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Swiss Science Concentrates

A CHIMIA Column

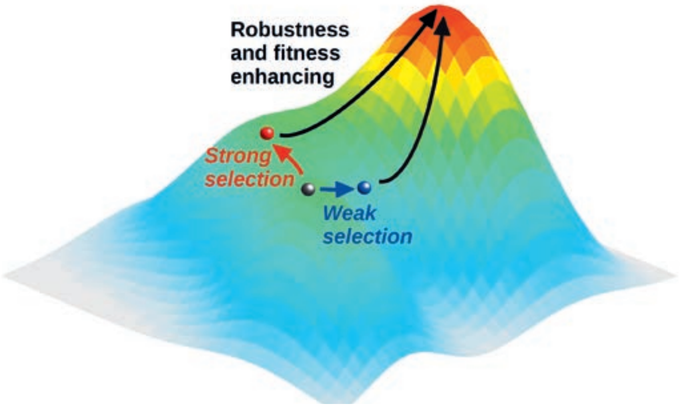
Short Abstracts of Interesting Recent Publications of Swiss Origin

Selection enhances protein evolvability by increasing mutational robustness and foldability

Jia Zheng, Ning Guo, and Andreas Wagner,* *Science* **2020**, *370,* 6521.
University of Zurich

Protein evolution has revolutionized the way proteins are regarded as catalysts, yet most of the background of how the intensity of selection affects their evolvability remains unclear. This question was addressed by the authors using a yellow fluorescent protein as a study model. It is commonly believed that deleterious mutations accumulating through weak selection events, act as a stepping-stone towards the evolution of new functionalities. Counterintuitively, the authors prove that strong rather than weak selection for yellow fluorescence led to a greater ability to evolve green fluorescence later on. The reason is that strong selection not only increased fitness but also enhanced the tolerance of proteins to deleterious mutations by helping them to accumulate foldability- and stability-improving mutations. In addition, more robust genetic backgrounds could tolerate more deleterious mutations and thus resulted in a greater increase of genetic diversity in evolving populations.

Authors' comments:
"We are excited by our discovery, because it proves not just that natural selection can create the conditions under which Darwinian evolution can succeed, but also because it identifies an important mechanism rooted in protein biochemistry by which it can do so."

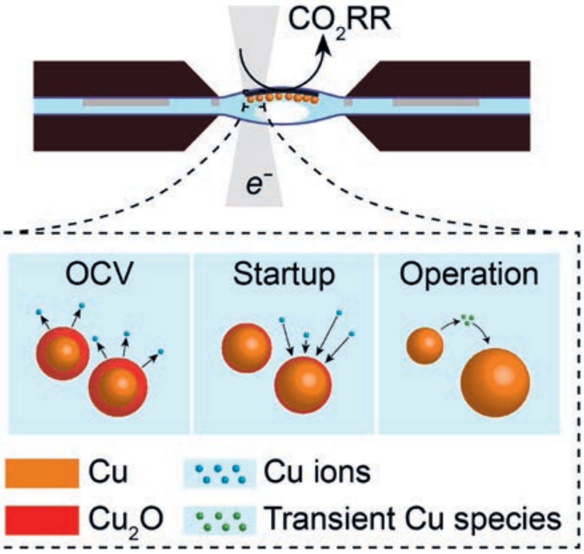


Real-time Monitoring Reveals Dissolution/Redeposition Mechanism in Copper Nanocatalysts during the Initial Stages of the CO_2 Reduction Reaction

J Vavra, T.H. Shen, D. Stoian, V. Tileli, and R Buonsanti* *Angew. Chem. Int. Ed.* **2020**, *60*, 1347-1354.
École Polytechnique Fédérale de Lausanne

With global pressure to find ways to reduce CO_2 emissions, the electrochemical CO_2 reduction reaction poses a promising way forward. Understanding how electrocatalysts change in terms of their morphology, size and surface composition is an effective approach to their rational design, with the goal to improve their stability while retaining activity and selectivity. With the aid of transmission electron microscopy and *operando* X-ray spectroscopy, the reconstruction of copper-based nanocatalysts during the start-up phase of the CO_2 reduction reaction, was investigated. Results revealed that dissolution and redeposition, rather than coalescence, is the mechanism responsible for the change in morphology of the electrocatalyst. In addition, the formation of copper oxides was found to play key a role in the process.

Authors' comments:
"The observed solution-mediated process of Cu catalyst dissolution/redeposition is rather surprising at the negative potentials required by the CO_2 reduction reaction, where metallic Cu is the thermodynamically stable phase. While the process is certainly accelerated by the nanocrystalline nature of the investigated catalyst, it is relevant for all the Cu based CO_2 reduction reaction catalysts. The exact nature of the transient species mediating the observed process remains yet to be discovered."



Prepared by Ana I. Benítez-Mateos, David Roura Padrosa, Gordon Honeyman, Keir Penston, and Francesca Paradisi*
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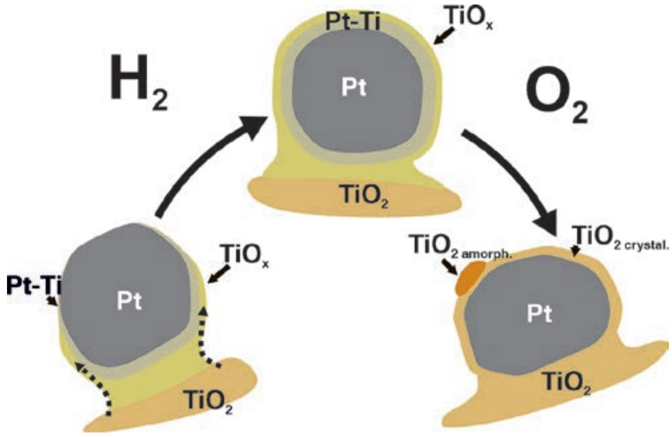
The dynamics of overlayer formation on catalyst nanoparticles and strong metal-support interaction

A. Beck, X. Huang,* L. Artiglia, M. Zabilskiy, X. Wang, P. Rzepka, D. Palagin, M. Willinger,* and J. A. van Bokhoven,* *Nat. Comm.* **2020**, *11*, 3220.
ETH Zürich and PSI

Activity and selectivity of a catalyst are determined by the absorption behaviour of molecules on its surface. For the heavily employed platinum metal catalysts, the combination with a reducible oxides support bares great potential to tune the absorption behaviour through a phenomenon named strong metal-support interaction (SMSI). This study provides, through complementary *in situ* characterization, a real-time holistic understanding of the transformations caused by SMSI. The study of a platinum-titania system revealed the dual role of hydrogen in this process. Hydrogen induces the migration of reduced titanium oxide and the formation of an alloy as competing processes. Exposure to oxygen segregates the titanium from the alloy, and a thicker titania overlayer forms. This unique role of oxygen shows that SMSI state can be also employed in catalytic oxidation reactions.

Authors' comments:

"The strong metal–support interaction is a phenomenon in which the support partially covers the surface of a catalytic nanoparticle, thereby affecting its catalytic performance. The formation of such overlayers was until our study poorly understood."



Untangling the Complexity of Mixed Lithium/Magnesium Alkyl/Alkoxy Combinations Utilised in Br/Mg Exchange Reactions

Leonie J. Bole, Neil R. Judge, and Eva Hevia* *Angew. Chem. Int. Ed.* **2021**, *10.1002/anie.202016422*.
University of Bern

The use of Group 1 metal alkoxides as additives to activate s-block organometallics is a well-established phenomenon in polar organometallic chemistry. However, despite its long-standing importance in organic synthesis, the nature of this activating effect still remains to be fully understood. Here the authors shed light on the origins of the role played by lithium alkoxides when added to dialkylmagnesium reagents, in Br/Mg exchange reactions of substituted bromoarenes. This origin lies on the cooperativity exhibited by mixed Li-Mg species that engage in a new type of bimetallic Schlenk equilibrium, which generates *in situ* a highly reactive alkyl rich lithium magnesiate. By trapping the key organometallic intermediates, the constitution of distinct mixed Li/Mg species with different ligand sets and Li:Mg ratios have been established, exposing the hidden complexity of this lithium alkoxide-mediated Br/Mg exchange processes.

Authors' comments:

"NMR monitoring studies were key for the success of this work. The three of us spent many hours discussing spectra, challenging each other with regards to the possible mechanism of these intriguing transformations. Every spectrum became a key piece of an exciting but intricate jigsaw!"