In-situ experiments applied to oxide catalysts:

A critical status report

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Understanding heterogeneous catalysis can only be achieved when the critical functions of technical systems are investigated with rigorous physicochemical experiments. These experiments require well-defined model systems such as oxide films, size-selected aggregates or metallic samples. The selection and preparation of these model systems requires knowledge of the structure of a working catalyst under practical conditions as only then the structural and electronic specifications of adequate model systems can be derived without guess-work.

Investigating metallic silver and heteropolymolybdates (HPA) as archetypical catalysts for methanol oxidation, it will be shown that a thorough in-situ analysis of the bulk structures is essential to grasp the difference between ideal model systems (clean single crystals) and working systems. The presence of substantial pressures of reactive molecules transforms the bulk structures of the clean models and hence profoundly modifies the surface chemical properties of the model systems. The formation of solid-solution structures between silver and oxygen restructures the polycrystalline surface. It induces local structural defects which are considered as vital components to the selectively oxidising surface. The removal of crystal water from the HPA leads to a collapse of their structure with changes in the electronic structure of the solid most relevant for the catalytic action. The reversible polycondensation of molecular units of HPA which require the absence of crystal water is the key step for the catalytic function of storage of reactive oxygen responsible for selective oxidation.

The examples will show that it is not sufficient to only probe surface properties directly in-situ but that it is equally relevant to study bulk structural transformations during catalysis in order to find relevant model structures for physicochemical experiments. Although we have a certain methodology at our disposal to achieve this complete in-situ characterisation, there remains a lot of method development to be done to reach the desired level of applicability and productivity of catalyst characterisation which is required to ask the relevant questions from catalysis to surface science.