

7 English Summary

The present doctoral thesis contributes to the understanding of the structure of the copper-oxygen-system in connection with the catalytic activity of copper as an oxidation catalyst for the partial oxidation of methanol to formaldehyde. A comparatively global approach was selected, in which the surface and the bulk structure were examined. Depending upon accessibility both in situ methods (EXAFS, Raman spectrometry, infrared and visual video records, temperature measurements) in combination with mass spectrometry and ex situ methods (ESCA, SEM) are applied.

The investigation of the bulk structure of carbon supported and unsupported copper catalysts took place in situ under real conditions of the catalytic partial oxidation of methanol at varying methanol turnovers with time-resolved X-ray absorption spectrometry (DEXAFS), combined with mass spectrometry.

A large section of the work is concerning different measurements executed with in situ methods concentrated on a state of the methanol-oxygen-copper-system, in which oscillations occurred. One assumes in particular from this dynamic state of the catalyst insights in functionality of the copper catalyst, such as contribution of bulk species to form the catalytic active surface.

The electronic and chemical structure of the surface of a Cu(111)-single crystal was examined with ex situ ESCA. A pre-oxidized Cu(111)-single crystal was treated stepwise with methanol ($T = 573$ K). By this treatment, the conditions of real catalysis were simulated. After the methanol treatment about ninety monolayers of the surface were removed by sputtering and then the sample was annealed in vacuum ($T = 573$ K).

In the process of the methanol treatment besides Cu_2O and Cu an unknown copper-oxygen-compound developed, this is probably a copper suboxide. Its UPS HeI spectrum shows a broad, smeared structure, which resembles the HeI CuO spectrum and is caused by a strong interaction between copper and oxygen, probably mainly Cu 3d-O 2p. In difference spectra from Cu Auger-spectra recorded before and after the methanol treatment bands appear which are in the proximity of the Cu_2O bands. This unknown copper-oxygen-compound is formed only temporarily and is unstable under the conditions of methanol treatment at high temperatures.

The state of the surface and the subsurface after the entire methanol treatment (250000 L) was characterized by HeI difference spectra, which were calculated from the spectra before and after He^+ -sputtering. According to whether a "rigid-band-shift" influences the difference formation or not, this state can be characterized differently.

The spectrum without a "rigid-band-shift" resembles roughly Cu_2O . The Cu_2O similar features are shifted all approximately -0.5 eV opposite to the Cu_2O reference spectrum. Altogether, it differs substantially from Cu- Cu_2O -phase mixtures. It contains bands, typically coming from the Cu 3d-orbital (around 3 eV) as well as bands, which probably come from the oxygen O 2p-orbital (~ 1 eV and $\sim 5-6$ eV). The intensity at the fermi-edge refers to the metallic characteristics of the copper oxygen surface phase, which would entail e.g., an increased electrical conductivity at the surface.

The correction of a possible "rigid-band-shift" ($-0,16$ eV) leads to a He I-difference spectrum, which resembles very strongly to Cu_2O . It contains however in the region above 5 eV additional strong emissions, that can be assigned to oxygen adsorbates. Other differences to the Cu_2O -spectrum, particularly in the region of the bands dominated by the Cu 3d (2-3 eV), point also to an unknown Cu-O-phase.

It was verified by an annealing experiment of an oxygen-containing Cu(111)-sample that the catalysts bulk makes oxygen-species available to the catalyst surface and is therefore a further source for the generation of the catalytic active surface. By means of UPS and Cu Auger difference spectra it was shown that during annealing of the sample a surface copper suboxide is formed from bulk oxygen, which resembles Cu_2O electronically. Additional hints for the formation of an unknown, unstable Cu-O-transient state were found. This transient state is either a metastable copper suboxide or dissolved or atomically adsorbed oxygen on the Cu- Cu_2O substrate.

A further evidence for the modification of the catalyst surface by species from the catalysts bulk represent the UPS spectra recorded during the stepwise methanol treatment of the pre-oxidized Cu(111)-sample. The UPS spectra show an oscillation behavior of the sample. In the course of the methanol treatment, the sample surface oxidized several times. This behavior under permanent reducing conditions is explained with a partial reoxidation of the surface by oxygen from the catalysts bulk.

In one excluding bulk-sensitive in situ EXAFS experiment, it was proven that the bulk structure of a copper catalyst under real catalytic conditions depends reversibly on the conversion or on the oxygen content in the gaseous phase. Under these conditions of a high formaldehyde yield, the catalysts bulk is metallic. The measured change of the Cu-Cu distance (max. around 0.03 Å) and a coordination number change reversibly dependent on the conversion, manifested dissolved oxygen in the catalysts bulk. The changes in distance were interpreted as size changes of the Cu crystallites inside the catalyst. Oxygen atoms are intercalated at the grain boundaries of a nano-crystalline network of copper crystallites. A size change of the crystallites or possibly also a modification of the distortion of the bulk structure is caused by changing the oxygen content. This oxygen stored in the bulk is obviously very mobile, since the measured Cu-Cu-distances react very fast to a modification of the oxygen content in the gas

phase.

The EXAFS experiment did not answer yet the question whether this bulk-dissolved oxygen is also crucial for the catalytic effectiveness of the copper catalysts. This question was positively clarified in an indirect manner by a part of the oscillation experiments that were performed under real catalytic conditions.

Catalytic oscillations in the Cu/O/Methanol system with copper powders are well-known from literature [26]. In this doctoral work catalytic oscillations combined with visible frontal oxidations and reductions of polycrystalline copper foil surfaces were found. The catalytic oscillations were observed under certain experimental conditions of temperature and methanol-oxygen-helium-flow after a high temperature methanol/oxygen pretreatment of the copper samples with permanently reduced or oxidized samples, as well as in connection with quasi periodic changes between more oxidized and completely reduced samples.

The oscillations are essentially attributed to temporal modifications of the copper catalyst. The oscillation mechanism depends on the experimental parameters and the pretreatment of the samples. Four oscillation models were derived. A part of the oscillations is due to thermal effects. An explanation of the oscillation behavior of the copper catalysts under certain conditions is only possible including the catalyst bulk (type III mechanism) into the explanation. Altogether thereby, sets of proofs for a catalytically relevant influence of the catalyst surface by bulk species were achieved.

The pretreatment (activation) of the catalyst (methanol/oxygen at high temperatures), necessary for the oscillations, produces probably the nano-crystalline network, postulated by the interpretation of the EXAFS experiments. This network stores the oxygen, which serves for the formation of the active surface phase. This activation is very stable. Turnover measurements with varying temperature show that the methanol/oxygen pretreatment increases the formaldehyde selectivity.

The dominating global coupling of the oscillations is made by the gas phase.

In small temperature ranges, the duration of the periods are inversely proportional to the reciprocal temperature (comparable to the behaviour of reaction rate constant according to Arrhenius equation).

The oscillations of the oxidation state (change between totally oxidized and totally reduced sample) ensure that the catalytic activation is regenerated and that in that way the conversion remains high, while with permanently oxidized samples it comes to a continuous deactivation, probably because of missing the periodic reduction of catalytically inactive Cu_2O .