



Characterisation of active phases of a copper catalyst for methanol oxidation under reaction conditions: An in situ X-Ray absorption spectroscopy study in the soft energy range

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Abstract

The oxidation of methanol over copper is investigated by X-ray absorption spectroscopy in the soft X-ray range under reaction conditions. This in situ method allows to correlate the surface electronic structure of the catalyst with its performance. The correlation reveals information about the catalytic function of various oxygen species on the surface. Oxide and metastable suboxide species affect in distinctly different ways the multiple action of copper as selective or unselective heterogeneous catalyst.

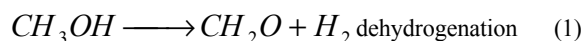
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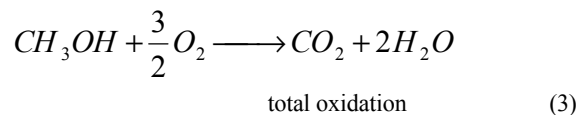
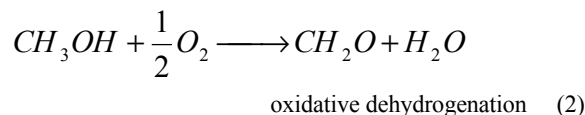
Introduction

In recent years an increasing number of high-pressure experiments on heterogeneous catalytic systems has been performed [1]. But only few of these experiments allow to investigate the catalyst under reaction conditions. An in situ investigation requires the simultaneous detection of quantities characterising the catalyst e.g. spectroscopic properties and the catalytic activity which is estimated by analysis of the gas phase composition. X-ray absorption spectroscopy in the energy range between 100-1000 eV represents a surface sensitive method to investigate the electronic structure of the catalyst under reaction conditions [2]. The absorption signal of the catalyst surface and the absorption of the gas phase, limiting the pressure in the reactor to about 10 mbar, are detected simultaneously. The method thus allows to interrogate correlations between the electronic structure of the catalyst surface and its activity. These correlations allow to

identify the role of surface species in heterogeneous catalytic processes.

Elemental copper is used as unsupported catalyst for the oxidehydration with air of alcohols to their respective aldehydes. In this work the oxidation of methanol to formaldehyde is investigated as a model reaction. This reaction exhibits conversions of about 75% with a selectivity of 80% and the temperature profile is only weakly sensitive to the total gas pressure. This is concluded from comparison of conversion-temperature profiles obtained in a copper tube reactor at 1 bar and respective profiles observed at 0.5 mbar [3]. The reaction paths for the catalytic oxidation of methanol over copper are very well known [4]:





The aim of this work is to find a correlation between the abundance of oxygen species on the copper catalyst surface and the catalytic activity. In this study the formation of different oxygen species and their respective interaction in the overall function of the catalyst are investigated.

Experimental

The experiments are performed in a special reactor cell consisting of two stainless steel chambers [2,5,6]. The high-pressure reactor chamber is mounted via a double flange to

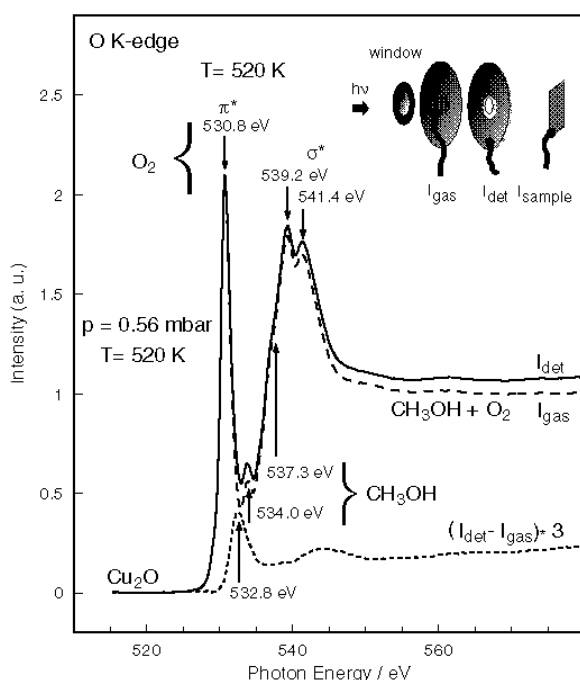


Fig.1: Subtraction of the gas phase from collection plate signal. The pre edge intensity of both spectra is subtracted. The spectra are normalised to the same intensity of the π^* resonance of molecular oxygen at 530.8 eV [13]. The difference spectra represent the X-ray absorption spectra of the copper catalyst. Under the given conditions it is Cu_2O . The inset shows a schematic drawing of the used detectors mounted in the reaction cell.

an UHV-chamber, which is adapted to the beamline of a synchrotron radiation facility. The UHV-chamber is equipped with an Au evaporated Cu-grid used as a conventional beam intensity monitor. A liquid nitrogen cooled, 200 nm thin polyimide X-ray window is fixed on the double flange. The monochromatic synchrotron radiation passes the X-ray window and the light irradiates the copper catalyst after travelling through the gas phase in the reactor. The

reactor chamber allows to detect three different signals simultaneously (see inset of Fig.1). An oxidation-resistant collection grid is mounted in the reactor cell, to record the total electron yield of the gas phase. An oxidation-resistant collection plate is installed in front of the catalyst to detect the surface-related XA spectra using the total electron yield method. The sample current induced by relaxations processes in the copper catalyst is recorded as well.

The catalyst-related signals of the collection plate and the sample current contain significant contribution from the gas phase signal. The way to extract the absorption spectrum of the catalyst is demonstrated in Fig.1. The spectra are normalised to the π^* -resonance of molecular oxygen at 530.8 eV, after subtraction of the pre-edge background [13]. The difference between the sample current, I_{sam} , or collection plate signal, I_{det} , and the collection grid signal, I_{gas} , reveals a surface-sensitive spectrum of the catalyst.

The copper foil can be heated up to 770 K. The measurements are carried out under flow-through conditions. A gas flow of 20ml/min methanol and 10ml/min oxygen is regulated by mass flow controllers. The total pressure in the reactor is controlled to 0.6 mbar during the experiment. The gaseous educts and products are detected by XAS and by a conventional mass spectrometer, which is connected to the reactor cell. Great care has been taken to avoid or passivate active materials in the reactor design. Without copper catalyst the blind activity of the set-up could be reduced to below 10% conversion.

Experiments are carried out at the beamline PM1 [7] and HE-TGM1 [8] at the Berliner Synchrotron Radiation Facility BESSY I. The spectral resolution of 1.6 eV and 2.3 eV are determined by the π^* -resonance of molecular oxygen at 530.8 eV at the PM1 and HE-TGM1 respectively. The photon energy is calibrated by the π^* -resonance of molecular oxygen with an accuracy of $\pm 0.2 \text{ eV}$.

Results

Spectral data

In Figure 2 the O K-NEXAFS of a copper catalyst is shown as a function of the $\text{O}_2 / \text{CH}_3\text{OH}$ gas flow ratio at a temperature of 670 K. A drastic change of the X-ray absorption spectra at a gas flow ratio of 0.5 is observed. For gas flow ratios below 0.5 the spectra are dominated by a broad structure at 536 eV consisting of two resonances B at 535.7 eV and C at 537.1 eV. This broad feature is not observed in the O K-NEXAFS spectra of known copper oxides. A further narrow resonance at 531.7 eV (A_1) is present at gas flow ratios below 0.5. The shape of the spectra is identical with spectra detected as a function of temperature at a $\text{O}_2 / \text{CH}_3\text{OH}$ ratio of 0.2 presented in [9]. The maximum A_2 at 532.8 eV is much more pronounced in the spectra detected in oxygen-rich gas phases ($\text{O}_2 / \text{CH}_3\text{OH} = 1.0-0.6$) and is shifted towards higher energies compared to A_1 . The detail of the assignment of oxygen species discussed in this paper are given below. The

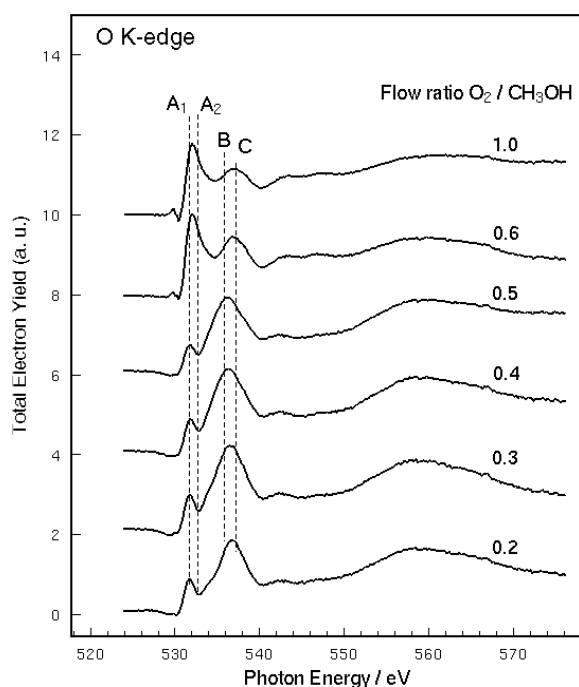


Fig. 2: O K-NEXAFS of a copper foil at 670 K as a function of O_2/CH_3OH flow ratio. The pressure was 0.5 mbar. The spectra are dominated by the oxidic structure A_1 for O_2/CH_3OH ratios above 0.6. The spectra change by increase the abundance of CH_3OH . A suboxidic structure (B+C) is dominating for O_2/CH_3OH ratios below 0.5.

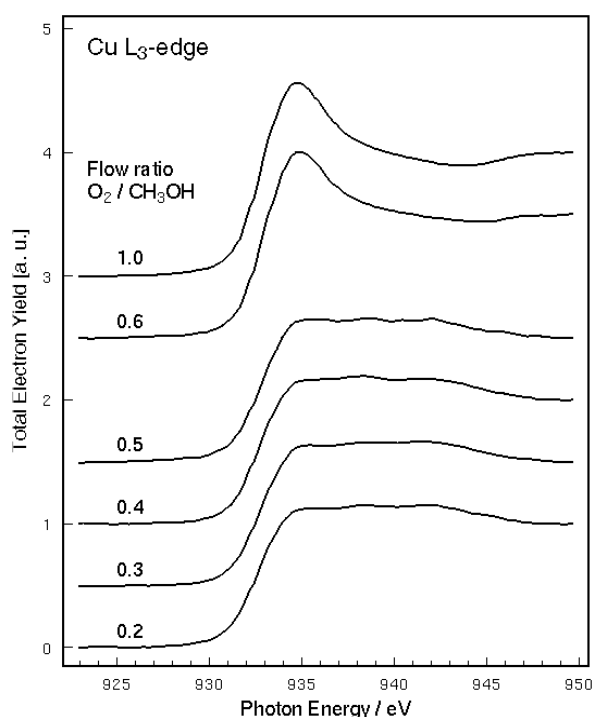


Fig. 3: The Cu L_3 -NEXAFS spectra corresponding to the spectra in Fig. 2. A transition from the oxidic phase to the metallic phase is observed. The white line at 934 eV characterising the oxidic phase is observed only for oxygen rich O_2/CH_3OH gas flow ratios.

Cu L_3 -NEXAFS spectra show an increase of the oxidic character with increasing O_2/CH_3OH gas flow ratios as well (see Figure 3). The step shape of the spectra characterising the metallic copper is gradually replaced by a resonance at 934 eV that is well known in Cu_2O [10,11]. The onset of catalytic activity coincides with the appearance of the feature B+C in the O K-NEXAFS and with the loss of the copper(I) oxide which seems to act as a passivating layer for the essential metallic character of the catalyst. In Figure 4 the conversion of methanol is plotted as a function of the O_2/CH_3OH gas flow ratio.

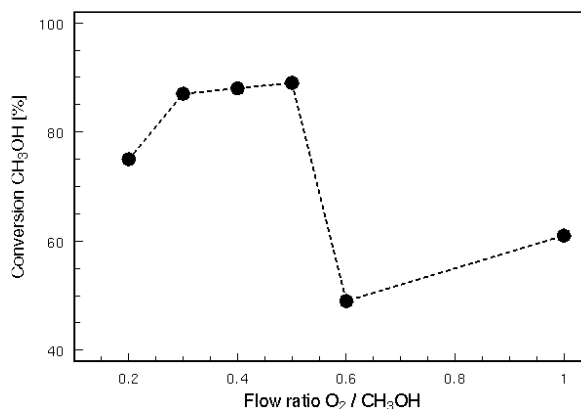


Fig. 4: The conversion of methanol increases drastically by decreasing the O_2/CH_3OH gas flow ration from 0.6 to 0.5 at 670 K. The enhanced activity coincidences with the transition from the oxidic phase to the suboxidic/metallic phase observed by the O K- and Cu L_3 - NEXAFS spectra in Fig. 2 and Fig.3 respectively.

Assignment of oxygen species

The O K-NEXAFS spectra are analysed quantitatively by a least square fit. The variation in abundance of the oxygen species with temperature and redox potential of the gas phase will be correlated to the activity in order to obtain information about the electronic structure and the catalytic function of relevant oxygen species. Figure 5 shows two O K-NEXAFS spectra and their deconvolutions obtained at a catalyst temperature of 670 K and at a gas flow ratio O_2/CH_3OH of 0.4 and 0.6 respectively. The analysis of NEXAFS spectra by superposition of Gaussian peaks describing resonances and an error function step structure characterising the absorption edge was earlier used for the oxygen-silver system [12]. Five oxygen resonances have to be included to reveal acceptable fits of the spectral shapes. These maxima are designated A_1 , A_2 , B, C and D. An additional weak structure E is observed, which is correlated to species A_2 . Two narrow structures (A_1 and A_2) are used to fit the peak at low energies around 533 eV characterising the $O1s \rightarrow O2pCu3d$ electron transition. The energy position of the maximum A_2 at 532.8 eV is identical with the

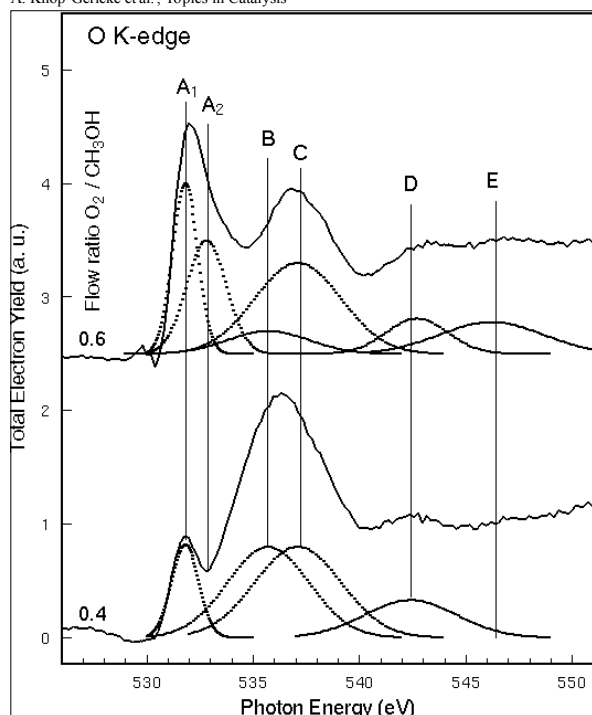


Fig. 5: Two spectra of Fig.2 are plotted to demonstrate the different oxygen species investigated in this paper. Two Gauss peaks A_1 and A_2 were used to fit the oxidic structure. The suboxide phase is characterised by three gauss peaks (B-D).

one of copper(I) oxide [10,11]. The feature is designated as Ox_{bulk} , meaning three-dimensional Cu_2O . The peak E is due to the σ^* -resonance of Cu_2O at 546 eV caused by $O1s \rightarrow O2pCu4sp$ electron transition. The peak A_1 at 531.7 eV is attributed to an oxidic species as well, because it exhibits a similar energy position and spectral shape than Ox_{bulk} . Peak A_1 is related to surface copper(I) oxide Ox_{surf} . The different resonance energies reflect the influence of the metallic substrate on thin layers of oxide whereas thicker layers appear indistinguishable from bulk oxide. The maximum B+C is assigned to a novel copper suboxide that is characterised by the $O2pCu4sp$ hybridisation. The Cu L-NEXAFS spectra of the copper foil indicate despite the presence of oxygen-species a metallic character of the catalyst under reaction conditions of partial oxidation as shown in Figure 3. Therefore the observed oxygen-species has to be attributed to a copper suboxide Ox_{sub} . The stoichiometry of this suboxide was estimated using the edge-jumps of the in-situ NEXAFS spectra at the Cu L- and at the relevant structure of the O K-edge. The found value for the Cu/O-ratio is around 10:1 [25]. This stoichiometry is much higher compared to the one of copper oxides. The O K-NEXAFS spectra of the Ox_{sub} is dominated by the structures B and C at about 536 eV. For Cu_2O this energy range is characterised by the $O2pCu4sp$ hybridisation. The atomic character of the Ox_{sub} species is indicated by the missing of an additional sharp π^* -resonance at lower binding energies that is very well known for molecular oxygen [13].

Correlation with catalytic function

The parameters of representative Gaussian profiles are listed in Table 1. The energy positions and the FWHM were fixed for the deconvolution of the spectra. The only free parameters for the fits are given by the intensities of the used Gaussian profiles. Acceptable fits of Ox_{sub} were achieved by using two Gaussian profiles (B and C). The different bonding of Ox_{sub} and Ox_{surf} and Ox_{bulk} ($O2pCu3d$ hybridisation) on the other hand induces a different catalytic activity of the suboxide and the oxidic species. This will be shown below.

Table 1: Energy position and FWHM of the used Gaussian profiles to deconvolute the in situ O K-NEXAFS spectra.

Designation	A_1	A_2	B	C
Energy	531.7 eV	532.8 eV	535.7 eV	537.1 eV
FWHM	1.5 eV	2.2 eV	4.5 eV	4.8 eV

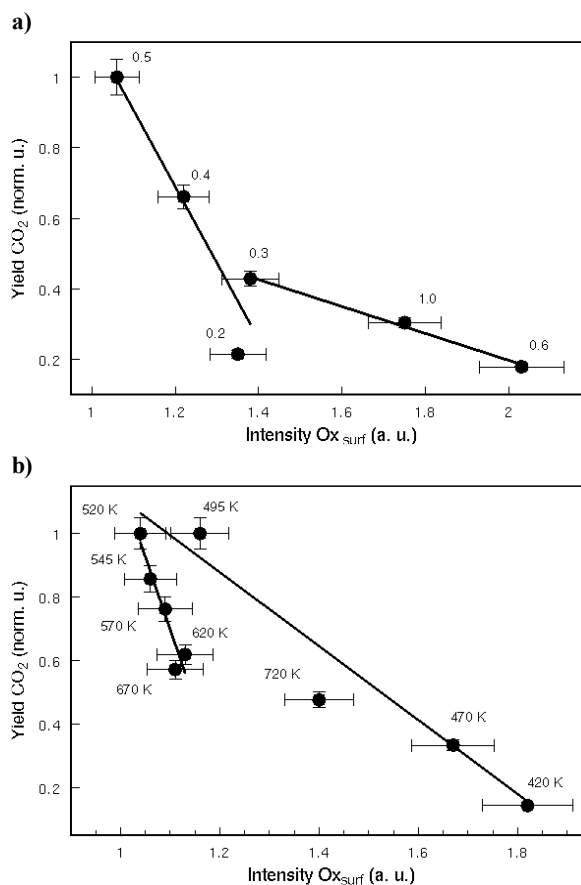


Fig. 6: a) The intensity of the surface oxide species Ox_{surf} is negatively correlated to the yield of CO_2 . The O_2/CH_3OH gas flow ratio was varied at 670 K. The gas flow ratio is given in the plot beside the data points.

b) The intensity of the surface oxide species Ox_{surf} is negatively correlated to the yield of CO_2 . The temperature of the catalyst was varied at a O_2/CH_3OH gas flow ratio of 0.2. The temperature is given in the plot beside the data points.

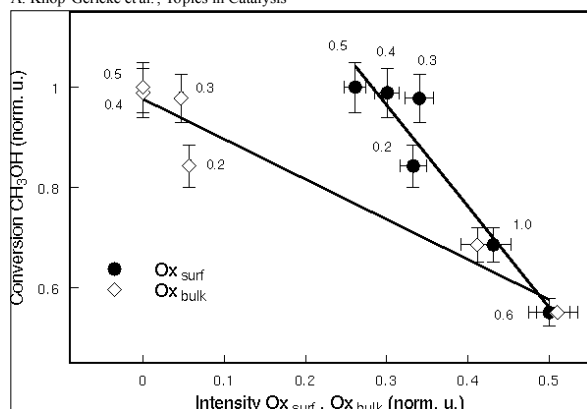


Fig. 7: The oxide species Ox_{surf} and Ox_{bulk} inhibit the conversion of methanol with different rates. The influence of Ox_{surf} is more pronounced. The intensities of the oxide species are normalised to the maximum intensity of $Ox_{surf} + Ox_{bulk}$.

Since the catalytic activity is determined by the topmost layer of the surface but the analytical method offers an information depth of several nanometers, the transition in the growth-mode from two-dimensional to three-dimensional is indicated by the change in the slopes shown in Fig. 6a,b [9]. The correlation between the conversion of methanol and the abundance of Ox_{surf} and Ox_{bulk} in Figure 7 shows a decrease of methanol conversion by the coverage of the copper surface with oxidic species. An increase of Ox_{bulk} by 30% reduces the methanol conversion by 10%, whereas an increase of Ox_{surf} by 30% reduces the methanol conversion by 20% which indicates an island growth of Ox_{bulk} because it covers less of the active phase compared to Ox_{surf} .

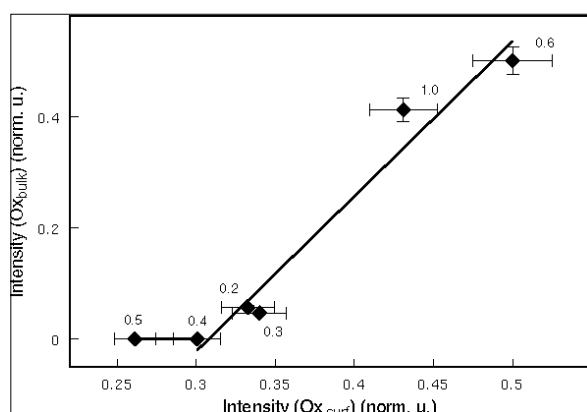


Fig. 8: The intensity of Ox_{bulk} increases with increasing intensity of Ox_{surf} after a short induction phase. The intensities of the oxide species are normalised to the maximum intensity of $Ox_{surf} + Ox_{bulk}$.

Figure 8 shows the result of a correlation between growth of the Ox_{bulk} species as a function of the Ox_{surf} abundance. At low coverages only the Ox_{surf} species is growing and Ox_{bulk} is not detectable. The growth of the Ox_{bulk} species sets in at a relative abundance of Ox_{surf} of 0.3. The species Ox_{bulk} and Ox_{surf} grow simultaneously for higher coverages.

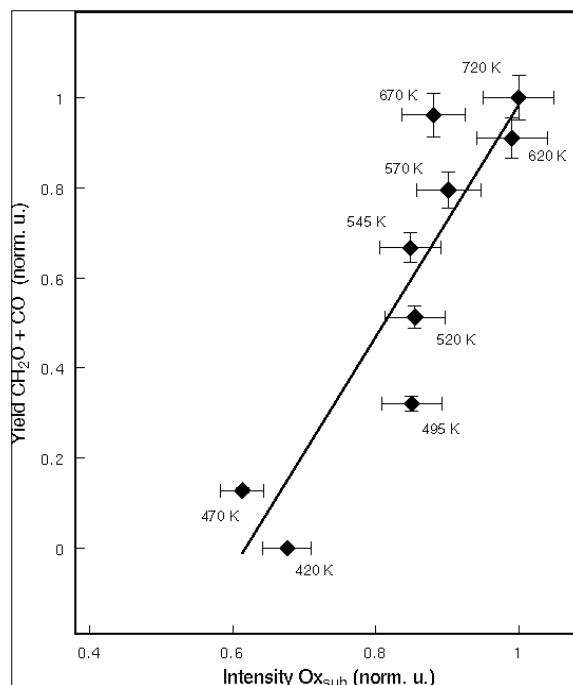


Fig. 9: The yield of $CH_2O + CO$ is plotted as a function of the suboxide. The temperature was varied at a O_2/CH_3OH gas flow ratio of 0.2. The pressure was 0.6 mbar.

The catalytic activity of the Ox_{sub} phase is not correlated to the total oxidation of methanol, but Ox_{sub} is connected with the partial oxidation of methanol. Figure 9 shows the correlation of the CH_2O -yield and the intensity of Ox_{sub} . The positive correlation between CH_2O and the intensity of Ox_{sub} points to a “marker function” of Ox_{sub} . The suboxide species marks the catalytically active sites for the partial oxidation of methanol and is therefore positively correlated to formaldehyde. The role of Ox_{sub} is different from the role of Ox_{surf} in the catalytic reaction. Ox_{surf} is consumed by the total oxidation of methanol as shown by the negative correlation between CO_2 and Ox_{surf} in Figures 6a and 6b.

Discussion

This in situ XAS study demonstrates the existence of three different oxygen species. Ox_{bulk} which is identical to the copper(I) oxide, the surface oxide Ox_{surf} which is negatively correlated to the total oxidation and the suboxide species Ox_{sub} which is positively correlated to the yield of formaldehyde. The atomic oxygen species Ox_{sub} presents a novel copper suboxide that was not detected in means of UHV studies of the Cu/O system [14]. It is formed only under reaction conditions [3, 5, 6, 9,25]. This fact demonstrates impressively the necessity to use in situ methods for the investigation of heterogeneous catalytic processes.

The formation of Ox_{surf} and Ox_{bulk} does not correlate linearly with the nominal abundance of oxygen in the gas phase as shown in Figures 6a,7 and 8. Since the catalytic reaction consumes oxygen in competition with the oxide formation, the abundance of Ox_{surf} and Ox_{bulk} is affected by the kinetics of the catalytic reaction as well. The convolution of reaction rates which are certainly different for the two oxygen consuming catalytic- and the three different processes of oxide

formation causes the complicated relation between the abundance of Ox_{surf} and Ox_{bulk} and the nominal partial pres-

sure of O_2 as shown in Figures 6a,7,8.

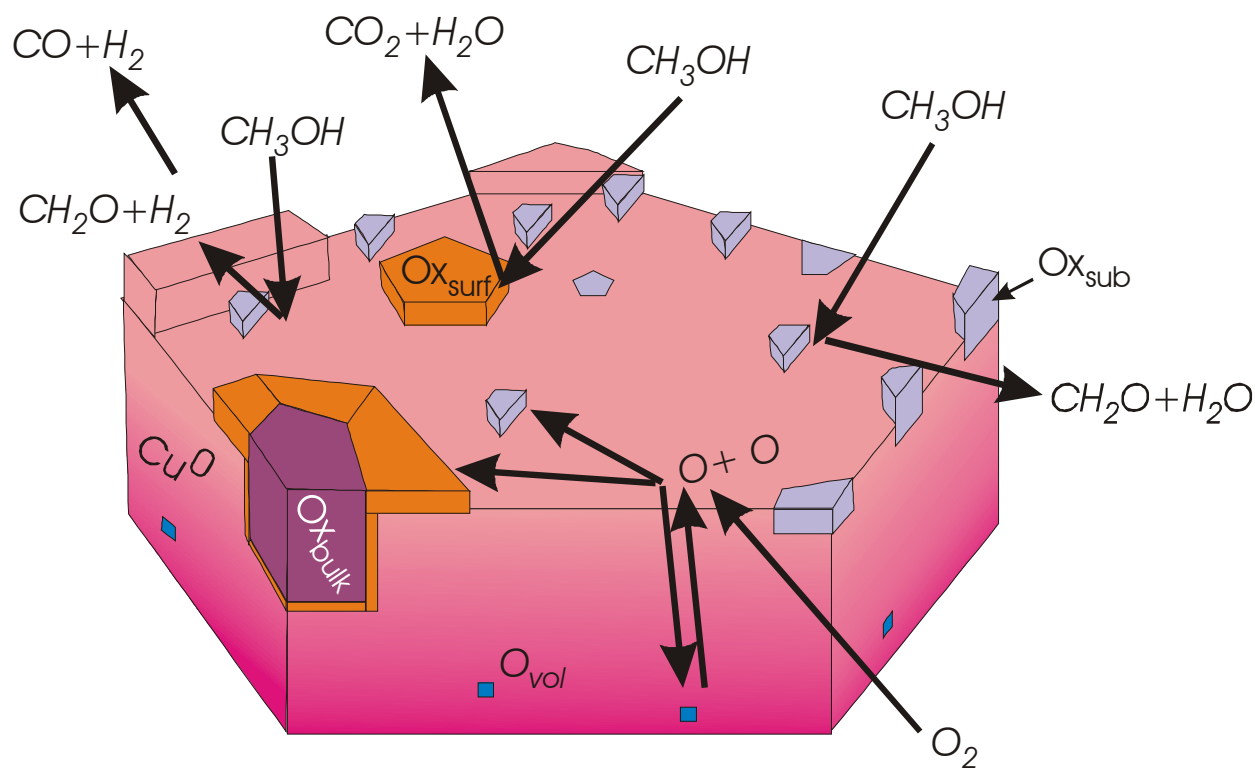


Fig.10: The active surface of the catalyst with different coexisting oxygen species is schematically drawn. The arrows indicate the interaction of the gas phase and the surface. Cu_2O (Ox_{bulk}) and Ox_{surf} convert methanol to CO_2 . The atomic suboxide phase Ox_{sub} is correlated to the yield of formaldehyde. Oxygen incorporated in metallic copper is exchanged with the surface oxygen species.

The results presented in Figure 8 allow to conclude that Ox_{surf} represents the first step in the formation of copper(I) oxide. At early stages of oxidation the copper surface oxide Ox_{surf} is formed as a two-dimensional film on the copper surface [15]. The conversion of methanol is negatively affected by the abundance of Ox_{surf} as shown in Figure 7. A higher oxidation potential of the gas phase adjusted by the gas flow ratio and / or by the temperature induces the deep oxidation of copper characterised by the onset of a three-dimensional growth of the oxide.

The lattice parameter of cubic Cu and cubic Cu_2O are given in the literature by 0.3608 nm and 0.427 nm respectively [16,17]. This large lattice mismatch of about 15% prevents the immediate growth of Cu_2O on Cu. The thin Ox_{surf} -layer may thus serve as buffer on the copper surface and allows the consecutive growth of Ox_{bulk} (see Figure 10).

It is important to note, that the investigated surface may not be static and well-defined under the present reaction conditions. Chemisorption of atomic oxygen and its reaction with Cu creates significant changes of the metal surface. In the literature the modification of the electronic structure of Cu by the incorporation of O in the matrix is discussed [18,19,

20, 21]. The induced strain fromed by sub-surface oxygen atoms influences the energy position of the Cu3d-band. This is evident in the shift of the white line in the O K-NEXAFS of Ox_{bulk} from 532.8 eV to 531.7 eV for Ox_{surf} . By this affect the penetration of O-atoms below the catalysts surface can affect the catalytic activity of metallic copper in the same way as the thin layer morphology of the Ox_{surf} is important for the surface chemistry. The shift of the valence band structure of this species characterised by the shift of the white line by 1.1 eV is a consequence of the modification of the oxide electronic structure by the presence of the metal and the function of subsurface oxygen as “adhesion agent” for the oxide buffer layer. When the Ox_{bulk} phase grows on top of Ox_{surf} , the local environment for Ox_{bulk} is not affected by the disturbed copper phase. The 3d-band is consequently not shifted and the white line of copper(I) oxide is detected at 532.8 eV where also the absorption for bulk Cu_2O is found [10,11]. The transition from Ox_{surf} to Ox_{bulk} cannot be determined in intermediate states by our present measurements due to the limited resolution allowing to distinguish only the state of Ox_{surf} from the final state of the three dimensional growth copper(I) oxide.

The most pronounced difference in the O K-NEXAFS of the active Cu catalyst relative to copper(I) oxide is the appearance of the structures B and C in the energy range of 535–540 eV. This additional spectra of an atomic oxygen species are assigned to a Cu-O compound with much weaker chemical bonding than in known oxides. The suboxide suggested is chemically to be considered as an intermediate between an oxide and a solid solution of oxygen atoms in a Cu matrix which is supported by the absence of any sign of Cu-d band interaction with this atomic species. The formation of $O_{x_{sub}}$ modifies the electronic structure of Cu and renders the adsorption of an additional oxygen species O_{ad} , which is directly involved in the oxidehydrogenation and acts as a co-catalyst for Cu.

The positive correlation of $O_{x_{sub}}$ and the yield of formaldehyde occurs due to the “marker” function of $O_{x_{sub}}$. The atomic oxygen species marks the active sites on which O_{ad} , that can not be detected directly by XAS, is chemisorbed. Defects in the copper matrix induced by the presence of $O_{x_{sub}}$ are good candidates for function as active sites. In this picture the detection of the modified metallic character of copper induced by metastable oxygen which is only present under reaction conditions compares well with the prediction of “oxygen modified” Cu from UHV single crystal studies [22].

The detected oxygen species may be suspected to represent intermediates of methanol. The formation of methoxy and formate as intermediates of the methanol oxidation over copper is discussed in the literature. On an oxygen-covered Cu single crystal methoxy was imaged by STM after a methanol treatment at room temperature [23]. At elevated temperatures no methoxy was found on the surface which was interpreted as the decomposition of methoxy to formaldehyde.

We did not observe any structure at the C K-edge that could be identified as methoxy or formate. All peaks in the C K-NEXAFS spectra are due to gas phase species of CH_3OH , CH_2O , CO and CO_2 . The O K-NEXAFS spectra of CH_3O and $CHOO$ on copper are described in the literature. The O K-NEXAFS of methoxy on Cu (100) is characterised by a broad structure at 539 eV and a less intense peak at 534 eV [24]. The broad structure exhibits a similar shape compared to the broad feature (B+C) in the present work. But its position disagrees with the methoxy feature by 1 eV and besides the temperature dependence of B and C is different, therefore the change in spectral shape of B+C can not be explained by one adsorbate [25]. In a recent work characteristic features of methoxy on Cu in the O K-NEXAFS at 531.5 eV, 536.5 eV and 538.5 eV are reported [26]. The spectral shape of the described structures are, however, different from the peak shape of feature (B+C). In addition we do not detect a peak at 538.5 eV.

The same arguments hold for the case of formate representing the second adsorbate, observed in UHV studies. The O K-NEXAFS of formate on Cu are given in the literature with pronounced features at 535.5 eV and 545.5 eV for the π^* - and σ^* -resonance respectively [24,27]. Sommers et al. gave resonance energies at 532.7 eV and 542 eV comparable to energy positions found in this work [28]. The different re-

sponses of the spectral features A_1 , A_2 and B towards changed reaction conditions are proofs of the existence of chemically different species. Furthermore, the intensity ratio of A and D does not fit to that given in ref. [28]. Altogether it can be concluded, that the oxygen species found in this work can not be attributed to methoxy or formate. The species represent rather atomic oxygen, that was not described in the literature before. The failure to detect fingerprints of intermediate species may be explained by high reaction rate causing a short lifetime of intermediates on the surface.

OH-groups are expected on the surface during methanol oxidohydrogenation. The reaction of chemisorbed OH with a activated H-atom from the dehydrogenation processes leads to the desorption of water. Pangher et al. investigated chemisorbed water on Ni (110) [29]. Since metal surfaces are reactive in the dissociation of water, OH-groups should be present on the surface. A broad resonance at 536.5 eV was found for the Ni/OH system. The energy position and the width of the feature might be compared to the feature (B+C) detected in this work. But the existence of OH-groups can explain only one of the species, because a different dependence on temperature and on O_2/CH_3OH ratio was found for the two contributions B and C to the overall shape [25]. But the formation of OH-groups seems to be suppressed since we did not observe methoxy, formed by the abstraction of hydrogen from methanol, on the surface.

The two resonances B and C may present two different types of defects, which explain the different temperature dependence of the two peaks. There may exist more different types of defects of the copper matrix induced by subsurface-oxygen atoms but the spectral resolution used in this investigation allows to distinguish only the resonances B and C.

Conclusion

The in situ O K-NEXAFS of an active catalyst looks different compared to copper oxides. It is characterised by atomic oxygen forming a copper suboxide by $O2pCu4sp$ hybridisation in contrast to additional $O2pCu3d$ hybridisation in Cu_2O . This novel oxygen species is correlated to the yield of formaldehyde. The copper suboxide is detectable only under reaction conditions and therefore it is not observed in UHV investigations.

The formation of intermediates like methoxy and formate on the copper surface was not observed.

The copper suboxide is formed by atomic oxygen penetrating the copper matrix. They cause strain in the copper network. This strain terminates by defects on the catalyst surface which are marked by the copper suboxide species. These copper defects present adsorption sites for an oxygen species that is directly involved in the partial oxidation of methanol but which was not detected by in situ O K-NEXAFS. A higher abundance of oxygen induces the formation of the surface oxide and the bulk oxide. The formation of these oxygen species is not directly correlated to the abundance of oxygen in the gas feed, because the conversion of the gas phase by the catalytic reaction affects the abundance of oxygen in the gas phase as well.

The conversion of methanol to formaldehyde is inhibited by the formation of oxidic species. The detected suboxide pre-

sents a novel weakly bond oxygen species that was not discussed in the literature before. Further experiments to iden-

tify the geometric structure of the copper suboxide are required to render calculations of this suboxide species.

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