



About the role of oxide phases in the methanol oxidation over copper foil studied by in situ XAS

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Since a long period the methanol oxidation over copper has been a topic of intensive investigations with various methods. Two main reaction paths occur: the total oxidation of methanol to CO_2 and water and the partial oxidation to formaldehyde and hydrogen or water. An interesting point is the role of the oxygen in the catalytic reaction. From ex situ surface science studies it is concluded that oxygen can both act as a promoter and as an inhibitor of the reaction [1]. A big variety of oxygen species can occur at copper surfaces. Moreover one often has to face the problem that the structure of the catalyst can be significantly different under reaction condition from that observed after the reaction or ex situ. Therefore it is very helpful to perform a surface sensitive experiment during the reaction to get direct hints about the oxygen species present under these conditions. To draw conclusions about their function it is necessary to monitor simultaneously the conversion of the gas phase. Such an experiment is usually referred to as in situ.

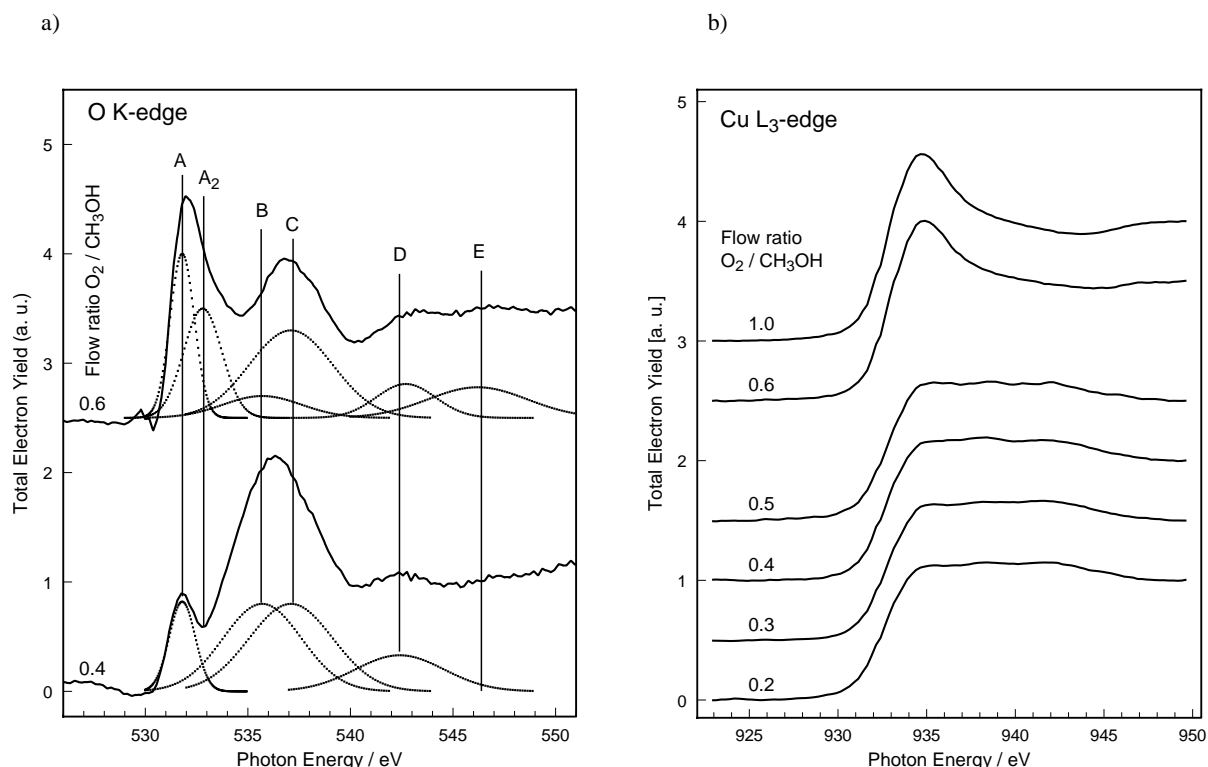


Figure 1: In situ NEXAFS of the active copper foil for different $\text{O}_2 / \text{CH}_3\text{OH}$ flow ratios at a sample temperature of 670 K. 1a (left) shows the O K-edge and 1b (right) the corresponding Cu L₃-edge. Profiles used for a least square fit describing the resonances A-E at the O K-edge are also shown.

We performed in situ XAS studies at the Cu L-, C K- and O K-edges during the methanol oxidation over polycrystalline copper with various methanol / oxygen mixtures as feed for the catalyst. Simultaneously we monitored the methanol conver-

sion and the yield of the products (CO_2 , formaldehyde) both by quantitatively analysing the NEXAFS of the gas phase and by conventional online mass spectrometry. Details of the experimental set-up and the data processing are given in [2,3].

Experiments were performed at the PM1 beamline at BESSY I. The spectral resolution was set to 1.6 eV at the O K-edge in order to get a sufficiently high photon flux at the position of the sample after the X-ray beam has traversed the gas in the reaction chamber.

Copper foil was heated up to 670 K in various oxygen / methanol gas mixtures with flow ratios from 0.2 to 1.0 ($\text{O}_2 / \text{CH}_3\text{OH}$). Examples of the resulting NEXAFS at the oxygen K- and Cu L_3 -edges are presented in figure 1. For further analysis the spectra at the O K-edge have been fitted with profiles A-E as indicated in figure 1a. It can be shown that resonances B-D belong to a new form of suboxide which is correlated to the partial oxidation of methanol to formaldehyde [3,4]. Resonances A and A_2 as well as E belong to oxidic types of oxygen on the copper surface. By comparison with literature and reference samples, resonance A_2 at 532.8 eV can be identified as the $\text{O}1s \rightarrow \text{O}2p\text{Cu}3d$ electron transition well known in the O K NEXAFS of Cu_2O . E is related to the $\text{O}2p\text{Cu}4sp$ electronic states of Cu_2O . So it is possible to observe in situ a transition from the metallic to an oxide surface phase characterised by the appearance of resonance A_2 and an intensity gain at the onset of the Cu L_3 -edge caused by a slightly higher oxidising potential of the gaseous environment.

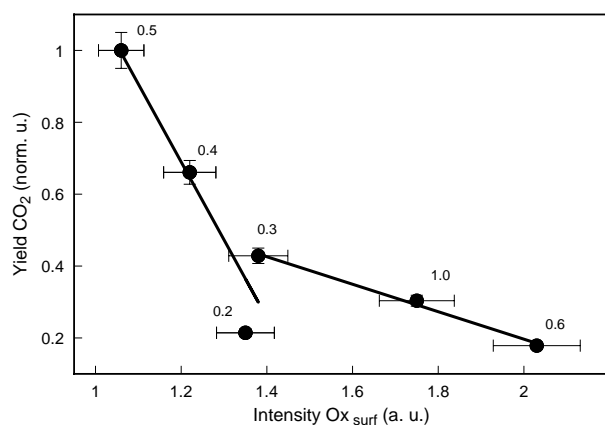


Figure 2: The integrated intensity of resonance A (Ox_{surf}) is negatively correlated to the yield of CO_2 of the catalytic reaction. The sample temperature was 670 K and the numbers indicate the oxygen / methanol flow ratio.

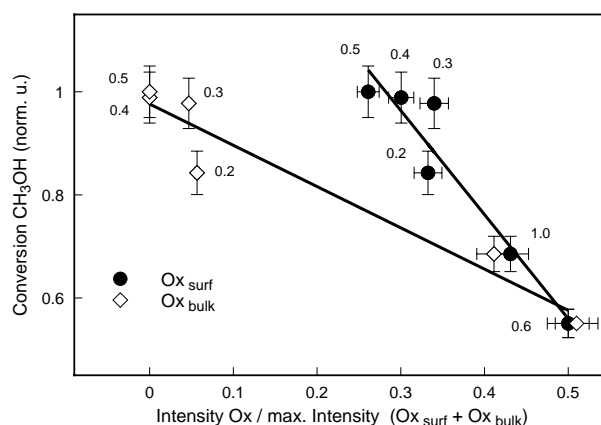


Figure 3: The integrated intensity of resonances A (Ox_{surf}) and A_2 (Ox_{bulk}) show a negative correlation with the conversion of methanol. The inhibiting impact of Ox_{surf} is stronger than that of Ox_{bulk} .

Resonance A at 531.6 eV also belongs to an oxidic phase which can be concluded by the position and the sharp spectral shape of the resonance and the catalytic functionality shown in figure 2. The integrated intensity scales negatively with the yield of CO_2 . It is suggested that this oxygen species is a thin surface layer of copper oxide (Ox_{surf}) and therefore the precursor state of the bulk oxide (Ox_{bulk} , resonance A_2). This would explain the different inhibiting impact of these two oxide species on the methanol conversion displayed in figure 3. This in situ observation is in full agreement with the conclusion from surface science experiments that a fully oxygen covered copper surface is inactive for the reaction [1]. Also the two activity regimes visible in figure 2 could be caused by the start of 3D growth of the surface oxide layer having in mind that catalysis first of all takes place at the outer surface of the catalyst. Thus high pressure in situ XAS can help to bridge the gap between UHV experiments and “real” catalytic conditions.

References:

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