Single particle XAS spectroscopy to elucidate fundamental processes in catalysis

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Nano-sized particles, such as platinum, are often the active component in heterogeneous catalysts. However, more often than not, the support for these particles is not innocent and it may actively participate in one or more catalytic steps. The process of spillover is often invoked. This phenomenon describes the reaction of a species on one particle, which then exerts an action on a different particle that is not in contact with the first (*R. Prins, Chem. Rev. 112 (2012) 2714–2738*). The reactive species is, thereby, spilled over onto the support and diffuses to reach and react with the second particle. This phenomenon is often assumed, however, experimentally very difficult to verify and is, therefore, controversially discussed.

To observe the phenomenon of hydrogen spillover, we designed a model system in which 15 pairs of platinum and iron oxide particles are deposited onto a specific support with a distance between the two starting from 0 nm (overlapping pair) and progressively increasing to 45 nm. This inter-particle distance is controlled with nanometer precision using top-down nanofabrication. Thus, the only difference between the iron oxide particles is their distance to the closest platinum particle. In addition, a lone iron oxide particle, which has no interaction with any platinum over a distance of 1 μm was also deposited within the same field-of-view. Two catalytically relevant supports, alumina and titania, were employed. Using an X-ray photoemission electron microscope installed at the SIM beamline of the Swiss Light Source, Fe $L_{2,3}$ edge XAS of all 16 iron oxide particles could be measured simultaneously at the single particle level. After the controlled dosing of hydrogen, the extent of reduction of the iron oxide particles as function of their distance to the hydrogen splitting platinum particle is a measure to what extend hydrogen spills over onto the support and diffuses from platinum to the iron oxide particle.

There is a strong difference in the extent of spillover over titania and alumina, which was interpreted with the help of theoretical calculations. The ability of reduction of the support, which readily occurs on titania, and the ability of a hydride and proton to diffuse, as in case of alumina, determines the degree of hydrogen spillover. The theory predicted that three-coordinate aluminum in the alumina surface is essential for hydrogen spillover on alumina to occur. Such low-coordinated aluminum sites were observed in Al K edge XANES spectra. These results provide a unique insight into what are the parameters that govern a fundamental process in heterogeneous catalysis (*W. Karim et al. Nature 541 (2017) 68-71*).