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Selective oxidation catalysis over Ag and Cu The role of a metallic catalyst

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Selective oxidation is a fundamental process for the production of a large range of basic and intermediate chemicals. It is of high significance for technological as well as for scientific reasons. Chemically one has to activate di-oxygen and also C-H bonds in low-functionalised hydrocarbon molecules.

These elementary processes require the existence of active sites with redox properties and with solid acid-base properties simultaneously. On metals the activation of di-oxygen in a reductive cycle is well-understood. The creation of acidity is, however, a problem as it requires very strong metal-oxygen bonds which are typically found in oxides.

The question arises about the electronic structure of metals in oxidation reaction catalysis. We investigate this problem with Ag and Cu using the reaction of methanol to formaldehyde as a practically exerted process and as a scientific probe reaction.

Ag cannot form stable oxides under practical reaction conditions. But it can create a variety of atomic oxygen species located on, in and under the metal surface. These

species exhibit very differently electronic structures and serve hence as basic or redox-active centres for methanol oxidation. The formation of the basic species requires a massive surface restructuring and the participation of the metal bulk which has been investigated with in-situ diffraction methods.

Cu can form oxides which will be shown, however, to be active only in the undesired total oxidation of methanol to CO₂. The selective oxidation occurs with a unique oxygen species which is neither an adsorbate nor an oxide. It occurs only under reaction conditions and transforms upon attempts to isolate it in UHV into islands of copper oxide. The creation of this species requires again the participation of the Cu bulk which becomes disordered as consequence of the activation in catalysis. In-situ X-ray absorption at high and low energies was used to illustrate the transformation of inactive blank copper into a nanocrystalline state of active copper which is highly metastable towards segregation into metal and oxide. This metastability is assumed to be responsible for the pronounced rate oscillation of the selective oxidation.