MAX-PLANCK-GESELLSCHAFT 49th International Symposium of the American Vacuum Society, Denver (03.-08.11.2002)

In situ XPS investigation of the methanol oxidation over copper

H. Bluhm[1]*, M. Hävecker[1], A. Knop-Gericke[1], R. Schlögl[1], D.F. Ogletree[2], M. Salmeron[2]

[1] Department of Inorganic Chemistry, Fritz-Haber-Institute of the MPG, Faradayweg 4-6, 14195 Berlin, Germany
[2] Lawrence Berkeley Laboratory, Berkeley, CA, USA

* Corresponding author: e-mail bluhm@fhi-berlin.mpg.de, phone +49 30 8413 4500, fax +49 30 8413 4401

We have used in situ X-ray photoelectron spectroscopy (XPS)[1] in combination with mass spectrometry to investigate the partial oxidation of methanol to formaldehyde over a polycrystalline copper sample. 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. The Oxygen 1s spectra reveal that at least two different oxygen species with binding energies (BE) of 529.7 eV and 531.4 eV, respectively, are present at the catalytically active Cu surface. The O 1s peak at 529.7 eV is assigned to chemisorbed oxygen at the Cu surface. The integrated intensity of the chemisorbed oxygen peak is proportional to the amount of formaldehyde that is produced in the catalytic reaction. The peak at 531.4 eV is assigned to subsurface oxygen. The formaldehyde yield increases linearly with the integrated intensity of the subsurface oxygen peak, up to a concentration of the equivalent of about one monolayer of subsurface oxygen. A further increase of the amount of subsurface oxygen does not lead to an increase of the formaldehyde yield.

References

[1] D.F. Ogletree, H. Bluhm, G. Lebedev, C.S. Fadley, Z. Hussain, M. Salmeron, submitted to Rev. Sci. Instrum.