

***In situ* X-ray photoelectron spectroscopy of the methanol oxidation over Cu(110)**

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Introduction

We have used *in situ* X-ray photoelectron spectroscopy (XPS) to investigate the partial oxidation of methanol over Cu(110) in the pressure range between 10^{-7} and 10^{-3} mbar. The aim of the present study was to investigate the adsorbate structures present on the Cu(110) surface and relate them to the observed catalytic reactivity. The identification of distinct adsorbate phases was achieved by resolving different components in the C 1s and O 1s core level peaks. Especially, the everlasting question, whether formate is present on the surface during the reaction and if yes, how it influences the reactivity of the Cu(110) surface was to be addressed [e.g. 1, 2, 3]. The systematic study mainly in the 10^{-5} mbar pressure range provided insight, why UHV experiments of the partial methanol oxidation and measurements under more technical conditions at higher total pressure monitor two separate reaction regimes. In the future it is planned to extend the study into the higher pressure range in order to resolve the still existing contradictive assignments of adsorbate species during the catalytic reactions.

Experimental

A Cu(110) single crystal was mounted onto a temperature-controlled sample stage in the experimental cell. The partial pressures were adjusted using leak valves. X-rays are admitted to the experimental cell through a 100 nm thick SiN_x window, where they illuminate the sample surface. The emitted photoelectrons enter a differentially pumped electrostatic lens system and are focused on the entrance slit of a standard electron energy analyser, where high vacuum conditions are maintained by another pumping stage. The setup allows tuning the total pressure in the reaction cell between 10^{-7} mbar and 1 mbar. The reaction products were monitored with the help of a differentially pumped mass spectrometer. The sample temperature was varied with the help of an infrared laser heating system in the range from 300 K ... 800 K. The experiments were performed at the undulator beam line U49/2-PGM1.

Results:

Fig. 1 A) shows a set of TPR spectra at varying total pressure. The occurrence of a low temperature peak at a total pressure $< 10^{-3}$ mbar is pronounced in the 10^{-5} mbar range at a $\text{CH}_3\text{OH}:\text{O}_2$ mixing ratio between 1:0.6 and 1:0.8 [4]. The question arising was, why it forms and what causes its decay. Fig. 1 B) shows the O 1s and C 1s spectra where separate peaks can be resolved that are related to O_{ad} , formate and methoxy species.

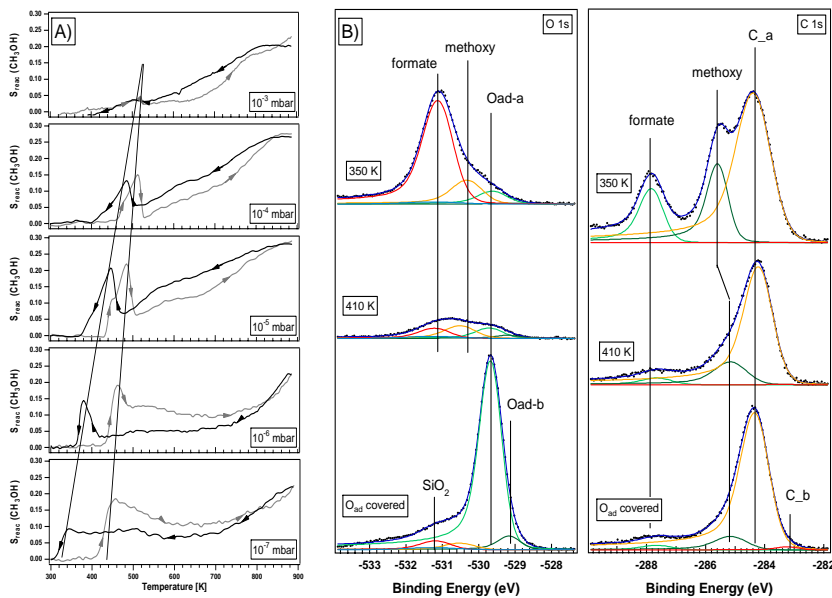


Fig. 1:

A) Reactive sticking S_{react} of Methanol over Cu(110) applying a $\text{CH}_3\text{OH}:\text{O}_2$ mixing ratio of 1:0.8 at different total pressures.

B) O 1s and C 1s components for different adsorbate species on Cu(110) formed applying unstationary reaction conditions: Oad-a (ordered O-(2 \times 1)), Oad-b (disordered), formate, methoxy, C_a and C_b contamination and a small SiO₂ impurity.

In order to obtain well resolved methoxy related

C 1s and O 1s peaks an oxygen covered Cu(110) sample was annealed in a methanol rich atmosphere of $P(\text{CH}_3\text{OH})=1.4\times 10^{-6}$ mbar and $P(\text{O}_2) = 0.2\times 10^{-6}$ mbar. Upon cooling down the sample a significant amount of methoxy was temporarily formed on the surface. The adsorption species indicated in Fig. 1 B) could be resolved in accordance with values found in the literature. Within a day a SiO₂ contamination below 0.06 ML was slowly accumulated, which could be readily removed by Ar^+ sputtering. A carbon contamination accumulated when a high methanol and a low oxygen partial pressure were chosen, as visible in Fig. 1 B). The C_a contamination (and a very small amount of C_b) occurred probably due to a C_xH_y species possibly generated at the chamber walls (note the negligible O 1s signal in the 2nd spectrum). Applying constant pressures and waiting for stationary conditions at 300 K (e.g. at $P(\text{CH}_3\text{OH})=0.5\times 10^{-5}$ mbar and $P(\text{O}_2) = 0.3\times 10^{-5}$ mbar) apart from the C-contamination exclusively formate is formed on the surface. Since under similar reaction conditions a c(2 \times 2) ordered structure was seen in LEED [4], we can state that the c(2 \times 2) described in [4] and possibly the one in [1] should correspond to formate and not to methoxy as controversially discussed in [2]. The adsorbate coverages were calibrated using the O 1s intensity of the well

known 0.5 ML of an O-(2×1) phase. Using the fact that the methoxy molecule consists of C:O=1:1, while for formate this is 1:2, the relative sensitivity factor for C 1s and O 1s can be obtained. Within the errors of the experiment the coverage of all adsorbates can be calculated, where coverage is defined as covered adsites (note that one formate molecule is bound to 2 adsorption sites via its two O atoms). Fig. 2 displays the different adsorbates present on Cu(110) during the partial methanol oxidation together with the corresponding formaldehyde production, determined by differentially pumped mass spectrometry.

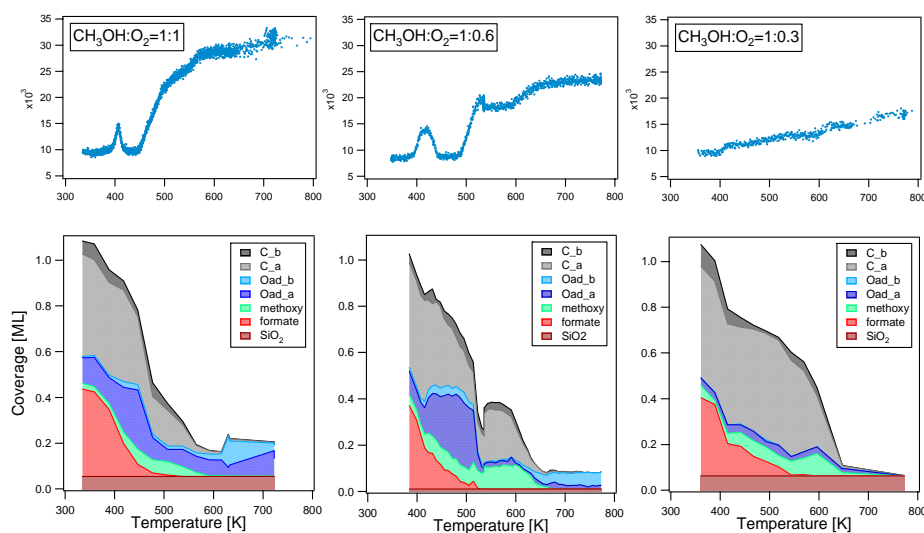


Fig. 2:
Adsorbates present on Cu(110) during the partial methanol oxidation at $P(\text{CH}_3\text{OH})=0.5 \times 10^{-5}$ mbar and different mixing ratios. The upper panel displays the formaldehyde production.

Note, that a maximum of 1 ML coverage is reached, which means that at least the C-

contamination can fill empty ad-sites in ordered adphases, e.g. in the O-(2×1) phase with a total O-coverage of 0.5 ML. The following facts can be extracted directly from the graph of Fig. 2, which will be used to identify the different reaction steps involved:

- 1) The surface at 300 K is completely adsorbate covered, while no reaction takes place.
- 2) Formate and C-contamination are the most prominent adsorbates at 300 K.
- 3) The decomposition of formate initiates the low temperature production of formaldehyde.
- 4) Parallel to the decrease of adsorbed formate, the O_{ad} coverage increases until the surface is O-poisoned and the reaction is blocked.
- 5) Above the second onset of the reactivity the oxygen coverage significantly drops and free surface area exists. To a small extend methoxy is present on the surface.
- 6) At $T > 700$ K oxygen and eventually C-contaminations are the only adsorption species.

Acknowledgements

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