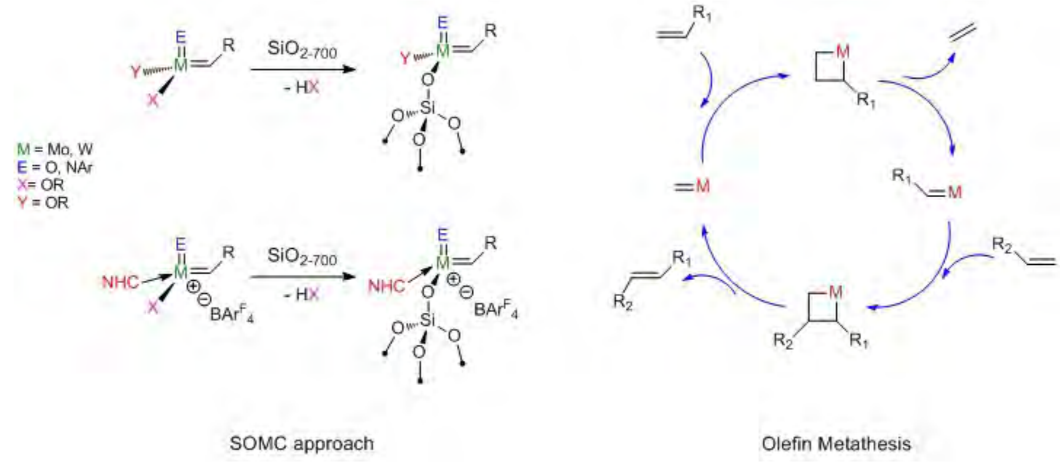
[1]ETH Zurich, [2]ETH Zürich

Olefin metathesis is a key reaction to the formation of new C=C bond, it extremely important both at academia and industrial level and the design of heterogeneous catalysts with high activity and stability is still a challenge. Several well-defined W=NAr, W=O, Mo=NAr alkylidene have been developed as homogeneous and supported systems.[1] While W- and Mo-Imido neutral complexes show similar reactivity towards internal olefins,[2] W Oxo species display greatly improved activity for terminal olefin metathesis,[3] in particular for cationic species containing NHC ligand.[4] After years of research, well-defined Mo-oxo alkylidenes have emerged as a new class of catalyst, once supported, these species show great activity towards both internal and terminal olefins.[5] Here, we present the synthesis of well-defined supported species of all these species and their compared activity in olefin metathesis.



SOMC approach

Olefin Metathesis

[1] R. R. Schrock, *Chem. Rev.,* **2009**, 109 (8), 3211; C. Copéret, F. Allouche, K. W. Chan, M. P. Conley, M. F. Delley, A. Fedorov, I. B. Moroz, V. Mougel, M. Pucino, K. Searles, K. Yamamoto, P. A. Zhizhko, *Angew. Chem. Int. Ed.*, **2018**,130, 2
[2] P. Zhizhko, V. Mougel, J. De Jesus Silva and C. Copéret, *Helvetica Chim. Act.*, **2017**, 101
[3] V. Mougel, M. Pucino and C. Copéret, *Organometallics*, **2015**, 34, 551
[4] M. Pucino, V. Mougel, R. Schowner, A. Federov, M. R. Buchmeiser and C. Copéret *Angew. Chem. Int. Ed.*, **2016**, 55, 1
[5] Margherita Pucino, Feng Zhai, Christopher P. Gordon, Deni Mance, Amir Hoveyda, Richard R. Schrock,Christophe Copéret, *Angew. Chem. Int. Ed.*, in press.

Fast Pyrolysis of Lignin Model Compounds

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Lignin is a highly abundant natural polymer with a structure that makes it an appealing source of fuels and chemicals with low carbon footprint [1,2].

A successful conversion of lignin to value-added products requires optimized depolymerization methods [3,4]. Fast pyrolysis has attracted interest in the last decades as it provides logistical and economic advantages over other thermochemical processes [5]. However, there is still a lack of deep mechanistic understanding and control of undesired side reactions that hinder significant advances in terms of yield and selectivity. In this regard, fast pyrolysis of model compounds with linkages that resemble those presented in lignin provide insight into the decomposition of this polymer [6,7].

A study of fast pyrolysis of lignin model compounds [e.g. 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol] and pyrolysis products is proposed. Pyrolysis experiments under collision-reduced high vacuum environment (py-iPEPICO) provide access to reactive molecules and the unimolecular chemistry. Batch-type reactor experiments using GC/MS detection (py-GC/MS) show only stabilized products but at more process-like conditions. Thanks to the combination of both techniques, reaction mechanisms will be proposed, achieving a better understanding of lignin model compounds and pyrolysis products in general.

[1] Sureerat Jampa, Allen Puente-Urbina, Zhiqiang Ma, Sujitra Wongkasemjit, Jeremy S. Luterbacher, Jeroen A. van Bokhoven, *ACS Sustainable Chemistry & Engineering,* **2019,** *7*, 4058-4068.
[2] Zhiqiang Ma, Ashim Ghosh, Navinchandra Asthana, Jeroen van Bokhoven, *ChemCatChem,* **2017,** *9*, 954-961.
[3] Patrick Hemberger, Victoria B. F. Custodis, Andras Bodi, Thomas Gerber, Jeroen A. van Bokhoven, *Nature Communications,* **2017,** *8*, 15946.
[4] Wouter Schutyser, Tom Renders, Sander Van den Bosch, Steven-Friso Koelewijn, Gregg T. Beckham, Bert F. Sels, *Chemical Society Reviews,* **2018,** *47*, 852-908.
[5] Anthony Bridgwater, Dietrich Meier, Desmond Radlein, *Organic Geochemistry,* **1999,** *30*, 1479-1493.
[6] Victoria B. F. Custodis, Patrick Hemberger, Jeroen A. van Bokhoven, *Chemistry – A European Journal,* **2017,** *23*, 8658-8668.
[7] Victoria B. F. Custodis, Patrick Hemberger, Zhiqiang Ma, Jeroen A. van Bokhoven, *Journal of Physical Chemistry B,* **2014,** *118*, 8524-8531.

Lignin Stabilization to Improve Fast Pyrolysis

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In recent decades, the use of lignocellulosic biomass as a renewable feedstock for chemicals, materials and fuels, has developed considerably [1]. Despite this, the potential of lignin, which constitutes ca. 30 % of lignocellulosic biomass, has not been reached [2]. Due to its recalcitrance, lignin is currently considered a low-value by-product of lignocellulosic processing plants and it is mainly combusted [3]. However, as it is highly rich in aromatic structures, lignin has great potential to produce value-added chemicals if it is depolymerized [4]. Fast pyrolysis is one of the most promising methods for lignin depolymerization [5]. However, side reactions (e.g. repolymerization reactions) should be hindered and reaction conditions optimized to increase the yield to specific desired products. One approach to achieve this is to convert lignin ´s reactive groups into more stable moieties [6,7]. A study of the influence of lignin extraction and chemical stabilization of the aliphatic and phenolic hydroxyl groups in fast pyrolysis is proposed. Lignin is extracted using the green solvent γ-valerolactone (GVL) and different stabilization methods are tested during or post extraction processes. Structural analysis is carried out using NMR spectroscopy, infrared spectroscopy and thermogravimetric analysis. Fast pyrolysis is achieved using a tandem pyrolysis reactor coupled to a gas chromatograph-mass spectrometer (py-GC/MS). Using this information, the effect of structural modifications on the yield and selectivity of lignin fast pyrolysis can be better understood.

[1] David M. Alonso, Sikander H. Hakim, Shengfei Zhou, Wangyun Won, Omid Hosseinaei, Jingming Tao, Valerie Garcia-Negron, Ali H. Motagamwala, Max A. Mellmer, Kefeng Huang, Carl J. Houtman, Nicole Labbé, David P. Harper, Christos T. Maravelias, Troy Runge, James A. Dumesic, Science Advances, 2017, 3, e1603301.
[2] Wouter Schutyser, Tom Renders, Sander Van den Bosch, Steven-Friso Koelewijn, Gregg T. Beckham, Bert F. Sels, Chemical Society Reviews, 2018, 47, 852-908.
[3] Joseph Zakzeski, Pieter C. A. Bruijnincx, Anna L. Jongerius, Bert M. Weckhuysen, Chemical Reviews, 2010, 110, 3552-3599.
[4] Sureerat Jampa, Allen Puente-Urbina, Zhiqiang Ma, Sujitra Wongkasemjit, Jeremy S. Luterbacher, Jeroen A. van Bokhoven, ACS Sustainable Chemistry & Engineering, 2019, 7, 4058-4068.
[5] Patrick Hemberger, Victoria B. F. Custodis, Andras Bodi, Thomas Gerber, Jeroen A. van Bokhoven, Nature Communications, 2017, 8, 15946.
[6] Li Shuai, Masoud T. Amiri, Ydna M. Questell-Santiago, Florent Héroguel, Yanding Li, Hoon Kim, Richard Meilan, Clint Chapple, John Ralph, Jeremy S. Luterbacher, Science, 2016, 354 (6310), 329.
[7] Wu Lan, Masoud T. Amiri, Christopher M. Hunston, Jeremy S. Luterbacher, Angewandte Chemie International Edition, 2018, 57 (5), 1356-1360.

Evolution of Pore Networks in the Synthesis and Catalytic Application of Hierarchical MFI Zeolites

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Understanding the organization of complex pore networks is essential in guiding the design of materials with enhanced functionality. Here, a multi-technique approach combining differential hysteresis scanning (DHS) measurements by high-resolution argon sorption,[1] positron annihilation spectroscopy (PAS), and electron microscopy is applied to quantitatively assess the evolution of the pore architecture in the preparation and application of hierarchical MFI zeolites.[2] Both direct (templated) and post-synthetic (desilication) synthetic routes are compared, studying the impact of key variables such as the degree of template removal, base concentration, and presence of pore-directing agents on the location, geometry, and connectivity of the mesopores developed (**Figure 1**). Evaluation in the conversion of methanol-to-olefins establishes the effectiveness of the different pore networks at alleviating deactivation due to the deposition of carbonaceous species (coke), confirming the increased blockage in the presence of occluded or constricted mesopores. The subsequent monitoring in the oxidative regeneration also provides insights into the comparative ease of coke removal. The synthesis-property-function relationships developed over these MFI zeolite catalysts provide unprecedented insights into the importance of controlling the hierarchical pore structure.

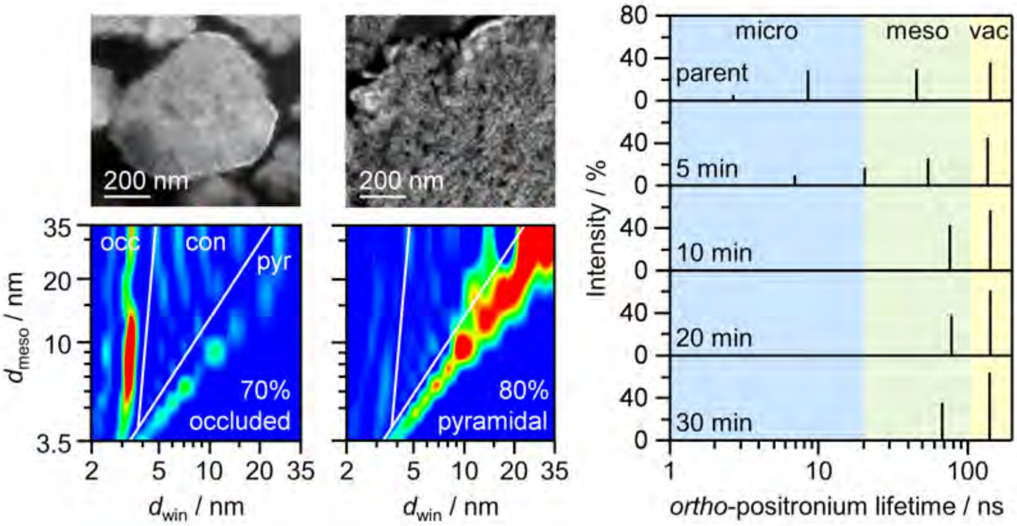

Figure 1 Advanced approach to monitoring the evolution of the location, geometry, and connectivity of mesopores during the synthesis and application of hierarchical MFI zeolites.

[1] J. Kenvin, S. Mitchell, M. Sterling, R. Warringham, T. C. Keller, P. Crivelli, J. Jagiello, J. Perez-Ramirez, *Adv. Funct. Mater.*, **2016**, 26, 6521.
[2] S. Mitchell, L. Gerchow, R. Warringham, P. Crivelli, J. Pérez-Ramírez, *Small Methods*, **2018**, 2, 1800268.

Trends and advances in the selective partial oxidation of methane

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Interests in valorizing methane, an abundant component of conventional associated gas deposits and shale gas, has resulted in considerable scientific effort in numerous directions, with one of them being, the selective partial oxidation to methanol. The objective of this presentation is to identify trends of the most promising systems and expand on them to discuss in-house experimental advances. The facile over-oxidation of methanol in conditions that activate methane impedes the 'direct methane to methanol' (DMTM) processes from reaching high yields.[1,2] The common denominator in better-performing systems is the ability to preserve the desired product and deter successive oxidation.[1,2,3]

One such approach is the derivatization to methyl esters, but such processes employ catalysts with complex organic ligands to reach high yields at relatively high temperature (>423 K) and pressure (20-70 bar).[4] We discovered the possibility to use a simple copper compound, copper (II) oxide, as a recyclable homogeneous catalyst to convert methane to methyl trifluoroacetate in high yields (up to 63%) at low pressure (5 bar).[5] However, from a product and catalyst recovery perspective, heterogeneous catalysis remains the more attractive choice. To this end, we identified a heterogeneous low-temperature activation of methane with hydrogen peroxide by aluminum in zeolites. Octahedrally coordinated framework-associated aluminum in zeolites, which has Lewis acidic character,[6] is the active site for the conversion of methane in trifluoroacetic acid.[7] The loading of copper to the zeolite makes the reaction selective to the ester (>90% at 6% methane conversion).[7] Despite their impressive performance, the aforementioned systems use potassium persulfate and hydrogen peroxide, which are both expensive oxidants. On this front, we have now engineered an aerobic liquid-phase process for the oxidation of methane to methyl trifluoroacetate. This isothermal low-pressure system with cobalt catalysts results in a space-time yield of above 20 $\mu mol.g^{-1}.h^{-1}$.[8] With further materials and process optimization, higher yields may be accomplished. Overall, there is a genuine paucity of such heterogeneously catalyzed aerobic processes for partial methane oxidation and consequently, these systems require increased attention.

[1] M. Ravi, M. Ranocchiari, J. A. van Bokhoven, *Angewandte Chemie International Edition* **2017**, *56*, 16464-16483.
[2] M. Ravi et al., *Nature Catalysis* **2019**, aceepted
[3] M. Ahlquist, R. J. Nielsen, R. A. Periana, W. A. Goddard III, *Journal of the American Chemical Society* **2009**, *131*, 17110-17115.
[4] R. A. Periana, D. J. Taube, S. Gamble, H. Taube, T. Satoh, H. Fujii, *Science* **1998**, *280*, 560-564.
[5] M. Ravi, J. A. van Bokhoven, *ChemCatChem* **2018**, *10*, 2383-2386.
[6] M. Ravi, V. Sushkevich, J. A. van Bokhoven, submitted to *Journal of Physical Chemistry C* **2019**
[7] M. Ravi et al., Manuscript in preparation
[8] M. Ravi et al., Unpublished results

Development of a Heterogeneous Pt/Zn Catalyst for Propane Dehydrogenation from Surface Organometallic Chemistry Principles

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A shift from oil-based naphtha cracking to shale-based ethane cracking has created an imbalance in the production and demand of propylene.[1,2] This has resulted in strong demands for alternative light olefin production routes. While on-demand propane dehydrogenation is practiced industrially, the current industrial catalysts suffer from fast deactivation and require frequent regeneration.[1,3] In attempts to deconvolve specific factors which effect catalyst stability and selectivity, and ultimately design more effective catalytic systems, we prepared a well-defined Pt/Zn catalyst using Surface Organometallic Chemistry.[4] This involves a two-step approach where a molecular Zn precursor was first grafted to the surface of a SiO_2 support followed by a thermolysis step. In a second grafting step a Pt precursor was grafted to the Zn doped SiO_2 support followed by a reduction treatment. The resulting catalyst shows unprecedented performance in the propane dehydrogenation reaction compared to other Pt/Zn catalysts. This contribution will present structural characterization of this heterogeneous system providing insight in the different factors leading to the increased catalytic performance, paving the way to future rational design of highly active catalysts in the field of multimetallic catalysis.

[1] Sattler, J. J. H. B.; Ruiz-Martinez, J.; Santillan-Jimenez, E.; Weckhuysen, B. M. *Chem. Rev.* **2014**, 114, 10613-10653.
[2] McFarland, E. *Science*, **2012**, 338, 340.
[3] Zhu, G.; Xie, C.; Li, Z.; Wang, X. (**2017**) Catalytic Processes for Light Olefin Production. In: Hsu C.S., Robinson P.R. (eds) Springer Handbook of Petroleum Technology. Springer Handbooks. Springer, Cham
[4] Copéret, C.; Comas-Vives, A.; Conley, M. P.; Estes, D. P.; Fedorov, A.; Mougel, V.; Nagae, H.; Núñez-Zarur, F.; Zhizhko, P. A. *Chem. Rev.* **2016**, 116, 323-421.

Polyol synthesis route of ceria/zirconia oxides for methane oxidation under stoichiometric conditions

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Natural gas vehicles (NGV) are an attractive solution for the reduction of greenhouse gas emissions arising from road transportation due to its low specific CO_2 and NO_X emissions. However, due to the high global warming potential of methane and to increasingly stringent legislation, post-combustion treatment of unburnt CH_4 is crucial. The scarce literature concerning three-way catalysts (TWC) for NGV applications and the observation that the chemistry of such a catalyst is different from that of a TWC for gasoline vehicles indicated the necessity to develop and optimise catalytic converters for stoichiometric gas engines[1]. In this context, a systematic study was initiated for the development of a palladium-based TWC (Pd-Al_2O_3-$CeZrO_4$) by applying a step-by-step methodology to get an in-depth comprehension of the implication of each element present in the material.

The synthesis method is critical in this work because we want to achieve qualitative and reproducible material compositions and structures. The polyol synthesis was selected as the method of choice because it allows the precise control of the elemental composition of the catalyst and the preparation of homogeneous nanoparticles with a narrow particle size distribution and a high surface area[1]. Moreover, the role of ethylene glycol (EG) as high-boiling solvent, complexing agent and reactant makes the use of a capping agent meaningless, and the reaction conditions milder.

As a first step, the catalyst support (ACZ) was optimized based on the activity and stability of the material. Ceria/Zirconia oxides with varying Ce/Zr ratio were synthesized and tested under operation conditions specific for a NGV catalytic converter. Then, after determination of the ideal CZ ratio, Al_2O_3 was incorporated in different fractions into the structure. Additionally, since the exhaust gas temperature in this application is high (> 550°C), the thermal stability of the supports is of main importance. Hence, the aged support materials (900°C) were characterized to assess the structural changes that had been generated.

The ICP-OES results confirmed that the synthesis allows a precise incorporation of the elements into the material structure. The XRD patterns, EXAFS data and TEM images demonstrated the presence of a single phase material with a face cubic centered structure. We observed that the addition of zirconia in the lattice improved the thermal stability of the samples (no phase separation compare to pure CeO_2). Oxygen storage capacity measurements were performed at different temperatures to assess the quantity of oxygen that the synthesized supports can exchange with the environment. Finally, BET analysis showed that CZ with an equimolar ratio exposed a significantly higher surface area of 33 m^2/g after ageing compared to 8-9 m^2/g for the other samples.

[1] Ferri, D., Elsener, M. & Kröcher, O. Appl Catal B,.2018, 220, 67–77.
[2] F. EPFL dissertation. EPFL_TH7937-1. 2017

Epitaxially-Directed Iridium Nanostructures on Rutile-Type Carriers for the Selective Catalytic Hydrodechlorination of Dichloromethane

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The valorization of methane (CH_4), the main component of underutilized natural gas (NG), into chemicals and fuels is a critical step for transitioning from the oil to the renewables era. Currently, the flaring of a staggering 3.5% of the global annual NG production,[1] emits more than 350 million tons of CO_2, thereby weakening international efforts to meet greenhouse gas reduction targets. This wasteful practice stems from the prohibitive expense of shipping NG from remote locations to centralized plants and the lack of viable options for on-site upgrading in compact, modular plants. For this purpose, chlorine-mediated processes have emerged as an attractive option, enabling direct methane functionalization under mild operating conditions in contrast to the traditional syngas chemistry (**Figure 1a**).[2] The methyl chloride (CH_3Cl) attained is a platform chemical for the manufacture of readily transportable commodities with similar conversion paths to methanol (CH_3OH). The industrial deployment of this new technology requires overcoming a challenge: under practically-relevant reaction conditions, high selectivity to dichloromethane (CH_2Cl_2, DCM, often exceeding 30%) in the methane chlorination/oxychlorination step compromises the production of the target CH_3Cl.[3,4] Therefore, innovative approaches for reforming polyhalogenated compounds are crucial to meet today's need for NG exploitation. This work describes the development of an iridium catalyst with unequaled specific activity in the hydrodechlorination of DCM to CH_3Cl, originating from the epitaxial direction of a noble-metal-based nanostructure *via* the sequential impregnation, thermal annealing, and reduction on rutile titanium oxide. Compared to iridium nanoparticles, the films attain superior methyl chloride selectivity (95%) and improved stability (**Figure 1b**). These findings constitute a basis towards the design of more efficient hydrodechlorination catalysts.

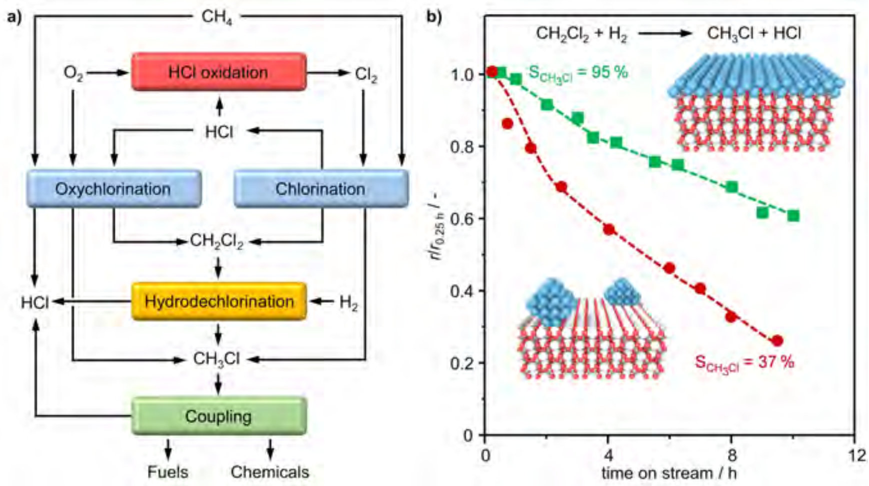

Figure 1 a) Process diagram for chlorine-mediated natural gas upgrading and b) Ir/TiO_2-rutile hydrodechlorination performance.

[1] J. Tollefson, *Nature*, **2016**, doi:10.1038/nature.2016.19141.
[2] E. McFarland, *Science*, **2012**, 338, 340.
[3] R. Lin, A. P. Amrute, J. Pérez-Ramírez, *Chem. Rev.*, **2017**, 117, 4185.
[4] V. Paunović, G. Zichittella, P. Hemberger, A. Bodi, J. Pérez-Ramírez, *ACS Catal.*, **2019**, 9, 1710.

Mechanism of preferential carbon monoxide oxidation on supported Pt-Fe catalysts

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Nowadays, preferential oxidation of carbon monoxide in hydrogen is of great importance due to the demand for carbon monoxide free hydrogen for proton-exchange membrane fuel cells [1]. Recent studies confirm that oxygen activation for carbon monoxide oxidation at low temperatures is possible by constructing an efficient Pt-MO_x interface, where MO_x – is a reducible metal oxide [2]. For example, in supported Pt-Fe catalysts, which can oxidize carbon monoxide in hydrogen streams even at room temperature [3].

However, the relations between the Pt-Fe structure and the catalytic performance remain debated. Whether the Pt-Fe interaction or blockage of Pt active sites by FeO_x species is responsible for the differences in the carbon monoxide adsorption mechanism is unclear. FeO_x species in contact with Pt could also take part in the formation of adsorbed water, hydroxyls and other species affecting the oxygen activation mechanism [4, 5]. Pt and Fe oxidation states significantly alter depending on the working conditions and it is not clear whether Fe^{2+}/Fe^{3+} redox pair is directly involved in the mechanism of oxygen activation [3].

In the current work, we synthesized bimetallic Pt–Fe/Al_2O_3 catalysts with different Pt:Fe ratios and also model Pt/FeO_x systems. We characterized them by transmission electron microscopy, X-ray diffraction analysis, hydrogen and carbon monoxide chemisorption. Catalytic activity depends on the pretreatment conditions, Fe content, oxygen and hydrogen concentration in the reaction stream. In situ time-resolved X-ray adsorption spectroscopy and infrared spectroscopy experiments are in progress to uncover structure-activity relationships and detect reaction intermediates involved in the activation of carbon monoxide and oxygen in the catalytic cycle.

[1] Frano Barbir, *PEM Fuel Cells – 2nd Edition, Elsevier*, **2013**, 305-372.
[2] Weiting Yu, Marc D. Porosoff, Jingguang G. Chen, *Chemical Reviews*, **2012**, 112, 5780–5817.
[3] Lina Cao, Wei Liu, Qiquan Luo et al., *Nature*, **2019**, 565, 631-635.
[4] Isaias B. Aragao, Jose M. Bueno, Daniela Zanchet, *Applied Catalysis A*, **2018**, 568, 86-94.
[5] Suying Li, Mingjun Jia, Jun Gao et al, *Journal of Physical Chemistry C*, **2015**, 119, 2483-2490.

Pyridylidene Amide Ligands for Highly Efficient Olefin Oxidation

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Electronically flexible ligands can vary their degree of donor ability and may stabilize several intermediates of the catalytic cycle. This can play a crucial role in catalysis as the metal center changes its oxidation state through the catalytic cycle. Pyridylideneamides (PYAs, see Figure 1) are an innovative class of such non-innocent ligands. They show a flexible electronic character depending on their environment and are suitable for metal coordination.[1,2] Their synthetic versatility can also be easily exploited by changing the chelating donor group or by changing the PYA position, resulting in different donor properties. Here we introduce bis-PYA ligands coordinated to the $[Ru(p\text{-}cym)Cl_2]_2$ precursor, which affords highly efficient catalysts suitable for olefin oxidation.

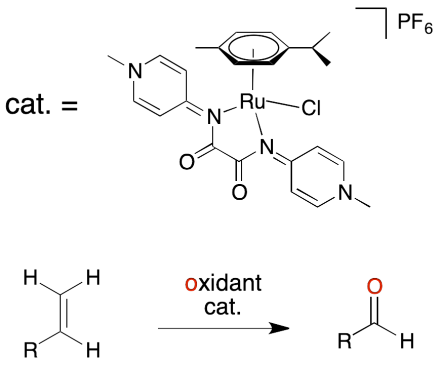

Figure 1 Schematic representation of a ruthenium complex containing a bis(pyridylidene amide) ligand that is suitable for olefin oxidation.

[1] M. E. Doster, S. A. Johnson, *Angew. Chem. Int. Ed.*, **2009**, 48, 2185-2187.
[2] M. Navarro, M. Li, H. Müller-Bunz, S. Bernhard, M. Albrecht, *Chem. Eur. J.* **2016**, 22, 6740-6745

Mining the C-C Cross-Coupling Genome using Machine Learning

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The speed and precision of machine-learning (ML) techniques in determining quantum chemical properties have resulted in a considerable computational speed up in comparison to traditional quantum chemical methods, and now allows a desired property of thousands of molecules to be assessed virtually instantaneously. The large databases that result from employing ML can, in turn, be mined with the goal of uncovering relationships that may be missed through the more commonly used small scale screening procedures. Due to its prominent place in chemistry, catalysis represents a particularly fruitful playground, where drawing connections between the quantum chemical properties of catalysts and their overall catalytic performance may lead to the identification of new highly functional species. In this spirit, we previously trained ML models to predict the performance of 18,000 prospective catalysts for a Suzuki coupling reaction using molecular volcano plots. Here, we apply concepts from big data to probe a type of “C-C cross-coupling genome” that explores results from many different named cross-coupling reactions. The use of dimensionality-reducing data-clustering algorithms facilitates the identification of relationships between the thermodynamics of different catalysts and the chemical properties of their constituent metal and ligands. Analyzing large numbers of species in this manner leads to the identification of not only unexpected catalysts that have thermodynamically ideal profiles to catalyze C-C cross-coupling reactions, but also reveals a wealth of interesting chemical trends regarding the influence played by different metals and ligands, as well as their unique combinations.

Anhydrous conditions enable the catalyst-free carboxylation of alkynes with CO_2 under ambient conditions.

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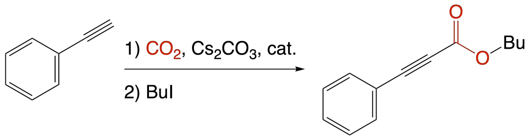
The direct carboxylation of C-H bond employing carbon dioxide as C1 source provides an attractive route to build higher value organic molecules starting from cheap feedstocks.[1] Recent years have seen the emergence of many reactions building organic molecules with CO_2 including the synthesis of cyclic carbonate[2], formylated amines[3], propiolic acid derivatives[4] and numerous other heterocycles. Among the mentioned reactions the carboxylation of terminal alkynes is of interest because of their importance as precursors in medicinal chemistry.[5] To date, many studies have been carried out to optimize the conditions for the carboxylation of terminal alkynes that is generally performed by using transition metal based catalyst (Cu, Ag) in presence of stoechiometric amounts of base (Figure 1).[6] Direct carboxylation of terminal alkynes with Cs_2CO_3 in the absence of catalyst has also been reported but requires high temperatures (120°C) and CO_2 pressures of 2-7 atm[7]. Here we show that if rigorously anhydrous conditions are used the direct C-H carboxylation of alkynes can be performed with high yield in mild conditions.



Cat. : CuX, AgX or others (0.05 - 1 mol%),
DSMO or DMF, 25-120 °C, 1-2.5 bar,
21 - 99 % yield

Figure 1. General reaction scheme. Catalysts and conditions used in literature.

[1] Qiang Liu, Lipeng Wu, Ralf Jackstell, Matthias Beller, *Nature Communications*, **2015**, 6, 5933
[2] Felix D. Bobbink, Dmitry Vasilyev, Martin Hulla, Sami Chamam, Florent Menoud, Gab́or Laurenczy, Sergey Katsyuba, Paul J. Dyson, *ACS Catalysis*, **2018**, 8, 2589-259
[3] Martin Hulla, Felix D. Bobbink, Shoubhik Das, Paul J. Dyson, *ChemCatChem*, **2016**, 8, 3338 – 3342
[4] Ye Yuan, Cheng Chen, Cheng Zeng, Bibimaryam Mousavi, Somboon Chaemchuen, Francis Verpoor, *ChemCatChem*, **2017**, 9, 882 – 887
[5] Filipe Manjolinho, Matthias Arndt, Kathe Gooßen, Lukas J. Gooßen, *ACS Catalysis*, **2012**, 2, 2014–2021
[6] Junting Hong, Man Li, Jianning Zhang, Beiqi Sun, Fanyang, *ChemSusChem*, **2019**, 12, 6–39
[7] Yu Dingyi, Zhang Yugen, *Green Chemistry*, **2010**, 13, 1275-1279

Evidences and Conjectures on the Initiation Process in Cr-based ethylene polymerization

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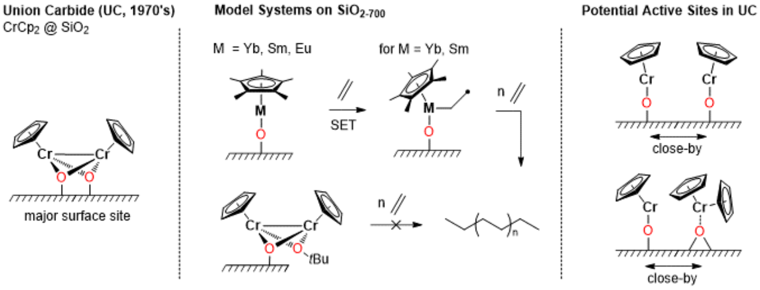
Following the Cr-based Phillips polymerization catalysts, CrO_3/SiO_2, Union Carbide discovered in 1970 an alternative system based on silica-supported chromocene. The catalyst is obtained by grafting bis-cyclopentadienyl chromium (II), Cp_2Cr, onto silica, probably one of the first industrial systems prepared via surface organometallic chemistry (SOMC).[1-3] Despite its industrial relevance, the nature of active sites and operating mechanism remains virtually unknown and parallels the debate related to the Phillips catalyst.

Recently, the corresponding silica-supported Sm(II) and Yb(II) systems, prepared by grafting Cp^*_2Ln

(Ln = Sm and Yb; Cp* = pentamethylcyclopentadienyl) onto silica, were shown to polymerize ethylene without co-catalyst, similarly to what is observed for the Union Carbide system.[4] The molecular and well-defined silica-supported species are highly active and proposed to initiate polymerization via a single electron transfer (SET), generating highly active Lanthanide(III)-alkyl species (see Scheme below). This proposed activation step was further supported by the inactivity of the Eu analogues that are much less reducing compared to Sm and Yb. Chromocene itself is slightly less reducing than Cp^*_2Eu but still activates ethylene after reaction with silica in the absence of additional alkylating co-catalysts.[5]

Here, we will discuss similarities and differences observed between Cr (II) and Ln (II) silica-supported systems prepared by grafting Cp_2Cr (II) and Cp^*_2Ln (II) onto silica partially dehydroxylated at 700 °C containing isolated OH group ($Q < 1\ OH^*nm^{-2}$). First, while monomeric species are obtained with Ln = Sm, Eu and Yb, dimeric species are predominantly obtained with Cr according to extended X-ray adsorption fine structure (EXAFS) studies, benchmarked with molecular analogues, consistent with previous findings.[6] Remarkably, even if the initial OH density is low and should yield isolated monomeric species, as observed with the lanthanide equivalents, mostly dimeric sites are formed for Cr. Considering reactivity towards ethylene, whereas isolated Yb and Sm surface sites are probably reducing enough to initiate polymerization, it is likely that dimeric Cr surface sites have low (or no) activity due to the presence of Cr-Cr bonding. In fact, silica-supported dimeric Cr species prepared by grafting [CrCpOtBu]2 using SOMC do not show any activity in ethylene polymerization. From these data, one may thus propose that proximal – not directly bonded – Cr (II) sites are potential active sites. Experimental evidences and conjectures in that direction will be discussed in detail.



[1] Karol, F. J.; Karapinka, G. L.; Wu, C.; Dow, A. W.; Johnson, R. N.; Carrick, W. L., Polym. Sci. A-1: 1972, 10 (9), 2621-2637.

[2] Union Carbide Corp. US Patent 3709853, 1973.

[3] Copéret, C.; Comas-Vives, A.; Conley, M. P.; Estes, D. P.; Fedorov, A.; Mougel, V.; Nagae, H.; Núñez-Zarur, F.; Zhizhko, P. A., Chem. Rev. 2016, 116, 323-421.

[4] Allouche, F.; Chan, K. W.; Fedorov, A.; Andersen, R. A.; Copéret, C., Angew. Chem. Inter. Ed.

2018, 57, 3431-3434.
[5] Finke, R. G.; Keenan, S. R.; Schiraldi, D. A.; Watson, P. L., Organometallics 1986, 5, 598-601.
[6] Schnellbach, M.; Köhler, F. H.; Blümel, J., Journal of Organomet. Chem. 1996, 520, 227-230.

Development of a microfluidics-based assay for the evolution of artificial metalloenzymes using a cell surface display strategy

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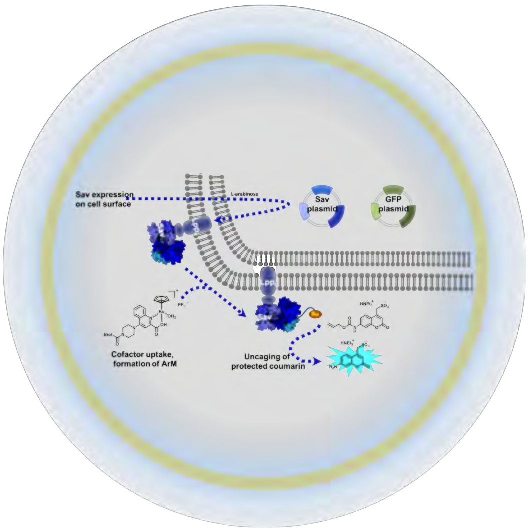
Incorporation of a transition metal catalyst within a protein scaffold enables the formation of artificial metalloenzymes (ArMs) with non-natural reactivities.[1]The catalytic activity and selectivity of such systems can be optimized by either chemical optimization of the metal cofactor or genetic evolution of the host protein. Integration of the biotinylated ruthenium complex[CpRu(Biot-Quinoline)(H_2O)][2]into the binding pocket of streptavidin (Sav) affords an artificial deallylase capable of uncaging a protected coumarin yielding a fluorescent readout.[3]

Herein, we present a microfluidics-based high-throughput assay[4]to evolve the catalytic activity of an artificial deallylase. Single *E. coli*cells with surface-displayed Sav are encapsulated in droplets together with the protected coumarin substrate and the biotinylated cofactor. The catalytically active mutants can be sorted by fluorescence-assisted droplet sorting (FADS) and the identified hits can be subjected to a further round of optimization. This method can be applied to evolve various ArMs *in vivo*and enable the screening of large libraries in an iterative and straightforward manner.



[1] Fabian Schwizer, Yasunori Okamoto, Tillmann Heinisch, Yifan Gu, Michela M. Pellizzoni, Vincent Lebrun, Raphael Reuter, Valentin Köhler, Jared C. Lewis, Thomas R. Ward, Chem. Rev., **2018**, 118, 142–231.
[2] T. Völker, F. Dempwolff, P. L. Graumann, E. Meggers, *Angew. Chem,. Int. Ed.*, **2014**, 53, 10536–10540.
[3] T. Heinisch, F. Schwizer, B. Garebedian, E. Csibra, M. Jeschek, J. Vallapurackal, V. B. Pinheiro, P.Marlière, S. Panke, T. R. Ward, *Chem. Sci.*, **2018**, 9, 5383–5388.
[4] R. Obexer, A. Godina, X. Garrabou, P. R. Mittl, A. D. Griffiths, D. Hilvert, *Nat. Chem.*, **2017**, 9, 50–56.

Nitride-Derived Copper Modified with Indium as a Highly Stable and Selective Catalyst for the Electroreduction of CO_2

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The lack of efficient catalysts prevents the electrocatalytic reduction of carbon dioxide from contributing to the pressing target of a carbon-neutral economy. In this study, we reveal indium-modified copper nitride as a highly stable electrocatalyst selective toward CO. In_2O_3/Cu_3N showed a Faradaic efficiency of 80% toward CO at an overpotential of 0.5 V for 100 h, in stark contrast to the very modest stability of the benchmark In_2O_3/Cu_2O (**Figure 1a**).[1,2] Microfabricated systems allowed to correlate the superior performance of indium-modified copper nitride with highly stable interfacial sites (**Figure 1b,c**).[3] Spectroscopic evidence suggested a modified reduction process of the nitride phase in the presence of indium. In the case of the copper oxide-based electrocatalyst, excessive indium diffusion m resulted in unstable interfaces (**Figure 1d**). Overall, this work uncovers the stabilizing properties of nitride-derived copper toward practical multicomponent catalysts.

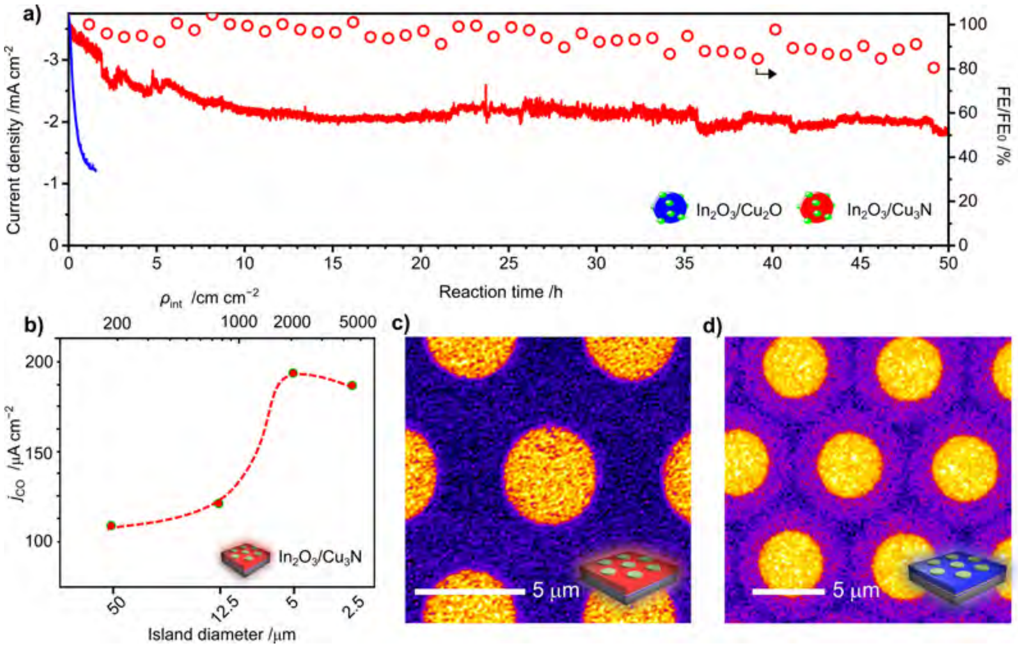

Figure 1 a) Electrocatalytic activity for In_2O_3/Cu_3N and the reference In_2O_3/Cu_2O. b) Relation between partial current density for CO and Cu-In interfacial density observed on microfabricated In_2O_3/Cu_3N electrodes. SEM-EDX indium distribution map for c) microfabricated In_2O_3/Cu_3N and d) microfabricated In_2O_3/Cu_2O after the reaction. The latter shows the Cu-In interface created by the diffusion of indium from the islands.

[1] S. Rasul, D. H. Anjum, A. Jedidi, Y. Minenkov, L. Cavallo, K. Takanabe,*Angew. Chem. Int. Ed.*, **2015**, 54, 2146.
[2] G. O. Larrazábal, A. J. Martín, F. Krumeich, R. Hauert, J. Pérez-Ramírez, *ChemSusChem*, **2017**, 10, 1255.
[3] G. O. Larrazábal, T. Shinagawa, A. J. Martín, J. Pérez-Ramírez, *Nat. Commun.*, **2018**, 9, 1477.

Atom-by-Atom Resolution of Structure-Function Relations over Low-Nuclearity Metal Catalysts

E. Vorobyeva[1], E. Fako[2], Z. Chen[1], N. López[2], O. V. Safonova[3], S. Mitchell[1]*, J. Pérez-Ramírez[1]*

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Controlling the structure sensitivity of catalyzed reactions over metals is central to developing atom-efficient chemical processes. Approaching the minimum ensemble size, the properties enter a nonscalable regime. Almost all trends in this ultra-small frontier derive from surface science approaches using model systems, because of both synthetic and analytical challenges. Exploiting the unique coordination chemistry of carbon nitride,[1-3] we discriminate through experiments and simulations the interplay between the geometry, electronic structure, and reactivity of palladium atoms, dimers, and trimers (**Figure 1**).[4] Catalytic tests evidence application-dependent requirements of the active ensemble. Pd trimers were more active in the selective hydrogenation of various functionalized alkynes, which was linked to the reduced hydrogen activation barrier with respect to single atoms and dimers. In contrast, Pd single atoms surpass ensembles in Suzuki coupling exhibiting distinct chemoselectivity to the dimers and trimers, which also ensured higher stability. This powerful approach will provide practical insights into the design of heterogeneous catalysts comprising well-defined numbers of atoms.

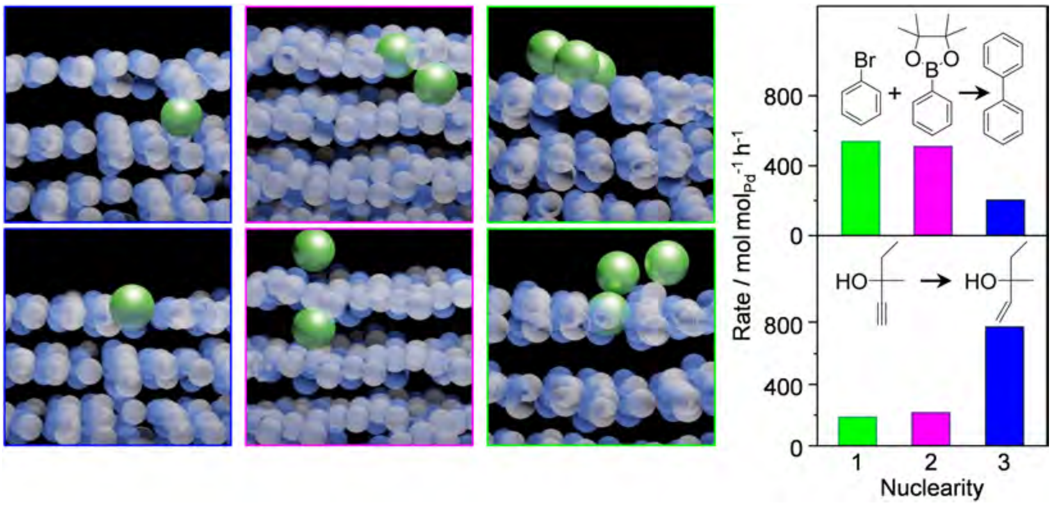

Figure 1 Calculated structures of palladium single atoms, dimers, and trimers stabilized on carbon nitride and catalytic performance in Suzuki coupling and alkyne semi-hydrogenation.

[1] Z. Chen, E. Vorobyeva, S. Mitchell, E. Fako, N. López, S. M. Collins, R. K. Leary, P. A. Midgley, R. Hauert, J. Pérez-Ramírez, *Natl. Sci. Rev.*, **2018**, 5, 642.
[2] E. Vorobyeva, Z. Chen, S. Mitchell, R. K. Leary, P. Midgley, J. M. Thomas, R. Hauert, E. Fako, N. López, J. Pérez-Ramírez, *J. Mater. Chem. A*, **2018**, 5, 16393.
[3] Z. Chen, E. Vorobyeva, S. Mitchell, E. Fako, M. A. Ortuño, N. López, S. M. Collins, P. A. Midgley, S. Richard, G. Vilé, J. Pérez-Ramírez, *Nat. Nanotechnol.*, **2018**, 13, 702.
[4] E. Vorobyeva, E. Fako, Z. Chen, S. M. Collins, D. Johnstone, P. A. Midgley, R. Hauert, O. V. Safonova, G. Vilé, N. López, S. Mitchell, J. Pérez-Ramírez, *Angew. Chem. Int. Ed.*, **2019**, doi:10.1002/ange.201902136.

Transition metal electrocatalysts encapsulated into N-doped carbon nanotubes on graphene nanosheets: Efficient water splitting through synergistic effects

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The development of efficient noble-metal free electrocatalysts is crucial for clean hydrogen production through water splitting. As carbon-based supports are expected to play a major role in low-cost electrocatalysis, improved synthetic methods and a deeper understanding of their mechanisms of action are now required. To this end, we synthesized transition metal catalysts for overall water splitting encapsulated into nitrogen-doped carbon nanotubes (M-N-CNTs, M = Ni, Co, Fe) through a direct and convenient pyrolysis of bulk g-C_3N_4. Furthermore, the addition of graphene oxide leads to a significant dispersion of the catalytic N-CNTs. Among the obtained catalyst series, NiFe-N-CNT with graphene (NiFe-N-CNT-G) exhibits extremely low overpotential of 270 mV (on glassy carbon) for the oxygen evolution reactions at a current density of 10 mA/cm^2. This performance is superior to most of the previously reported noble metal-free catalysts for OER. Our comprehensive study unravels that the growth of CNTs follows a “reduction-nucleation-growth” process. The thermally reduced metallic nanoparticles (NPs) serve as nucleation sites of carbon species on their surface to further promote N-CNT growth. Density functional theory (DFT) calculations reveal that the CNT walls and N-dopants in the catalysts modify the electronic structure and adjust the free energy toward the adsorption of intermediates. The one-step HER process is influenced more strongly by N-centers when compared to the four-electron transfer OER process. The scalable and straightforward synthesis together with excellent electrocatalytic performance renders the NiFe-N-CNT hybrid catalyst quite promising for large-scale water splitting applications.

[1] L. Zhang, J. Xiao, H. Wang, M. Shao, *ACS Catal.,* **2017**, 7, 7855.
[2] X. Zhang et al., *ACS Catal.,* **2016**, 6, 580.
[3] X. Cui, X. Bao et al., *Energy Environ. Sci.,* **2016**, 9, 123.
[4] X. Zou, X. Huang, A. Goswami, R. Silva, B. R. Sathe, E. Mikmeková, T. Asefa, *Angew. Chem. Int. Ed.,* **2014**, *126*, 4461.

Stability of atomically dispersed platinum catalysts on low index and stepped CeO_2 surface from density functional theory

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Atomically dispersed catalysts attract great attention due to high atomic utilization efficiency as well as their catalytic activity and selectivity. [1] Pt-CeO_2 is widely used in a range of important catalytic applications, such as vehicle emissions control, water-gas shift reaction, methanol reforming and carbon monoxide oxidation. Recently, Jones et al. [2] showed that volatile platinum species can be trapped by the ceria step sites to form atomically dispersed platinum, which can be stabilized at temperature as high as 800°C. At the same time, atomically dispersed platinum atoms often exhibit highly dynamic behavior, and thus the geometrical structures of active sites of atomically dispersed Pt-CeO_2 is still highly debated.

Herein, through the combination of first-principles calculations and *ab initio* atomistic thermodynamics, we demonstrate that atomically dispersed platinum species on ceria surfaces can adopt a range of local coordination configurations and oxidation states that depend on the surface structure, coverage and environmental conditions. Unsaturated oxygen atoms on the ceria surfaces play the leading role in stabilization of PtO_x species. Any Pt^0 species are thermodynamically unstable compared to the bulk phase, and oxidation of Pt^0 to Pt^{2+} or Pt^{4+} is necessary to stabilize mono-dispersed platinum atoms. Both Pt^{2+} and Pt^{4+} prefer to form square-planar [PtO_4] structures. The two most stable Pt^{2+} species on the (223) and (112) surfaces are thermodynamically favorable between 300 and 1200 K. The most stable Pt^{4+} species on the (100) surface tends to desorb from the surface as gas phase above 900-1000 K. The resulting phase diagrams of the atomically dispersed PtO_x species on various ceria surfaces under a range of experimentally relevant conditions can be used to predict dynamic restructuring of atomically dispersed platinum catalysts and design new catalysts with engineered properties.

[1] A. Wang et al. Nature Reviews Chemistry, 2018, 2, 65–81
[2] J. Jones. et al. Science, 2016, 353, 150–154.

On the photoionization of the vinyl radical

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Vinyl radicals were produced in flash pyrolysis of divinyl sulfone, and their photoionization investigated at the Swiss Light Source using double imaging photoelectron photoion coincidence (i^2PEPICO) spectroscopy in the 8.10–10.45 eV photon energy range. Three features could be identified in the rising edge of the photoionization spectrum (PIE curve), at onset energies of ca. 8.25, 8.43, and 8.60 eV. Autoionizing fine structure has also been observed as previously reported by Berkowitz et al.[1] The threshold photoelectron spectrum (TPES) has been recorded for the first time. In agreement with the photoelectron spectrum,[2] no vibrational structure was observed in the ground state band. The vertical ionization energy (IE_v) of the vinyl radical was found to be 9.20 eV. Based on the Active Thermochemical Tables and confirmed by our calculations, the adiabatic IE of C_2H_3 is 8.477 ± 0.007 eV, significantly above the ionization onset at 8.25 eV. However, the Frank–Condon factors for the transition from the bent Y-shaped neutral minimum to the bridge-shaped ionic minimum are negligible, and we propose that this transition does not contribute to the photoionization signal. Instead, it is ascribed to the three transitions between straight Y-shaped $C_2H_3^‡$ --> bridged $C_2H_3^+$, straight Y-shaped $C_2H_3^‡$ -->straight Y-shaped $C_2H_3^+$ and bent Y-shaped $C_2H_{3\,\text{-->}}$ straight Y-shaped $C_2H_3^+$, tentatively assigned to the observed PIE features.

[1] Berkowitz J., Mayhew C., Ruščić B., *J. Chem. Phys.* **1988,** *88* , 7396-7404.
[2] Blush J. A., Chen P., *J. Phys. Chem.* **1992,** *96* , 4138-4140.

Revising the mechanism of alcohol oxidation over V_2O_5/TiO_2 catalysts

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Supported metal oxides are widely used in industrial catalysts for a large variety of reactions. Vanadium oxide is a common component of selective oxidation catalysts. Interaction of highly dispersed vanadium species with oxide supports (SiO_2, Al_2O_3, TiO_2, CeO_2, ZrO_2 etc.) strongly influences the catalytic properties [1]. In spite of a number of spectroscopic studies on supported vanadia species over the past 50 years, details about the reaction mechanisms on the atomic scale remain debated. The mechanism of selective oxidation of alcohol into aldehyde exists in a number of visions starting with different mechanisms of alcohol adsorption and ending with different locations of oxygen vacancy [2-4]. So far, no direct spectroscopic evidence has been provided for the involvement of the support in the reaction mechanism. In part, this is due to the limitations of spectroscopic methods, such as lack of chemical specificity, insufficient sensitivity to low concentration of active species and the short life times of reaction intermediates.

The aim of this project is to revise the mechanism of alcohol oxidation over titania-supported vanadia. To facilitate probing the reactivity of Ti and V in this reaction, we focused our study on a series of tailored bilayered (1-5wt.%)V_2O_5/(0-40wt.%)TiO_2/SiO_2 catalysts [5]. After careful examination of catalytic properties, we performed operando time-resolved V K-edge and Ti K-edge quick-XAS experiments on selected $V_2O_5/TiO_2/SiO_2$ and V_2O_5/SiO_2 systems. Experiments have been performed under steady state and under transient conditions, upon switching on and off oxygen in a flow of ethanol. We observed changes in height of the pre-edge peak and shape of the edge in the spectra of vanadium upon reversible adsorption of ethanol at low temperatures and its oxidation above 160 °C. Both processes produced identical spectroscopic signatures according to V K-edge XANES but can be distinguished by V K-edge EXAFS. In situ Raman, NMR, and EPR experiments are in progress to clarify the mechanisms of ethanol adsorption and the location of oxygen vacancies in the first coordination shell of vanadium. Ti K-edge XANES could not detect significant changes in the structure of titanium sites upon adsorption and oxidation of ethanol, which we plan to confirm using the more sensitive modulation-excitation approach.

[1] Benjamin Beck, Manuel Harth, Neil Hamilton, Carlos Carrero, John Uhlrich, Annette Trunschke, Shamil Shaikhutdinov, Helmut Schubert, Hans-Joachim Freund, Robert Schlögl, Joachim Sauer, Reinhard Schomäcker*, Journal of Catalysis,* **2012**, 296, 120-131.
[2] Vasily Kaichev, Yuriy Chesalov, Andrey Saraev, Alexander Klyushin, Axel Knop-Gericke, Tamara Andrushkevich, Valerii Bukhtiyarov, *Journal of Catalysis,* **2016**, 338, 82-93.
[3] Bert Weckhuysen, Daphne Keller, *Catalysis Today*, **2003**, 78, 25-46.
[4] Beata Kilos, Alexis Bell, Enrique Iglesia, *The Journal of Physical Chemistry C*, **2009**, 113, 2830-2836.
[5] Xingtao Gao, Simon Bare, Jose Fierro, Israel Wachs, *The Journal of Physical Chemistry B*, **1999**, 103, 618-629.

The role of copper-zinc alloy in catalytic carbon dioxide hydrogenation to methanol

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Carbon dioxide is a greenhouse gas and major anthropogenic pollutant responsible for climate change and ocean acidification [1]. The development of an appropriate heterogeneous catalyst that will actively and selectively convert mixtures of CO_2 and H_2 to methanol, can significantly contribute to a more widespread large-scale utilization of CO_2 and renewable energy. One of the most active catalyst in CO_2 to methanol hydrogenation is based on alumina supported copper-zinc, which is widely used for syngas transformation to methanol. The activity is still far from commercial utilization and further catalyst improvement is still required [2]. Most previous studies, investigating mechanistic aspects of methanol synthesis, are based on experiments made under conditions (low temperature, vacuum) that are far away from the real catalytic experiment (>15 bar; 220-280 ºC). Hence, even the structure of active sites and especially the role of copper-zinc alloys in this catalytic system, are subject of intense debate [3-4].

This situation has motivated us, to perform *operando* investigations using time-resolved XAS (at both Cu and Zn K-edges) and XRD under relevant catalytic conditions, supported by theoretical modelling and TEM, in an effort to bridge the “pressure gap” and provide unambiguous understanding of the role of the alloy in this reaction. We show that surface CuZn alloy, which for a long time was considered an active site for methanol synthesis, is only present under highly reductive atmosphere and is rapidly reacted away upon switching to the catalytic CO_2/H_2 reaction mixture. Formation and decomposition of the CuZn alloy facilitate formation of a well-developed Cu/ZnO interface, where metallic Cu activates hydrogen, while the zinc phase is responsible for CO_2 adsorption and followed hydrogenation. The intimate contact between these two phases promotes efficient methanol synthesis. Ultimately, the role of CuZn alloy formation and its decomposition in forming the active interface represents a novel paradigm in this much-research system. It can be considered as an exemplar model for structural changes in multicomponent materials and catalysts.

[1] S.J. Davis et al., *Science,* **2010,** 329, 1330–1333.
[2] M.D. Porosoff et al., *Energy Environ. Sci.*, **2016**, 9, 62–73.
[3] S. Kattel et al., *Science*, **2017**, 355, 1296–1299.
[4] J. Nakamura et al., *Science*, **2017**, 357, eaan8074.

ZnO-Based Catalysts through Atomic Layer Deposition for CO_2 Hydrogenation to Methanol

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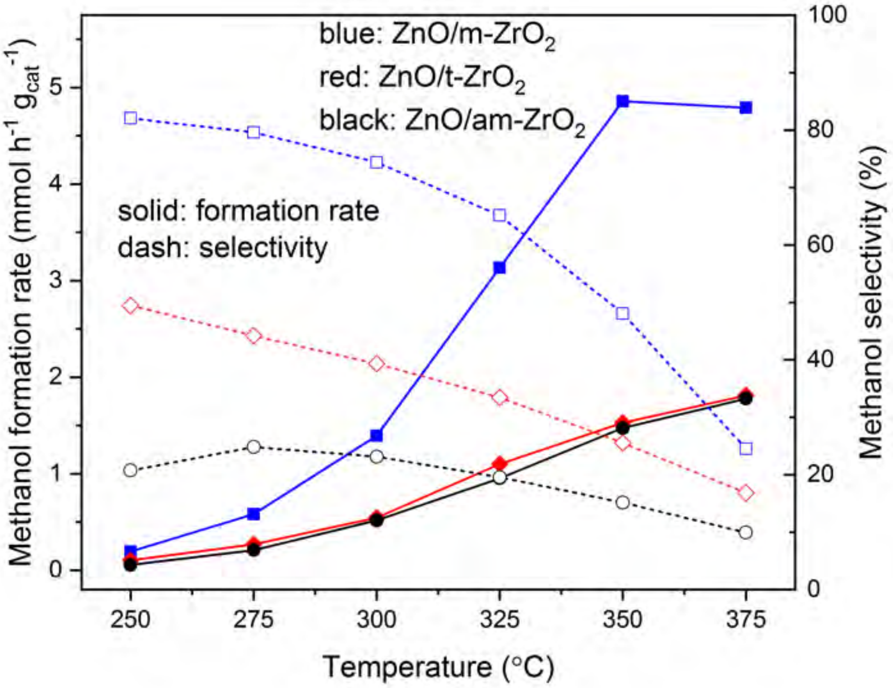
While hydrogenation of CO_2 to methanol is a promising technology for energy storage, its full scale industrial implementation is hindered by the deactivation of the Cu-ZnO/Al_2O_3 catalyst, in addition to the low selectivity to methanol.[1,2] Recently, Cu-free oxides have emerged as catalysts for CO_2 to methanol reaction and displayed a high stability and selectivity to methanol.[3,4] In this study, we have synthesized a series of ZnO coatings on different polymorphs of ZrO_2 while controlling the thickness of the ZnO layer by atomic layer deposition (ALD) with Ångstrom resolution. We found that ZnO coated on monoclinic ZrO_2 (m-ZrO_2) with 20 ALD cycles could achieve a methanol selectivity of ~70% at 25 bar (H_2/CO_2 = 3:1) and 325 °C. Moreover, no deactivation was found during a 100 h stability test. We also probed the effect of the support on the catalytic performance by comparing monoclinic, tetragonal (t-ZrO_2), and amorphous ZrO_2 (am-ZrO_2) and found that m-ZrO_2 is the most effective support. We observe further that the reduction of ZnO/m-ZrO_2 at 500 °C under H_2 promotes the interaction between these oxides and enhances the methanol selectivity compared to reduction at 300 °C.



[1] A. Goeppert, M. Czaun, J.-P. Jones, G. K. Surya Prakash and G. A. Olah,*Chem Soc Rev*, 2014, **43**, 7995–8048.

[2] M. Behrens, F. Studt, I. Kasatkin, S. Kühl, M. Hävecker, F. Abild-Pedersen, S. Zander, F. Girgsdies, P. Kurr and B.-L. Kniep, *Science*, 2012, 1219831.

[3] O. Martin, A. J. Martín, C. Mondelli, S. Mitchell, T. F. Segawa, R. Hauert, C. Drouilly, D. Curulla-Ferré and J. Pérez-Ramírez, *Angew. Chem. Int. Ed.*, 2016, **55**, 6261–6265.

[4] J. Wang, G. Li, Z. Li, C. Tang, Z. Feng, H. An, H. Liu, T. Liu and C. Li, *Sci. Adv.*, 2017, **3**, e1701290

Direct Conversion of Methane to Methanol over Cu-Erionite Zeolite

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Direct conversion of methane to methanol has been an attractive yet challenging process in hydrocarbon chemistry field. In recent year, copper-exchanged zeolites have emerged as a promising class of materials capable of selectively oxidizing CH_4 into surface-bound methoxy species by hosting active sites akin to those found in CH_4 monooxygenases.[1,2] So far, the most studied zeolites for direct conversion of methane to methanol are mordenite and ZSM-5, and the overall methanol yield has been continuously increasing through efforts of decades.[3,4] The direct conversion of methane to methanol over Cu-zeolites requires a stepwise procedure, where a high-temperature activation (typically, 450 °C) is needed to create the active sites and subsequently the system is cooled down to a lower temperature (*ca.* 200 °C) in the reaction stage to avoid the over oxidation and thus achieve an optimal methanol yield. In this study, we show for the first time that a Cu-erionite (Cu-ERI) zeolite achieved a high methanol yield under an isothermal condition, which was comparable to those obtained on other zeolites in the conventional condition.

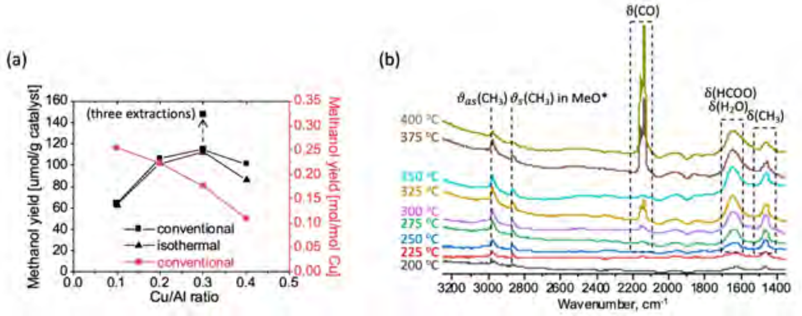

Figure 1. (a) Methanol yield as a function of Cu/Al ratio in Cu-ERI catalysts under conventional and isothermal conditions. (b) *In-situ* FTIR spectra of surface species formed on Cu-ERI (Cu/Al=0.3) during the reaction with methane at 300 ° C for 30 min.

Figure 1(a) shows the methanol yield over the Cu-ERI zeolites with different Cu/Al ratios. With high temperature activation at 450 °C, the Cu-ERI sample with Cu/Al=0.3 produced 150 umol-methanol/gram catalyst at 300 °C under 30 bar methane (after three extractions, see the arrowed point). The yields obtained under the isothermal condition were close to those in the conventional condition, indicating that the same amounts of active sites were generated. The methanol yield per copper (red line) decreased with the increase in copper loading, suggesting only a small fraction of the additional copper was active with the majority remaining inactive. *In-situ* FTIR spectra in Figure 1(b) demonstrate that the Cu-ERI zeolite showed superior selectivity towards methanol even at 300 °C, which is probably due to a unique environment of the active sites. Identification of Cu speciation in the Cu-ERI zeolite, for example through the in-situ Cu K edge XAS, is crucial to understand the possible mechanisms, which will be pursued in the near future.

[1] P. Tomkins, M. Ranocchiari, J. A. van Bokhoven, *Acc. Chem. Res.* (2017) 50, 418. [2] K. T. Dinh, M. M. Sullivan, P. Serna, R. J. Meyer, M. Dincă, Y. Román-Leshkov, *ACS Catal.* (2018) 8, 8306. [3] J. S. Woertink, P. J. Smeets, M. H. Groothaert, M. A. Vance, B. F. Sels, R. A. Schoonheydt, E. I. Solomona, *Proc Natl Acad Sci U S A.* (2009) 106, 18908. [4] E. M. C. Alayon, M. Nachtegaal, A. Bodi, J. A. van Bokhoven, *ACS Catal.* (2014) 4, 16.

Designer 3D Yolk@Shell TiO_{2-x}/LDH Architecture for Powerful Visible Light CO_2 Conversion

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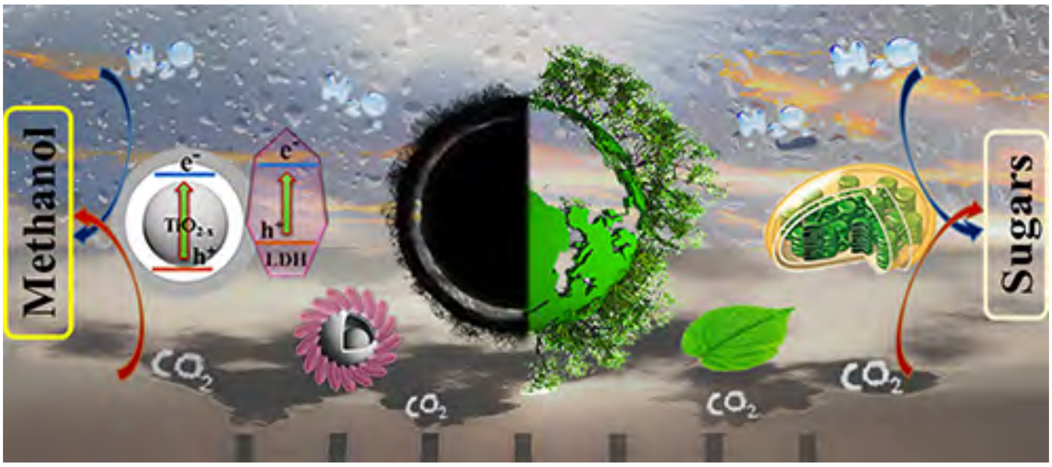
The world's increasing population and prompt growth of economy and industry comes along with huge amount of fossil fuel combustion. The resulting increase of carbon dioxide (CO_2) concentration on earth contributes to the greenhouse effect. Different strategies are proposed at mitigating CO_2 emissions including carbon recycling used in energy supply. Similar to photosynthesis in plants, direct photo conversion of CO_2 to fuels or organic raw materials for chemical products by extracting protons and electrons from water molecules can be the ultimate way to realize a sustainable carbon-neutral society. The main challenge in this respect is production of appropriate, stable, and effective photocatalytic materials. To achieve these aims a promising route is the design of engineered hybrid semiconductors with high efficiency of visible light utilization. In this regard, three dimensional yolk@shell hydrogenated TiO_2/Co-Al layered double hydroxide (3D Y@S TiO_{2-x}/LDH) architecture was successfully assembled by sequential solvothermal, hydrogen treatment and hydrothermal preparation steps. This architecture revealed a high activity and selectivity for the photocatalytic reduction of CO_2 to solar fuels, without a noble metal co-catalyst. The time dependent experiment indicated that the production of CH_3OH was almost selective until 2h (up to 251 $\mu mol/g_{cat.}$ h.), whereas the CH_4 was produced gradually by increasing the time of reaction to 12h (up to 63 $\mu mol/g_{cat.}$ h.). This superior activity can be attributed to the design of 3D Y@S TiO_{2-x}/LDH architecture with high CO_2 adsorption ability in mesoporous yolk@shell structure, and LDH interlayer spaces. Also, oxygen vacancies in TiO_{2-x} could provide excess sites for adsorption, activation and dissociation of CO_2. Furthermore, the generated Ti^{3+} species on the surface of Y@S TiO_2 as well as connecting of structure with LDH plates, can facilitate the electron-hole separation and decrease the band gap of nanoarchitecture to the visible region. This research can pave the way to further progress in the design of advanced structures with greatly improved photo-efficiencies (e.g. hydrogen production, solar cells, and solar enhanced fuel cells) that will be reported in due course.



[1] Kan Li, Bosi Peng, Tianyou Peng, ACS Catalysis, **2016**, 6, 7485-7527.
[2] Abolfazl Ziarati, Alireza Badiei, Rafael Luque, Weiyi Ouyang, Journal of Materials Chemistry A, **2018**, 6, 8962-8968.
[3] Abolfazl Ziarati, Alireza Badiei, Rosella Grillo, Thomas Burgi, ACS Applied Materials & Interfaces, **2019**, 11, 5903-5910.

Selective Propylene Production via Propane Oxychlorination on Metal Phosphate Catalysts

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Catalytic propane oxychlorination (POC), comprising the reaction of this alkane with O_2 and hydrogen chloride (HCl), represents a very interesting route for the direct and selective production of propylene, a key commodity of the chemical industry.[1] Few catalytic systems have been disclosed for this reaction, generating great potential for new discoveries. Here, we assessed the performance of phosphates of transition metals, including Ti, V, Cr, Mn, Fe, Co, Ni, and Cu in POC. Four categories of catalysts were identified, depending on the preferentially generated products; propylene (Cr and Fe phosphates), cracking products (Mn, Ti, Co, Ni phosphates), chlorinated hydrocarbons (Cu phosphate), or carbon oxides (V phosphate). Among them, chromium phosphate (CrPO) stood out as a selective (up to 98%) catalyst for propylene production. Its olefin yields of up to 50% render it one of the best catalysts among those applied to any propane-to-propylene technology. Furthermore, long-term runs and in-depth characterization demonstrated that this catalyst can preserve its structure and performance for over 60 h on stream. Finally, representative systems of each category were assessed in the oxidation of propane and of HCl as well as in propyl chloride dehydrochlorination to gather insights enabling rationalization of the catalytic performance (**Figure 1**). This kinetic analysis revealed that the reactivity of the phosphate catalysts linearly correlates with the material's ability to evolve chlorine, while a high propylene selectivity originates from fast dehydrochlorination kinetics in combination with a hindered ability to generate molecular chlorine in the gas phase and a low propensity towards propane cracking and combustion.

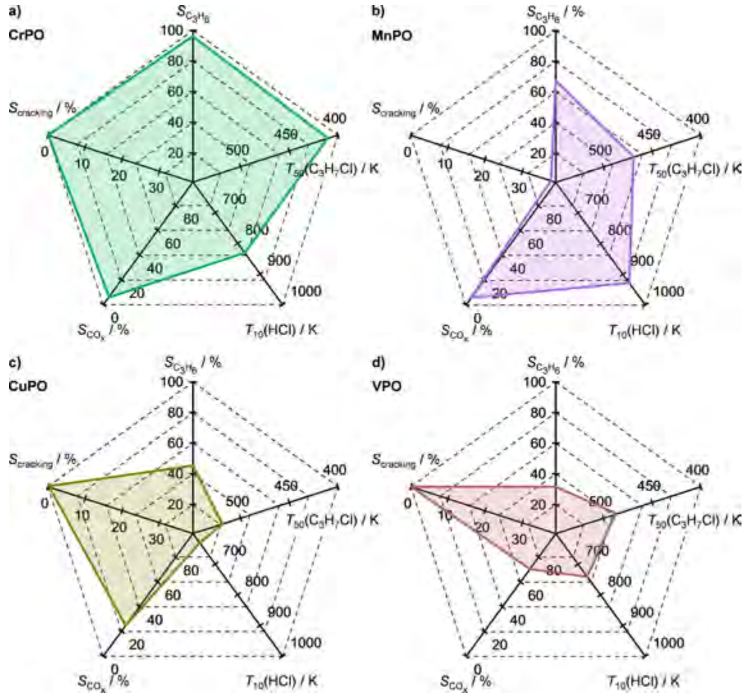

Figure 1 Rationalization of the selectivity patterns in POC over representative catalysts of each of the categories identified.

[1] G. Zichittella, N. Aellen, V. Paunović, A. P. Amrute, J. Pérez-Ramírez, *Angew. Chem. Int. Ed.* **2017**, 56, 13670.

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Redefining Nucleoside Analog Total Synthesis and Manufacturing

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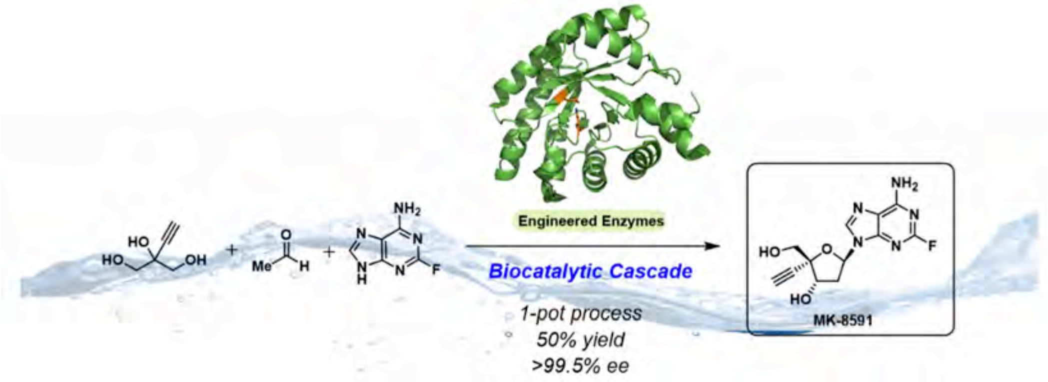
Nucleoside analogues are ubiquitous in nature and are critical component of life-saving therapies used in the treatment of viral disease and cancer. Despite their widespread use and commercial value, the state-of-the-art methods for their preparation in drug discovery, drug development and eventual commercialization are lacking and remain a poorly solved problem in organic synthesis. In addition to posing synthetic challenges, custom nucleoside total synthesis presents several challenges with respect to green and sustainable chemistry, where current methods largely rely on chiral pool feedstocks and protecting group chemistry. We have developed a suite of novel methods for the synthesis and scale-up of nucleosides, as exemplified by the synthesis of MK-8591 for the treatment of HIV infection. These efforts have culminated in an aspirational synthesis from commodity chemicals using a biocatalytic in-vitro cascade for construction of the nucleoside.



Nature of the synergy between Brønsted and Lewis acid sites in Sn-Beta zeolites for the synthesis of polyoxymethylene dimethyl ethers (OME)

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Diesel consumption is expected to grow between 46 and 200 % compared to its 2010 level during the next four decades, according to the World Energy Council.[1] Meanwhile, air pollution has reached alarming levels in large cities forcing governments to adopt more stringent emission standards. In this context, polyoxymethylene dimethyl ethers (OME) have recently gained attention as a new type of diesel additive or substitute due to their appealing properties.[2] Their large-scale implementation requires stable and acidic catalysts. However, the role of Lewis and Brønsted acid sites, and their potential synergy remains ambiguous for the synthesis of OME. Therefore, the goals of this study were twofold. First, we sought to acquire a deeper understanding of the type of acidity which is involved in the different OME synthesis steps. Second, we aimed at investigating the nature of the synergy between Lewis and Brønsted acid sites.

These objectives were pursued by synthetizing a series of BEA zeolites with various amounts of Brønsted and Lewis acid sites applied to several reactions for OME synthesis. Lewis acidity was introduced in the zeolite framework via Sn incorporation by grafting in dichloromethane, as it was shown to lead to high Sn content with little extra-framework Sn. Various characterization techniques such as N_2 physisorption, solid-state NMR or infrared spectroscopy of adsorbed pyridine were used to study the catalysts structure and acidity. The synthesized catalysts were used to produce OME using various reactions involving different reactants. Additionally, attenuated total transmittance Fourier-transform infrared spectroscopy was used to study the adsorption modes of $OME_1$and trioxane (TRI) on the synthesized catalysts.

The characterization results confirmed that Sn grafting resulted in the incorporation of Sn in a tetrahedral coordination within the dealuminated BEA framework. Then, our reaction results demonstrated that Brønsted sites were active in all steps of OME synthesis while Lewis acid sites were only active in OME growth, paraformaldehyde (PF) decomposition and hemiacetal acetalization. Notably, TRI dissociation and OME_1activation did not occur on Lewis acid sites. The presence of both sites resulted in a synergy when $OME_1$was used with PF or TRI. Partially dealuminated, Sn-modified Beta zeolites exhibited a significant increase in turnover frequency and reduction in byproduct generation compared to the parent H-Beta zeolite. This synergistic effect is explained by a more efficient formaldehyde (FA) insertion into OME on Lewis acid sites, while generation of FA units by TRI or PF decomposition occurred on Brønsted acid sites. The interaction between tetrahedral Sn and the carbonyl group of FA resulted in an activated FA, likely to be inserted into OME.

[1] World Energy Council, Global Transport Scenarios 2050, **2011**, DOI: 10.1016/j.enpol.2011.05.049.
[2] C. J. Baranowski, A. M. Bahmanpour, O. Kröcher, *Appl. Catal. B Environ,* **2017**, 407, DOI: 10.1016/j.apcatb.2017.06.007.

Understanding the Nature of Surface Sites in Ga_2O_3-Based Catalysts for Propane Dehydrogenation: Acidity, Deactivation, and the Support Effect

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Ga_2O_3-based catalysts for the dehydrogenation of propane (PDH) feature hexa- and tetracoordinated Ga^{3+} sites, the latter are likely the active centers for PDH.[1] However, little is known about the distribution and nature of surface sites in Ga_2O_3-based PDH catalysts and the influence of surface acidity, structural defects and the support on the catalytic activity. Here, we report that the specific activity of silica-supported γ–Ga_2O_3 nanoparticles (γ–Ga_2O_3/SiO_2) in PDH is higher than that of β–Ga_2O_3/SiO_2 and a $Ga(NO_3)_3$-derived benchmark, Ga/SiO_2. We characterized surface sites by pyridine-FTIR and ^{15}N DNP NMR and developed structure-activity relationships for this class of catalysts. γ–Ga_2O_3/SiO_2 is a more active but less selective catalyst than unsupported γ–Ga_2O_3 (Fig. 1, A, B). Surface acidity studies reveal mild Brønsted acid sites only for γ–Ga_2O_3/SiO_2. Such sites likely result from the interaction between γ–Ga_2O_3 and SiO_2 and may be associated with the high specific activity and lower selectivity of γ–Ga_2O_3/SiO_2. The defect-spinel structure of γ–Ga_2O_3 contains structural vacancies susceptible to cationic substitutions,[2] which could promote an interaction with the silica support, thus yielding mild Brønsted acidity with distinct catalytic performance. Interactions between Lewis acid sites and surface silanol groups generating Brønsted acidic sites have been described for zeolites and silica-aluminas,[3,4] but to our knowledge, they have not yet been characterized for interfacial sites in SiO_2-supported metal-oxide nanoparticles. In contrast to all other catalysts in this work, Ga/SiO_2, the benchmark featuring only tetracoordinated Ga sites, does not deposit any coke and does not deactivate on stream. ^{15}N DNP NMR spectra (Fig. 1C) show features at ca. 235 ppm ascribed to Ga(IV) sites for all catalysts except α–Ga_2O_3. This suggests that higher-coordinated Ga sites could be associated with coke-related deactivation in PDH. Overall, we establish structure-activity relationships for Ga_2O_3-based PDH catalysts by elucidating the surface sites of silica-supported and unsupported polymorphs of Ga_2O_3, also providing insight for the interaction between γ–Ga_2O_3 and the silica support.

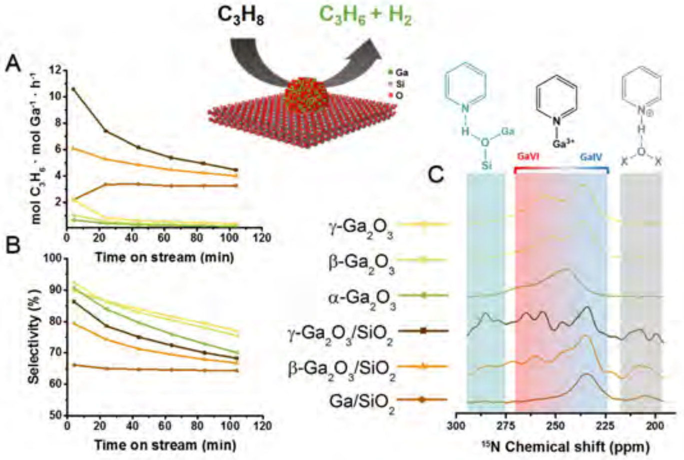

Figure 1. PDH specific activity (A) and selectivity (B) for Ga_2O_3 catalysts. ^{15}N DNP NMR results, relating features at different chemical shifts with the pyridine-bound surface Ga sites (C).

[1] Fan, K.N., *et al., J. Catal.*, **2008,** *256*, 293–300.
[2] Gupta, P, et al., J. Phys. Chem. C., **2018,** 122, 22094−22105.
[3] Meriaudeau, P., *et al., J. Mol. Catal.*, **1990,** *59*, L31 - L36.
[4] Hensen, J. M., *et al., J Phys. Chem. C.*, **2012,** *116,* 21416–21429.

A Silicon-based Microfluidics Platform for Heterogeneous Catalysis in Wall-coated Flow Reactors

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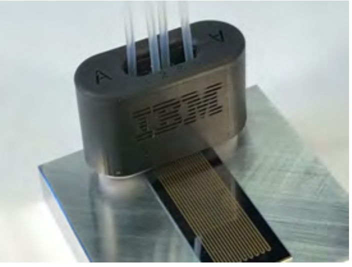
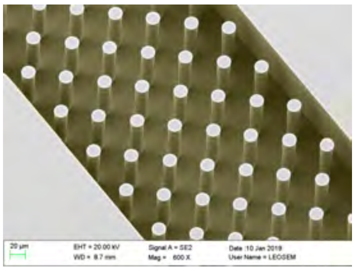
On-chip flow microreactors may increase space-time efficiency for reaction screening and compound library synthesis (e.g. for drug discovery) as they enable miniaturization and process automation. Cutting-edge microfabrication of highly chemically inert silicon-based microfluidics compatible with MEMS (microelectromechanical systems) and CMOS (complementary metal-oxide-semiconductor) fabrication technologies allows novel reactor designs and functionalities to be realized and thus the exploration of new chemical reactivities and testing of new compounds [1]. On-chip features such as electrically driven joule heaters, electrodes or field-enhanced nanophotonic surface textures may allow site-selective electrochemical surface functionalization [2,3], precise reaction control and on-line analytics.



Silicon-based milli- and microfluidic devices are developed for solid-phase synthesis of catalytically active surfaces. In contrast to frequently utilized glass channel walls as catalyst adhesion layers [4], we use metallic coatings along microchannels that permit the formation of segregated thin-films patterns to site-selectively functionalize surfaces along a single channel. The metallic adhesion layers thereby act as electrodes for electrosynthesis, catalyst immobilization and electrochemical analysis. These wall-coated microreactors with a high surface-to-volume ratio are employed to screen single- and multistep chemical reactions with organo- and organometallic catalysts. In addition, nanofabricated resonant plasmonic nanohole arrays embedded in the electrodes are designed to characterize catalyst monolayers by surface-enhanced Raman spectroscopy (SERS).



[1] R. Munirathinam, J. Huskens, W. Verboom, *Adv. Synth. Catal.,* **2015**, 357, 1093-1123.
[2] M. Hellstern, M. Gantenbein, L. Le Pleux, G. Puebla-Hellmann, E. Lörtscher, M. Mayor, *Adv. Mater. Interfaces,* **2019**, 6, 1801917.
[3] M. Hellstern, M. Gantenbein, G. Puebla-Hellmann, M. Mayor, E. Lörtscher, “Electrochemical Deprotection for Site-selective Immobilization and Local Assembly of Molecules by Click-Chemistry” US Patent Application No. P201701725US01 (**2018**).
[4] R. Ricciardi, J. Huskens, W. Verboom, *J. Flow Chem.,* **2013**, 3, 127-131.

Post-synthesis deposition of mesoporous niobic acid with improved thermal stability by kinetically controlled sol–gel overcoating

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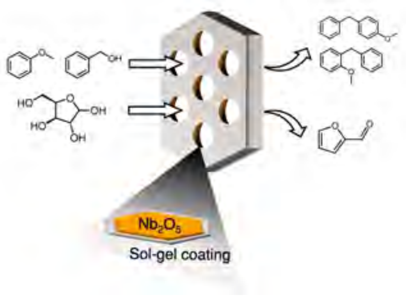
Niobia is a well-known solid acid catalyst owing to its intrinsic Brønsted and Lewis acidity. However, catalyst development with this oxide has been limited by our ability to control its pore structure and thermal stability. Here we report a novel post-synthetic approach for preparing mesoporous niobia catalysts. This method relies on controlling the kinetics of niobium(v) ethoxide to deposit conformal Nb_2O_5 overcoats on SBA-15 in a typical Stöber solution. Full Nb_2O_5 coverage over the mesopores of SBA-15 was achieved by adding 4 monolayer equivalents of precursor ($4Nb_2O_5$@SBA-15), which was verified by X-ray photoelectron spectroscopy. This overcoated SBA-15 had a high surface area and retained a narrow as well as ordered pore size distribution. Importantly, the typical structural transition from the amorphous to pseudo-hexagonal Nb_2O_5 phase did not occur with the overcoat after calcination at 773 K. Limiting this crystallization imparts an unprecedented thermal stability to our niobia overcoat, which enables the acid sites to be well preserved after catalyst regeneration. Furthermore, $4Nb_2O_5$@SBA-15 showed higher yields than commercial niobia (HY-340) and lab-synthesized bulk niobia in two probe reactions: xylose dehydration to furfural and Friedel–Crafts alkylation. In both cases, the improvement could be explained by the unique structural features of the niobia overcoat, including a favorable ratio of Brønsted and Lewis acid sites in the case of xylose dehydration and a high proportion of isolated Nb–OH groups for the alkylation reaction. Such structural features and unprecedented thermal stability provide additional tools for synthetizing unique solid acid catalysts using a simple post-synthesis deposition method.



Metal Dependent Structure-Activity Relations in Acetylene Hydrochlorination

S. K. Kaiser[1], R. Lin[1], G. Manzocchi[1], J. Pérez-Ramírez[1]*

[1]ETH Zurich, Switzerland

The substitution of the toxic mercuric chloride catalyst in polyvinyl chloride production *via* acetylene hydrochlorination is an imperative step to reduce the environmental impact of this long-established industrial technology.[1] In this context, merging fundamental and applied research to derive structure-activity relations of promising metal-based catalysts (Au, Ru, Pt, Ir, and Rh) is key to guide the development of a more sustainable process. For this purpose, we synthesized a platform of metal nanostructures, ranging from single atoms with tunable oxidation state to metallic nanoparticles, by varying the structure of functionalized carbon and controlled thermal activation. Combining advanced characterization techniques, steady-state experiments, density functional theory, and mechanistic studies, we identified two main catalyst families, (*i*) Au-, Pt- and (*ii*) Ru-, Ir-, Rh-based systems, which show fundamental differences regarding the structure of the active site (single atoms versus nanoparticles, **Figure 1**) and the prevailing deactivation mechanisms (single atom agglomeration versus nanoparticle re-dispersion). With this understanding, we developed system-oriented optimization strategies, including single-layer graphene encapsulation of metal nanoparticles to prevent undesired re-dispersion and oxygen co-feeding to inhibit coke formation at the metal sites, fostering the design of high-performance hydrochlorination catalysts.[2]

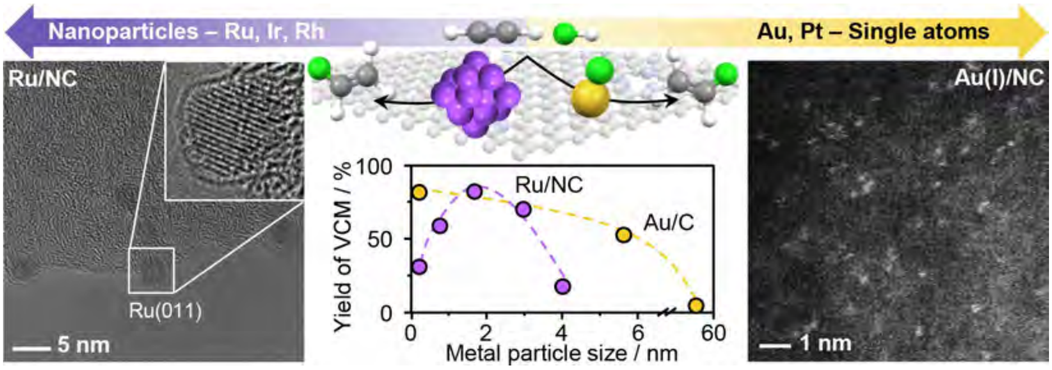


Figure 1 Single atoms versus nanoparticles as the active site in acetylene hydrochlorination.

[1] R. Lin, A. P. Amrute, J. Pérez-Ramírez, *Chem. Rev*. **2017**, 117, 4182.
[2] K. Kaiser, R. Lin, S. Mitchell, E. Fako, F. Krumeich, R. Hauert, O. V. Safonova, V. A. Kondratenko, E. V. Kondratenko, S. M. Collins, P. A. Midgley, N. López, J. Pérez-Ramírez, *Chem. Sci*. **2019**, 10, 359.

Process Related Aspects of Industrial Fluorine Chemistry

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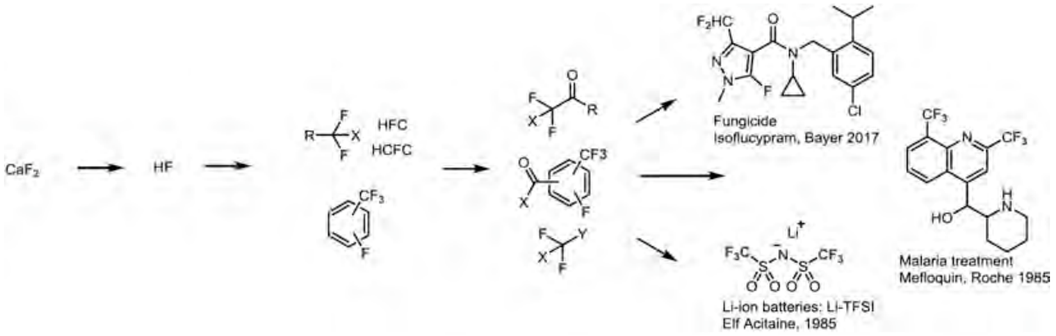
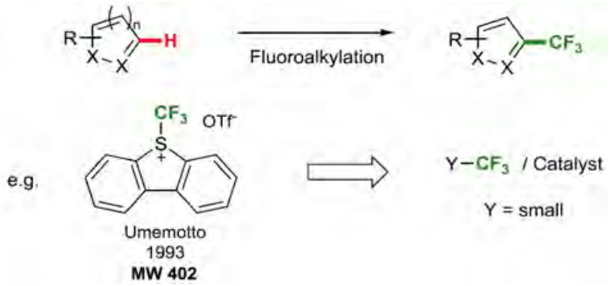
Numerous active ingredients in the pharmaceutical and agro chemical industry as well as material sciences[1] contain fluorine as a crucial part, determining the desired properties of the ingredient to a large extent[2].



The production of fluorine containing ingredients on an industrial scale, however, poses several challenges addressing reactivity, toxicity, material of construction and more. The combination of these challenges with increasingly complex actives as well as the expectations for fast and cost efficient launch of new products forces one to use efficient ways to make these products.

Some aspects of such new ways may not only involve the use of typical modern industrial concepts but also require new chemical methods such as catalytical fluoroalkylations avoiding the use of costly and waste intensive reagents.



[1] G. Siegemund, W. Schwertfeger, A. Feiring, B. Smart, F. Behr, H. Vogel, B. McKusick, P. Kirsch, in *Ullmann's Encyclopedia of Industrial Chemistry*, **2016**.

[2] H. Groult, F. Leroux, A. Tressaud, *Modern Synthesis Processes and Reactivity of Fluorinated Compounds*, Elsevier, **2016**.

Structure-activity descriptors for the rational design of materials in direct conversion of methane to methanol

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Methane, the simplest alkane, is the principal component of natural gas, which is one of the cheapest and most abundant sources of hydrocarbons. Its direct conversion to an oxygenate, such as methanol, a large-scale product in the chemical industry, is an exciting goal. However, the low chemical reactivity of methane and the tendency of methanol towards oxidation to carbon oxides mean that the direct oxidation of methane with oxygen in one step is challenging, if not impossible.[1] One of the approaches to the selective oxidation of methane to methanol is so-called "chemical looping", implying cyclic exposure of the material possessing redox properties to an oxidant and methane at different temperatures with the subsequent extraction of the oxidation products.[2-5] Despite multiple studies in this field and the partial identification of the active species and reaction mechanism, it has not been possible to design the best material and determine the ideal process conditions for industrial implementation. Our present study shows how to design a significantly better performing material and the reaction parameters to enhance the methanol yield. This led to the highest methanol productivity to date, using a material that until recently was considered to be inactive, opening a novel direction for the design of active materials.

We performed a systematic study of the copper-exchanged zeolites with MOR, MFI, BEA and FAU structures with similar Si/Al ratio and copper loading in the conversion of methane to methanol. FTIR spectroscopy of adsorbed nitrogen monoxide and molecular hydrogen determined the copper speciation, while the redox properties of the materials were evaluated by means of the temperature-programmed reaction (TPR) with methane, monitored by mass spectrometry and in situ X-ray absorption spectroscopy. The redox properties of the Cu(II)-oxo sites in copper-exchanged zeolites, governed by the zeolite framework and copper speciation, correlate with activity and selectivity in the direct synthesis of methanol from methane. Such redox properties can be extracted with ease from TPR experiments and then serve as a guide for selecting the conditions when testing new materials and predicting the optimal temperature for activation of methane. The data on the copper-oxo reducibility can be used to optimize the reaction conditions to achieve the highest methanol yield. In this way, it was established that the reaction of CuFAU(Si/Al = 3) with methane in an isothermal regime at 633K and 15 bar leads to a methanol yield of 360 μmol/g, which is the highest methanol yield achieved over copper-exchanged zeolite in one cycle.

The discovered process answers needed advancement for industrial feasibility of the direct conversion of methane to methanol and provides a route for further optimization of the reactive material and reaction conditions.

[1] M. Ravi, M. Ranocchiari, J. van Bokhoven, Angew. Chem. Int. Ed., 2017, 56, 16464-16483. [2] M. H. Groothaert, P. J. Smeets, B. F. Sels, P. A. Jacobs, R. A. Schoonheydt, J. Am. Chem. Soc., 2005, 127, 1394. [3] J. S. Woertink, P. J. Smeets, M. H. Groothaert, M. A. Vance, B. F. Sels, R. A. Schoonheydt, E. I. Solomon, Proc. Natl. Acad. Sci. U. S. A., 2009, 106, 18908. [4] S. Grundner, M. A. C. Markovits, G. Li, M. Tromp, E. A. Pidko, E. J. M. Hensen, A. Jentys, M. Sanchez-Sanchez, J. A. Lercher, Nat. Commun., 2015, 6, ncomms8546. [5] V. L. Sushkevich, D. Palagin, M. Ranocchiari, J. A. van Bokhoven, Science, 2017, 356, 523. [6] V. L. Sushkevich, D. Palagin, J. A. van Bokhoven, Angew. Chem. Int. Ed., 2018, 57, 8906-8910.

Development of a microfluidics-based assay for the evolution of artificial metalloenzymes using a cell surface display strategy

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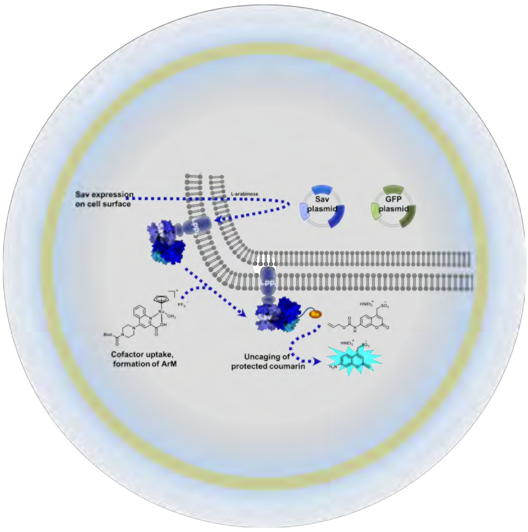
Incorporation of a transition metal catalyst within a protein scaffold enables the formation of artificial metalloenzymes (ArMs) with non-natural reactivities.[1]The catalytic activity and selectivity of such systems can be optimized by either chemical optimization of the metal cofactor or genetic evolution of the host protein. Integration of the biotinylated ruthenium complex[CpRu(Biot-Quinoline)(H_2O)][2]into the binding pocket of streptavidin (Sav) affords an artificial deallylase capable of uncaging a protected coumarin yielding a fluorescent readout.[3]

Herein, we present a microfluidics-based high-throughput assay[4]to evolve the catalytic activity of an artificial deallylase. Single *E. coli*cells with surface-displayed Sav are encapsulated in droplets together with the protected coumarin substrate and the biotinylated cofactor. The catalytically active mutants can be sorted by fluorescence-assisted droplet sorting (FADS) and the identified hits can be subjected to a further round of optimization. This method can be applied to evolve various ArMs *in vivo*and enable the screening of large libraries in an iterative and straightforward manner.



[1] Fabian Schwizer, Yasunori Okamoto, Tillmann Heinisch, Yifan Gu, Michela M. Pellizzoni, Vincent Lebrun, Raphael Reuter, Valentin Köhler, Jared C. Lewis, Thomas R. Ward, Chem. Rev., **2018**, 118, 142–231.
[2] T. Völker, F. Dempwolff, P. L. Graumann, E. Meggers, *Angew. Chem,. Int. Ed.*, **2014**, 53, 10536–10540.
[3] T. Heinisch, F. Schwizer, B. Garebedian, E. Csibra, M. Jeschek, J. Vallapurackal, V. B. Pinheiro, P.Marlière, S. Panke, T. R. Ward, *Chem. Sci.*, **2018**, 9, 5383–5388.
[4] R. Obexer, A. Godina, X. Garrabou, P. R. Mittl, A. D. Griffiths, D. Hilvert, *Nat. Chem.*, **2017**, 9, 50–56.

Stable and tunable phosphonic acid dipole layer for band edge engineering of photoelectrochemical and photovoltaic heterojunction devices

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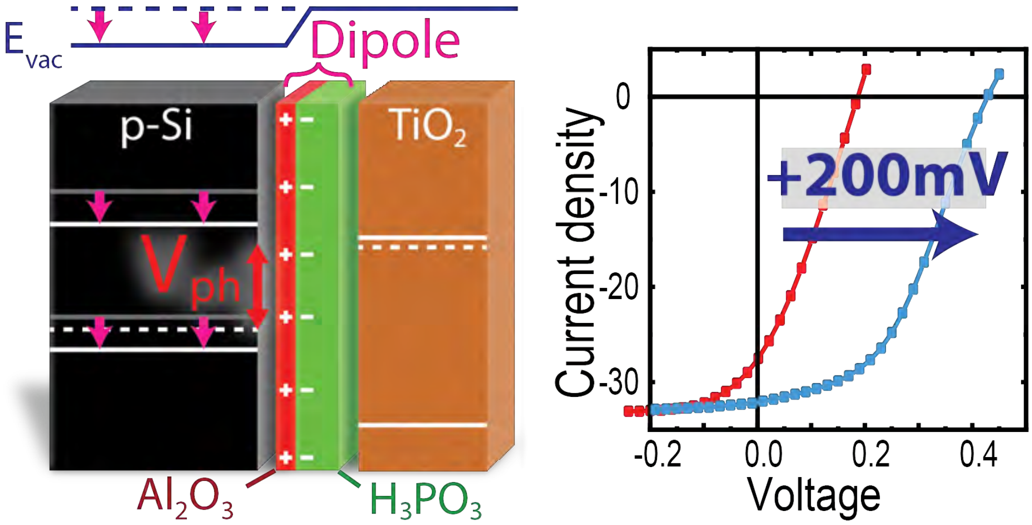
[1]University of Zurich, [2]Empa

Photoelectrochemical water splitting is performed in aqueous electrolyte. High performance semiconductors are not stable under those conditions and a corrosion protection layer, such as TiO_2, has to be used. The photoabsorbing material and the TiO_2 form a heterojunction and the photovoltage of such a device is usually small since most high performance semiconductors (e.g. Si) have a poor band alignment with TiO_2. We present a method to overcome this limitation by placing a phosphonic acid (H_3PO_3) dipole layer in between p-Si and n-TiO_2. The dipole induced band shift leads to an increase in photovoltage by 200 mV (see Figure).



We found that the photovoltage can be tuned by varying the thickness of the phosphonic acid layer, which was confirmed by DFT calculations. The versatility of the method was demonstrated by increasing the photovoltage of TiO_2 protected emerging materials, Cu_2O and Sb_2Se_3.

[1] René Wick-Joliat, Tiziana Musso, Rajiv Ramanujam Prabhakar, Johannes Löckinger, Sebastian Siol, Wei Cui, Laurent Sévery, Thomas Moehl, Jihye Suh, Jürg Hutter, Marcella Iannuzzi, S. David Tilley, *Energy Environ. Sci.*, **2019**, DOI: 10.1039/C9EE00748B.

Active Site Structures in Titanium-Silicalite 1: An NMR Point of View

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[1]ETH Zürich, [2]BASF SE

Titanium-Silicalite 1 (TS-1) is a unique oxidation catalyst that allows for the efficient activation of hydrogen peroxide (H_2O_2) as a terminal oxidant.[1] In particular, it allows for the catalytic epoxidation of propene on industrial scale leaving only water as byproduct. TS-1 has been studied in great detail, with the aim to understand the nature of the active sites that are still highly debated. Numerous studies based on both spectroscopic methods (IR, UV-VIS, EXAFS, NMR, XRD, neutron diffraction)[2] and computational approaches (MM, QM/MM, DFT)[3] led to isolated titanium peroxo and titanium hydroperoxo species being most commonly proposed as active sites.

Here, through the use of solid-state NMR spectroscopy augmented by computational studies and complementary spectroscopic methods, we will discuss the nature of the active sites in the TS-1 catalyst. Contrary to what is reported in the literature, non-isolated Ti sites are proposed to be key to the unique catalytic properties of TS-1.

[1] a) Bruno Notari, *Catal. Today,* **1993**, *18*, 163-172. b) Mario G. Clerici in *Metal Oxide Catalysis.* Eds. S. David Jackson, Justin S. J. Hargreaves, *Wiley-VCH*, **2009**.
[2] Silvia Bordiga, Alessandro Damin, Francesca Bonino, Carlo Lamberti in *Surface and Interfacial Organometallic Chemistry and Catalysis. Topics in Organometallic Chemistry.* Eds. Christophe Copéret, Bruno Chaudret, *Springer,* **2005**.
[3] Xavier Solans-Monfort, Christophe Copéret, Odile Eisenstein in *Quantum Chemical Calculations of Surfaces and Interfaces.* Eds. Vladimir A. Basiuk, Piero Ugliengo, *American Scientific Publishers,* **2009**.

Uncovering the interfacial carrier dynamics in emerging photoelectrodes for solar fuel production – an operando spectroelectrochemical study

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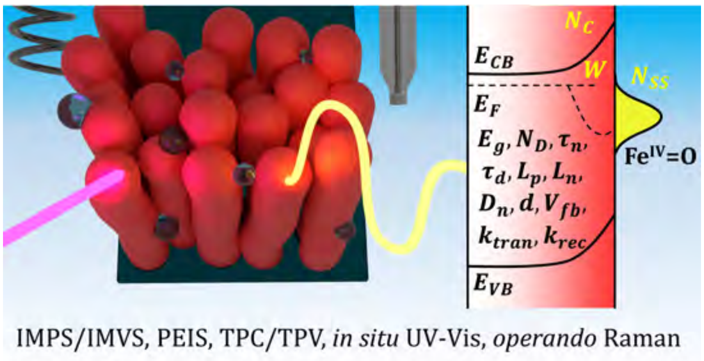
Storing solar energy in chemical form (*e.g.* hydrogen from water splitting), represents a promising route to enable a carbon-neutral society. Photoelectrochemical (PEC) water splitting holds the key to perform this process with simplicity and at high theoretical conversion efficiency. However, the realization of PEC H_2 production at a global scale is limited by the current performance of semiconductor materials suitable for PEC. To advance the field, an improved fundamental understanding of the semiconductor-liquid junction (SCLJ), wherein the photoelectrosynthetic reaction is occurring, is urgently needed to identify the parameters limiting the performance and direct actions for their improvement.



Here, we show how a toolbox of *operando* and *in situ* characterization techniques, namely, intensity-modulated photocurrent/photovoltage spectroscopy (IMPS/IMVS), transient photocurrent/photovoltage spectroscopy (TPC/TPV), photoelectrochemical impedance spectroscopy (PEIS), *in situ* UV-Vis spectroscopy, and *operando* Raman spectroscopy can be used to gain deep insight of the competing processes at the SCLJ. We highlight our recent studies with emerging semiconducting photoelectrodes ($CuIn_{0.3}Ga_{0.7}S_2$, $CuFe_2O_4$,[1] $ZnFe_2O_4$,[2] SnS_2,[3] and $LaFeO_3$), which have provided insights into the interfacial carrier behavior, *i.e.*, energetic across the interface, kinetics of charge transfer and recombination, nature of the surface states, and chemical identity of intermediate species. In particular, we implement light modulation techniques (IMPS/IMVS) on $CuFe_2O_4$ to reveal an unfavourable kinetic competition which significantly hampers the charge transfer efficiency. Likewise, by fitting the impedance response with equivalent circuits, a clear map of the density of surface states is shown. Overall, these findings provide a better understanding on the electrochemical phenomena at the SCLJ, establishing a precise roadmap to engineer the interface and optimize the performance of solar fuel devices.

[1] Yongpeng Liu, Florian Le Formal, Florent Boudoire, Liang Yao, Kevin Sivula, Néstor Guijarro, *Journal of Materials Chemistry A*, **2019**, 7, 1669-1677.
[2] Xiaodi Zhu, Néstor Guijarro, Yongpeng Liu, Pascal Schouwink, Rebekah A. Wells, Florian Le Formal, Song Sun, Chen Gao, Kevin Sivula, *Advanced Materials*, **2018**, 30, 1801612.
[3] Yong Zuo, Yongpeng Liu, Junshan Li, Ruifeng Du, Xiaoting Yu, Congcong Xing, Ting Zhang, Liang Yao, Jordi Arbiol, Jordi Llorca, Kevin Sivula, Néstor Guijarro, Andreu Cabot, *ACS Applied Materials & Interfaces*, **2019**, 11, 6918-6926.