International congress on operando spectroscopy, Lunteren (02.-06.03.2003)

IN SITU X-RAY PHOTOELECTRON SPECTROSCOPY OF THE METHANOL OXIDATION ON COPPER

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Introduction

We have used *in situ* X-ray photoelectron spectroscopy (XPS) to investigate the catalytic oxidation of methanol over a polycrystalline copper foil. There are two main reaction paths: a partial oxidation to formaldehyde, and a total oxidation, which would be thermodynamically favored under equilibrium conditions:

(1) $CH_3OH + ½O_2 \rightarrow CH_2O + H_2O$
(partial oxidation) $\Delta H = -159$ kJ/mol

(2) $CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O$
(total oxidation) $\Delta H = -674$ kJ/mol

In situ near-edge X-ray absorption spectroscopy results at the O *K*-edge revealed that the formaldehyde yield is correlated to the presence of a suboxide species at the sample surface that could only be detected under *in situ* conditions. [1] The goal of our experiments was to use *in situ* XPS [2] to determine the nature of the active species during the catalytic reaction, and to measure their abundance as a function of reaction conditions. By varying the incident photon energy we have also performed depth-profiling of the active species at the copper surface under reaction conditions.

Results and discussion

A polycrystalline Cu foil was mounted onto a temperature-controlled sample stage in the experimental cell. The combined methanol and oxygen pressure in the experimental cell was 0.6 mbar at a methanol-to-oxygen flow ratio of 3:1. The experiments were performed at BESSY in Berlin at the undulator beam line U49/2-PGM1, and at the bending magnet beamline 9.3.2 at the Advanced Light Source in Berkeley. Fig. 1 shows the O1s region of photoemission spectra (hν = 720 eV) taken at 25 °C and 400 °C in the reaction mixture. Since the incident X-ray beam irradiates part of the gas phase in front of the sample in addition to the sample surface, the spectra in Fig. 1 contain gas phase peaks alongside the surface peaks. Peaks with a binding energy (BE) higher than 534 eV are due to gas phase species, those with a BE smaller than 534 eV are due to oxygen species at the surface.

Both gas phase and surface peaks in the spectra in Fig. 1 show a strong dependence on the sample temperature. At 25 °C, only gas phase peaks of the two reactants (O_2 and CH_3OH) are present in the spectrum, indicating that there is no catalytic conversion. The presence of gas phase peaks of the reaction products (CH_2O, H_2O, and CO_2) in the spectrum taken at 400 °C shows that the Cu foil is catalytically active at this temperature.

In the spectra in Fig. 1 we can distinguish three different species at the surface or in the near-surface region (apart from some residual hydrocarbon-related contamination at 25

°C). At 25 °C the Cu_2O peak (BE 530.4 eV) dominates the spectrum. Two smaller peaks at 529.8 eV and 531.5 eV are also present at room temperature. These peaks dominate the O1*s* spectra of the catalytically active Cu surface at 400 °C, while the oxide peak is not present, i.e. the surface has now a metallic character. This is confirmed by the valence band spectrum taken at 400 °C, which shows the characteristic spectrum for metallic copper.

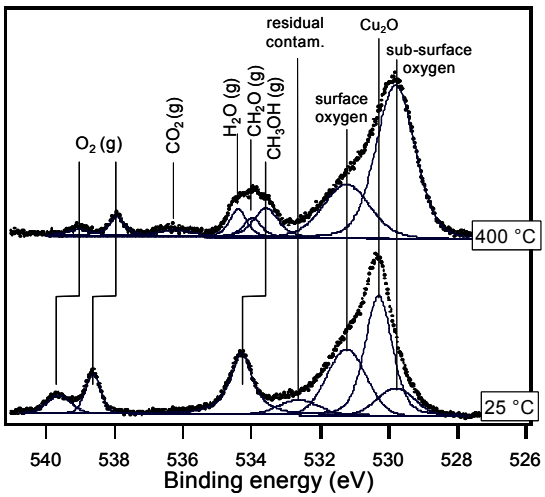

Fig. 1: In situ XPS O 1s spectra of copper foil in 0.15 mbar O_2 + 0.45 mbar CH_3OH. At 25 °C the sample is oxidic and catalytically inactive. At 400 °C the surface is metallic and shows a strong sub-surface oxygen peak. There are also peaks from the gaseous reaction products at 400 °C. The BE scale is referenced to the surface peaks. The BE difference of the gas phase peaks at 25 °C and 400 °C is due to a change in the work function of the sample surface.

The nature of the peaks at BE 529.8 eV and 531.5 eV was investigated using depth-profiling. To this end O1*s* spectra were recorded at different incident photon energies. The 531.5 eV peak intensity decreased with increasing mean free path length, whereas the 529.9 eV peak intensity increased with increasing mean free path length. This implies that the 531.5 eV species is located at the surface, while the 529.9 eV species is distributed in the sub-surface region. We can rule out that either of these species is a carbon-oxygen compound, since the C1*s* region of the photoemission spectrum does not show surface peaks that correlate to the O1*s* peaks under our reaction conditions. The 529.9 eV peak due to sub-surface oxygen was only observed in *in situ* measurements. When the oxygen flow to the cell was stopped the sub-surface oxygen peak vanished in less than one second.

Fig. 2 shows the dependence of the CH_2O yield on the abundance of sub-surface oxygen in the sample (expressed in terms of its peak area) for different temperatures between 25 °C and 450 °C. There is a clear correlation between the abundance of sub-surface oxygen and the yield of CH_2O. Sub-surface oxygen could increase the catalytic activity by inducing stress in the Cu lattice, which could lead to an upward shift of the *d*-states and thereby to a stronger surface-adsorbate interaction. [3] The role of the sub-surface oxygen in the catalytic oxidation of methanol is subject of further investigations in our laboratory.

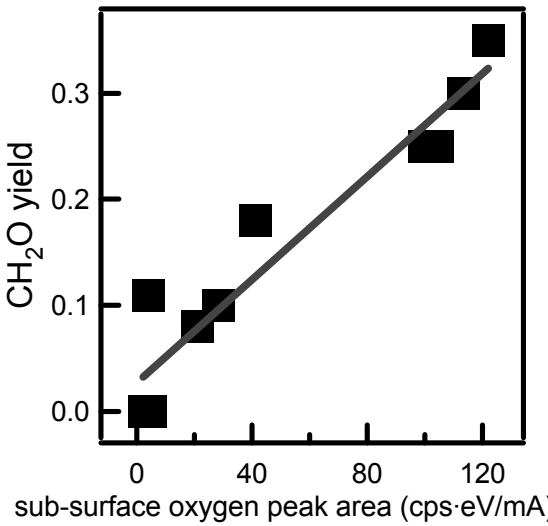

Fig. 2: CH_2O yield as a function of the sub-surface oxygen peak area.

References

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