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Why subnanometer ultrasmall metal-clusters on support open avenues for novel rational design of nanocatalysts?

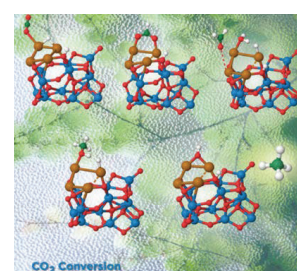
Supported subnanometer clusters with few metallic atoms (3-10) present advantages in catalysis field due to their unique chemistry which is different and tunable than for larger systems. This is due to the fact, that for ultra-small clusters in which “each atom counts”, the structures and properties change drastically by size and composition. Therefore, creation of materials based on metal-cluster components is appealing for new classes of catalysts. Despite of this expectation, ultra-small metal catalysts have not been sufficiently explored mainly due to the lack of knowledge on structures and their properties. Altogether subnanometer clusters offer to physical chemistry the opportunity to monitor catalytic reactions allowing to gain a fundamental understanding of catalytic processes necessary for the development of new classes of catalysts. For this purpose, theoretical and experimental approaches are needed, not only from a complementary point of view, but mainly using theoretical predictions to initiate the design of novel nano-catalysts which could be experimentally confirmed and realized.

The geometry of a cluster on a support, the cluster-support interaction as well as changes of these properties as a function of conditions under which reactions occur, determine the catalytic activity. The cluster size-dependence plays a key role and influences also small cluster-support interactions. In addition, the cluster size influences also the interaction between electronic states of adsorbed reactant molecules and of clusters.

Let us have a look on an attractive and useful example. In order to reduce the dependence on fossil fuels, it is necessary to mitigate the emission of greenhouse gas CO₂ and to increase the resources of chemical feedstock compounds. For this purpose, cheap catalysts with optimal performance need to be developed. This can be realized by a subnanometer copper tetramer-zirconia catalyst or introducing bimetallic tetramer Cu₃Pd at a zirconia support.

In a joint theoretical and experimental study, we have recently found that subnanometer copper tetramers supported by zirconia

are highly efficient for CO₂ hydrogenation and its conversion to methane at high temperatures. The catalytic performance is dependent on the cluster size and substrate morphology. DFT simulations on the Cu₄O₂ cluster supported by a Zr₁₂O₂₄ subunit provided a mechanism for CO₂ hydrogenation (cf. illustration above). This occurs along the way to the conversion to methane, confirming the experimental findings but also identifying methanol formation.

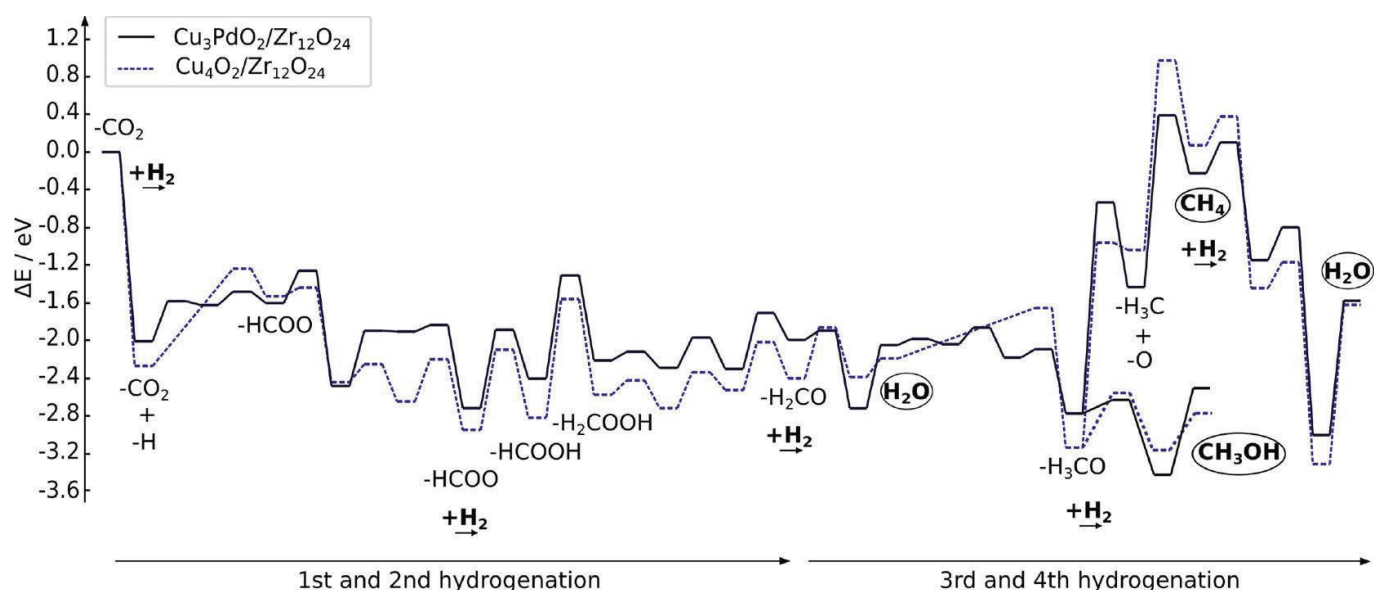


These results stimulated us to investigate the effect of exchanging a single Cu atom in the cluster with a Pd atom in the tetramer on the example of Cu₃PdO₂ at Zr₁₂O₂₄ on changing the performance. Pd was chosen due to its well-known role in dissociation of H₂. The aim is to optimize the catalytic performance of these copper-based tetramers in CO₂ hydrogenation. For this purpose, the role of Pd in the efficient activation of molecular hydrogen is used. This provides the possibility to fine-tune the catalysts performance in an atom by atom doping. We took into account partially oxidized tetramers due to reported oxidation states of Cu and Pd in mono and bimetallic clusters used in similarly cluster-based catalysts for hydrogenation and dehydrogenation reactions. We compared the predictive performance of the mixed tetramer with that of the monometallic cluster at the same support. A parallel investigation of methanol formation on these catalysts has also been performed. These sets of calculations are to support the main hypothesis whether a modification of the composition of the catalyst by an exchange of a single metal atom is preferable or not. The aim is to predict the functioning of the chosen model catalysts that will lead to the computational design of catalysts performing on demand.

Energy profiles of the monometallic versus Pd-doped bimetallic oxidized tetramer clusters at the support is shown in the figure below.

The following trends have been found: (i) In the case of the bimetallic cluster, the CuPd unit presents an interface with the support and has a key role in the hydrogenation steps; (ii) Hydrogenation steps on the Cu₄O₂ cluster at the support are energetically similar to those occurring at the Cu atom of Cu₃PdO₂. In contrast, the difference between the Pd-doped bimetallic

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and monometallic cluster is evident when dissociation of H₂ occurs due to the presence of the Pd atom; (iii) In both cases, the support plays the key role since the metal atoms of tetramers interact directly with Zr and O atoms of the support; (iv) Production of methane and methanol on both mono- and bimetallic clusters at the zirconia support is temperature-dependent.

Therefore, the incorporation of palladium in new catalysts might be advantageous, which is also more general, including other reactions where addition or removal of hydrogen takes place. Altogether, very small metallic clusters with extraordinary structural and electronic properties stabilized and affected by the support and doped by other metal atoms show their potential in improving catalyst activity.

Our aim is to show how computationally explore new ways of tuning the catalyst performance. This illustrates the role of the theoretical contribution to the rational design of novel nano-catalysts that can be experimentally realized.

ZITATE ZUM KLIMAWANDEL

„Der härteste und wichtigste Kampf des 21. Jahrhunderts wird ohne Waffen geführt. Die Werkzeuge dieses Kampfes heißen: Energieeffizienz, Energie sparen und erneuerbare Energien.“

Franz Alt

„In Deutschland gilt derjenige als viel gefährlicher, der auf den Schmutz hinweist, als der, der ihn gemacht hat.“

Carl von Ossietzky

Quelle: <https://www.careelite.de/klimaschutz-zitate-sprueche/>

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Vlasta Bonačić-Koutecký is a Professor at the Department of Chemistry, Humboldt University, Berlin. Since 2010 she has established the Interdisciplinary Center for Advanced Science and Technology (ICAST) at the University of Split, Croatia and became a head of the Center of Excellence STIM in 2014. Her scientific achievements are characterized by introducing novel theoretical concepts into traditional fields which initiated the development of new research areas having general impact in chemical and physical sciences in particular stimulating novel experimental research. During her scientific career she has pursued unconventional front field research in theoretical organic photochemistry, cluster science and femtochemistry.

In the field of nanoscience she has recognized that metal nanoclusters (with only few atoms) have unique structural, optical and reactivity properties which combine molecular-like with metallic features. This has added a new unexpected dimension to traditional nanoscience, introducing small metal nanoclusters into material science within the field of nanocatalysis for renewable energy as well as nano-optics and nano-bio-sensing for medical diagnostics. Among other awards, she has received an honorary Dr. h. c. (honoris causa) from the Université Claude Bernard Lyon 1 (UCBL) for introducing the nano-bio hybrids in the quantum nanocluster community.