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Controlled deposition of metal oxide layers by non-hydrolytic sol-gel for tailored acid sites generation and beyond

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Bulk materials are omnipresent in catalysis due to their ease of production, but they often suffer from low selectivity and stability due to the lack of precise design of their surface functionalities. We present a new technique for the controlled deposition of metal oxides layers, where precise tuning of material surface functionalities yields optimal performances for various applications.

The method is based on non-hydrolytic sol-gel chemistry using mixtures of metal alkoxides and metal halides. For instance, addition of a 1/3 mol/mol mixture of $\text{Ti}(\text{iPrO})_4$ and TiCl_4 to a toluene suspension of SiO_2 spheres led to the formation of a thin conformal TiO_2 overcoat with tunable porosity (Fig. 1, left). Thickness can be adjusted by the number of deposited layers with a growth rate of 0.5 nm/layer. Furthermore, this method allows deposition of TiO_2 layers inside the pores of mesoporous silica SBA-15 while maintaining 2D hexagonal structure and high porosity (Fig. 1, right). The mixed oxide created at the interface generates medium strength Lewis acid sites which catalyze 1-phenylethanol dehydration to styrene. High Lewis acid sites density with medium acid strength was obtained with 6 TiO_2 layers which lead to the highest yields of styrene and the highest catalyst stability. In contrast, a zeolitic catalyst often used for this reaction (HZSM-5) deactivates due to polystyrene formation on strong Lewis acid sites. The technique has also been employed to overcoat supported metal nanoparticle catalysts leading to metal-acid bifunctional catalysts that are highly selective for 3-propylguaiaicol hydrodeoxygenation, a key transformation for lignocellulosic biomass valorization. Finally, an analogous method was developed for deposition of alumina, yielding strong acid sites after deposition on silica substrates. We anticipate that the method reported can be used for the rational design of catalytic materials used in a wide range of applications.

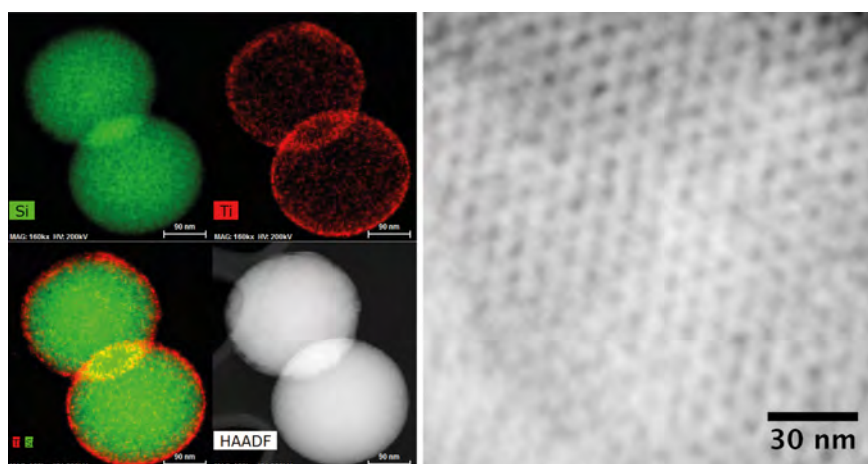


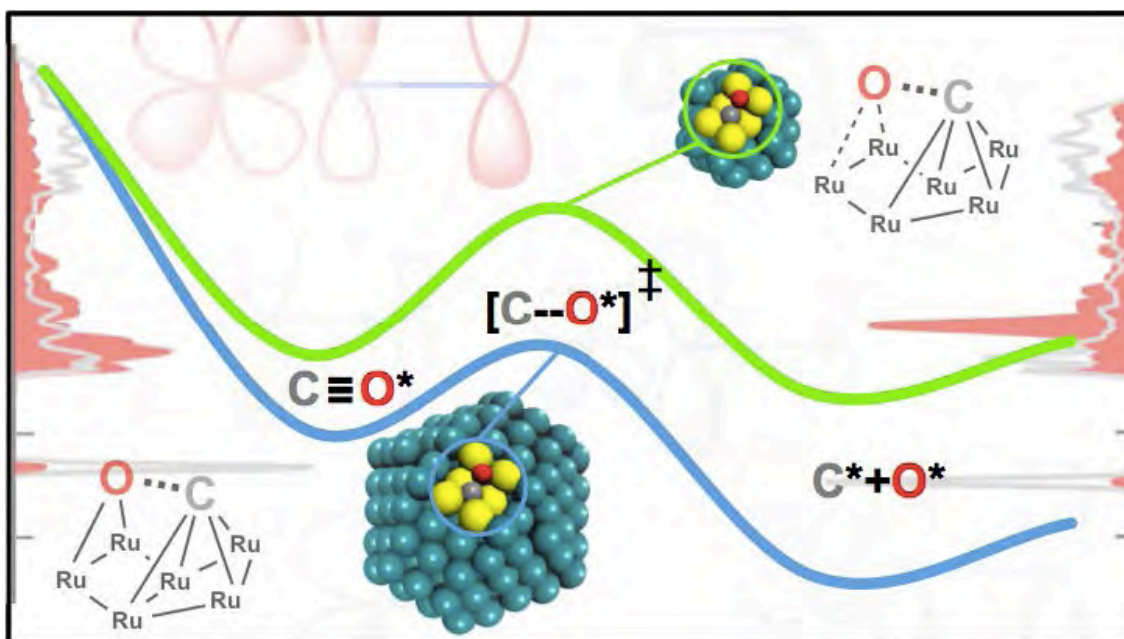
Fig. 1. Left: EDS mapping and HAADF STEM image of SiO_2 sphere after deposition of 10 layers TiO_2 (Si: green; Ti: red). Right: HAADF STEM image of SBA-15 after deposition of 10 layers TiO_2 .

Modeling Heterogeneous Catalysts by First Principles

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Metallic nanoparticles supported on oxides are one of the most important industrial heterogeneous catalysts. They are used in the ammonia synthesis, the formation of hydrocarbons from CO/H₂ (Fischer-Tropsch Synthesis), the reforming of methane or the water-gas shift reaction. In most cases, the evaluation of the reactivity of these systems via *ab initio* simulations is performed on a metallic facet (either a terrace or a step), usually neglecting the effect of the oxide support. While this approach allows the screening of different catalysts for a particular reaction at reasonable computational cost, it is not always able to explain how such systems work at atomic level. In this contribution, we will show how the use of realistic models for oxide supported nanoparticles can be key to properly describe the active site(s) of such systems and to rationalize experimental observations. In particular, we will illustrate how this approach combined with bonding analysis provides an additional explanation of the particle size effect in the Fischer-Tropsch reaction catalyzed by Ru nanoparticles; i. e. why bigger particles are more reactive towards CO than smaller ones.[1] Moreover, we will show how the inclusion of the support provides new interface sites, which are active in the methanol synthesis (from CO₂ and H₂) and the water gas-shift reaction catalyzed by oxide-supported Cu and Ni nanoparticles, respectively.[2,3]



[1] Lucas Foppa, Christophe Copéret, Aleix Comas-Vives, *J. Am. Chem. Soc.*, **2016**, 138, 16655-16668.

[2] Kim Larmier, Wei-Chih Liao, Shohei Tada, Erwin Lam, René Verel, Atul Bansode, Atsushi Urakawa, Aleix Comas-Vives, Christophe Copéret. *Angew. Chem. Int. Ed.*, **2017**, 129, 2358-2363.

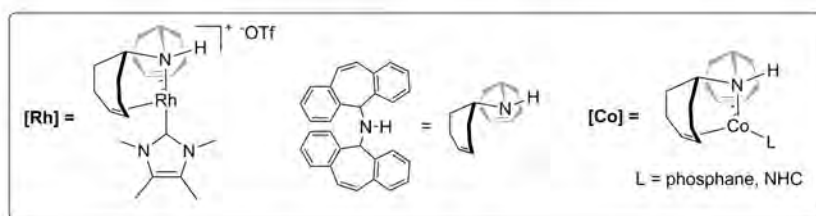
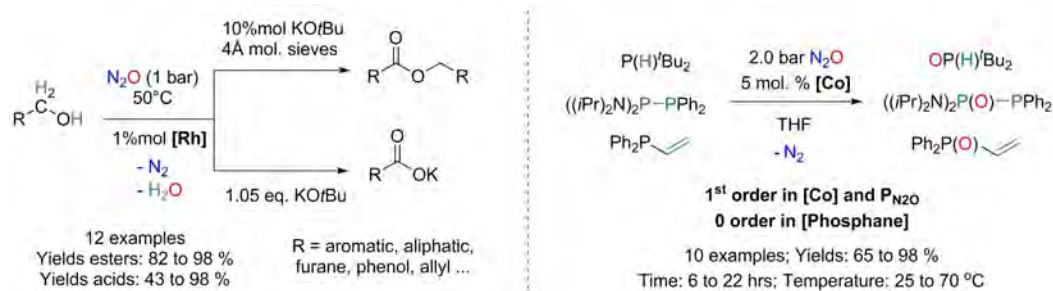
[3] Marius-Christian Silaghi, Aleix Comas-Vives, Christophe Copéret *ACS Catal.*, **2016**, 6, 4501-4505.

Toward a useful catalytic transformation of N₂O using group 9 organometallic complexes

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Nitrous oxide (N₂O) gases have been recently identified as the largest global ozone depleting agents and as the 3rd largest emitted greenhouse gases worldwide and 300 times more powerful than CO₂.^[1] N₂O is naturally produced via nitrification and denitrification of nitrate during nitrogen cycle, but is also an industrial waste. N₂O emission has increased significantly during industrialization as a result of agricultural soil management, N-fertilizer use, livestock waste management, mobile & stationary fossil fuel, combustion and industrial processes. Its transformation to less harmful chemicals is of particular interest but very challenging, since even if thermodynamically unstable, nitrous oxide is kinetically inert.^[2] We have successfully design low valent and reactive organometallic species containing group 9 metals (Rh^[3] and Co^[4]) that activate and catalytically transform, under mild conditions, this environmentally unfriendly molecules to valuable chemicals.



[1] a) A. R. Ravishankara, J. S. Daniel, R. W. Portmann, *Science*, **2009**, 326, 123-125. b) J. Hansen, M. Sato, *Proc. Natl. Acad. Sci. USA.*, **2004**, 101, 16109-16114.

[2] a) E. Eger, I., II. In *Nitrous Oxide N₂O*, Elsevier: New York, **1985**. b) K. Severin *Chem. Soc. Rev.*, **2015**, 44, 6375-6386.

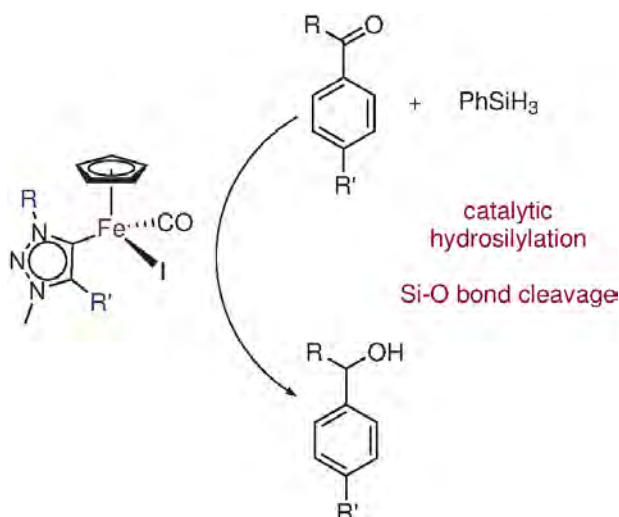
[3] T. L. Gianetti, S. P. Annen, G. Santiso-Quinones, M. Reiher, M. Driess, H. Grützmacher, *Angew. Chem. Int. Ed.*, **2016**, 55, 1886-1890.

[4] T. L. Gianetti, R. E. Rodriguez-Lugo, J. Harmer, M. Trincado, M. Vogt, G. Santiso-Quinones, H. Grützmacher, *Angew. Chem. Int. Ed.*, **2016**, 55, 15323-15328.

Triazolylidene iron(II) piano-stool complexes: synthesis and catalytic hydrosilylation of carbonyl compoundsC. J. Johnson¹, M. Albrecht^{1*}¹Universität Bern

1,2,3-Triazolylidenes are a recently developed sub-class of NHC ligands which have tremendous versatility due to the synthetic flexibility of the copper catalysed cycloaddition of alkynes with azides (CuAAC).^{1,2} These ligands are strong σ -donors, exhibiting stronger donor properties than classic Arduengo-type imidazole-2-ylidenes.² This property, coupled with the electronic flexibility of the mesoionic ligands makes them a powerful class of ligands for a large variety of catalytic transformations.

Iron is inexpensive, earth-abundant, non-toxic, biologically relevant, and environmentally benign. Thus, iron catalysts offer an attractive alternative to the systems based on rare and precious platinum group and coinage metals which dominate current literature.³ Herein we present a new class of triazolylidene iron(II) piano stool complexes and their activity in catalytic hydrosilylation reactions.



[1] P. Mathew, A. Neels, M. Albrecht, *J. Am. Chem. Soc.*, **2008**, *130*, 13534-13535.

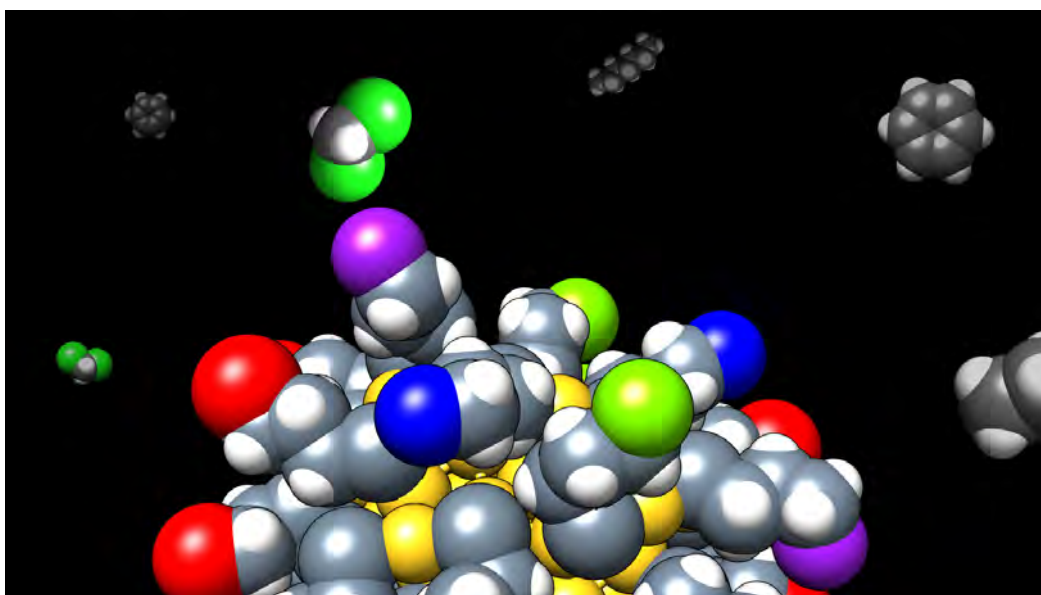
[2] K. F. Donnelly, A. Petronilho, M. Albrecht, *Chem. Commun.*, **2013**, *49*, 1145-1159.

[3] K. Riener; S. Haslinger, A. Raba, M. P. Högerl, M. Cokoja, W. A. Herrmann, F. E. Kühn, *Chem. Rev.*, **2014**, *114*, 5215-5272.

Understanding of self-organization process in monolayer protected gold nanocluster.G. Salassa¹, T. Bürgi^{1*}¹University of Geneva

The ultimate goal of nanotechnology is the realisation of “nanomachines” capable to perform sophisticated task as real machines or biological systems. In the searching of effective approaches toward such goal, nanoparticles have become principal protagonists due their unique features arising from their self-organized, multifunctional and topologically defined nature. Among nanoparticles monolayer protected gold nanoclusters (AuNCs) have risen a lot of interest due to their versatility and applicability in many fields of chemistry and nanotechnology.[1] Notwithstanding the high degree of sophistication, their self-organized nature make their synthesis straightforward. Indeed, AuNCS formation occurs via a self-assembly procedure where gold atoms form a nanocrystal of defined size (atomically precise) covered by tens of functionalised molecules forming a tridimensional monolayer.[2]

Our research activity will focus to investigate the mechanism and thermodynamic of the formation and organization of the monolayer of organic molecules coating the gold nanoclusters. The idea is to conjugate the thermodynamic information obtained by exchange experiments with morphological information obtained by MALDI and NMR experiments to understand the parameters that control the organization of the monolayer and possibly to use such parameters to control such organization.



[1] H. Häkkinen, *Nat. Chem.*, **2012**, 4, 443–455.

[2] T. Bürgi, *Nanoscale*, **2015**, 7, 15553–15567

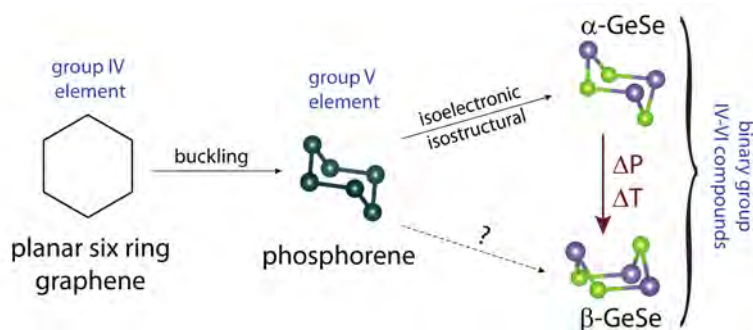
High-Pressure Synthesis and Characterization of β -GeSe — A Six-Membered-Ring Semiconductor in an Uncommon Boat Conformation

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Two-dimensional materials such as graphene and transition metal dichalcogenides have shown good potential to act as the basis for future electronics technologies [1,2]. Similarly, black phosphorus is considered a promising candidate for many applications in electronics and optoelectronics, because, for a small band-gap semiconductor, it displays high mobility charge carriers and can be easily exfoliated [3,4,5]. The intrinsic lack of a band gap in graphene has been an obstacle for the construction of devices. Black phosphorus on the other hand has an intrinsic small band-gap, which can be tuned into a Dirac semimetal [6]. Black phosphorus is the thermodynamically stable phosphorus form, but it oxidizes when exposed to water and oxygen. Therefore, related layered semiconductors are of significant interest.

In this presentation, we report the electronic and structural properties of β -GeSe [7], a previously unreported polymorph of GeSe, with a unique crystal structure that displays strong two-dimensional structural features. β -GeSe is made at high pressure and temperature and is stable under ambient conditions. Here, we will compare it to its structural and electronic relatives α -GeSe and black phosphorus. The new β form of GeSe displays a boat configuration for its Ge-Se six-membered ring, while the previously known α form, and black phosphorus, display the more common chair configuration for their six-rings. Electronic structure calculations suggest that β -GeSe has a bulk band gap of $\Delta \approx 0.5$ eV, and, in its monolayer form, $\Delta \approx 0.9$ eV. These values fall between those of α -GeSe and black phosphorus, making it a promising candidate for future applications.



[1] X. Ling, H. Wang, S. Huang, F. Xia, and M.S. Dresselhaus, *Proc. Natl. Acad. Sci.*, 2015, 112, 4523.

[2] H. Liu, Y. Du, Y. Denga, and P.D. Ye, *Chem. Soc. Rev.*, 2015, 44, 2732.

[3] L. Li, *et al.*, *Nat. Nanotech.*, 2014, 9, 372.

[4] L. Li, Yang, *et al.*, *Nat. Nanotech.*, 2016, 11, 593.

[5] J. Guo, H. Wang, F. von Rohr, W. Yi, Y. Zhou, Z. Wang, S. Cai, S. Zhang, X. Li, Y. Li, J. Liu, K. Yang, A. Li, S. Jiang, Q. Wu, T. Xiang, R. J. Cava, L. Sun, *arXiv:1611.03330*, 2016.

[6] J. Kim, S.S., *et al.*, *Science*, 2015, 349, 723.

[7] F.O. von Rohr, H. Ji, F. A. Cevallos, T. Gao, N. P. Ong, and R. J. Cava, *J. Am. Chem. Soc.*, 2017, 139, 2771.