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In situ photoemission spectroscopy investigation of the methanol oxidation over copper

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Abstract

Photoelectron spectroscopy has been a powerful tool in surface science for decades. It has been extensively used for the ex-situ characterization of catalysts' surfaces. Due to the short mean free path of electrons in a gas phase electron spectroscopies generally must operate in high vacuum. Traditional electron spectrometers are therefore not suited for the much needed characterization of catalysts' surface under reaction conditions. To overcome these limitations, we have developed a new high-pressure electron spectrometer. Our setup utilizes a differentially pumped electrostatic lens system that refocuses the photoelectrons that are emitted from the sample (which is in a gaseous atmosphere of up to several torr) into the focal plane of a standard electron energy analyzer situated downstream, in the high vacuum region.

Using this instrument we have investigated the methanol oxidation over a polycrystalline copper catalyst, where two main reaction paths are known: the total oxidation of methanol to carbon dioxide and water, and the partial oxidation of methanol to formaldehyde and water. The experiments were performed at a methanol to oxygen flow ratio of 3:1 (total pressure 0.4 torr) in the temperature range from 300 K to 750 K. The correlation of in-situ XPS spectra of the copper surface and the simultaneously obtained mass spectrometer data (which show the catalytic activity) allow us to draw conclusions about the electronic state of the catalyst under reaction conditions. Valence band and Oxygen 1s spectra show that after the onset of the catalytic reaction at $T > 550$ K the copper surface has a metallic character. During the partial oxidation the Oxygen 1s spectra show the presence of chemisorbed oxygen at the surface. In addition, there is also a strong photoemission peak at 531.6 eV. This peak could be caused by either surface hydroxyles or sub-surface oxygen. The amount of formaldehyde that is produced in the catalytic reaction is proportional to the integrated intensity of the O1s peak of chemisorbed oxygen. In Fig.1 the O1s spectra

of a Cu-foil are shown under reaction conditions at different temperatures.

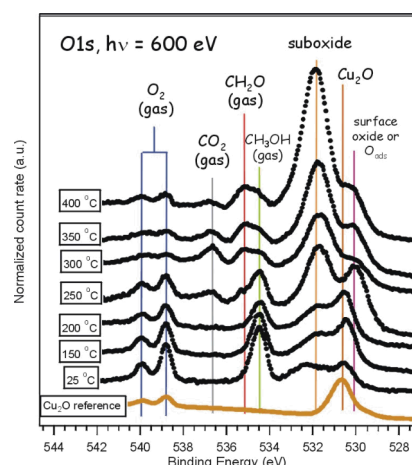


Fig.1: Oxygen 1s spectra of a polycrystalline Cu catalyst at different temperatures. The gas feed consists of methanol and oxygen in the ratio 3:1 at a pressure of 0.4 torr.

In situ XAS spectra in the soft energy range have shown already the metallic character of the active Cu surface in the selective oxidation of methanol [1]. In situ O K-edge spectra show an unknown oxygen species under working conditions caused by the formation of a suboxide or the adsorption of OH-groups. Since the suppression of the gas phase works much more better in the in situ photoemission set up compared to the in situ XAS measurements, the stoichiometry

can be estimated. The active surface is shows a oxygen/copper stoichiometry of 1:2.

The Carbon 1s spectra shows methoxy on the catalyst surface for temperature below 200°C. Furthermore a graphitic carbon species is observed on the surface below 350°C. At higher temperatures this species is oxidized to CO₂.

In summary it will be shown that in situ photoemission spectroscopy is a very powerful tool to investigate the electronic structure of a working catalyst surface.

References

- [1] A. Knop-Gericke, M. Hävecker, T. Schedel-Niedrig, R. Schlögl; Topics in Catalysis 15 (2001) 27