



Probing the Electronic Structure of an Active Catalyst Surface under High Pressure Reaction Conditions: The Oxidation of Methanol over Copper

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Abstract

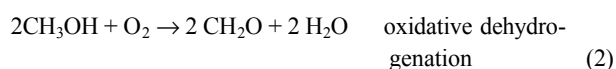
The active phase of a bulk metallic copper catalyst is investigated by surface sensitive X-ray absorption spectroscopy at the oxygen K-edge and the Cu L-edges in the total electron yield mode under practical steady state flow-through conditions. The active catalyst surface contains oxygen atoms revealing significant spectral differences compared to those of known copper oxides. The partial oxidation of methanol to formaldehyde is correlated to the abundance of this copper suboxide. These oxygen atoms probe defects of the copper lattice, which represent catalytically active sites. The suboxide is undetectable under UHV-conditions. The total oxidation of methanol is catalysed by a conventional copper(I) oxide species and the abundance of carbon dioxide in the gas phase is increasing with decreasing integrated intensity of the oxide species.

Keywords: catalytical oxidation of methanol over copper, partial oxidation, copper suboxide, copper (I) oxide, total oxidation, in situ O K-XANES

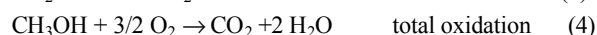
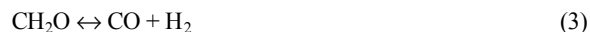
Introduction

In the past few years in situ techniques have attained great importance in the field of heterogeneous catalysis [1,2]. Studies under reaction conditions close to those found in practice are necessary, because the structure of a catalyst under reaction conditions can be significantly different from that after the reaction or ex situ. An in situ study requires for any relevant interpretation the simultaneous detection of catalytic conversion data together with the spectroscopic information of the catalyst.

Several reaction paths are known for the oxidation of methanol. Two reaction paths of the selective oxidation of methanol are discussed in the literature [10]:



Formaldehyde decomposes partly on the hot catalyst surface in carbon monoxide and hydrogen [8].



NEXAFS (Near Edge X-ray Absorption Fine Structure) spectroscopy in the energy range $250 \text{ eV} \leq h\nu \leq 1000 \text{ eV}$ applied in the total electron yield mode represents an established, surface sensitive method to investigate the electronic structure of solid state surfaces [3]. The formation of a copper suboxides Cu_xO ($2.2 \leq x \leq 2.7$) was found ex situ in UHV after pretreatment with various $\text{CH}_3\text{OH}/\text{O}_2$ -mixtures[5]. The electronic structure of these suboxides is very similar to the electronic structure of copper(I) oxide. Nevertheless, Cu_2O is supposed to catalyse only the non selective total oxidation of methanol to carbon dioxide and water [6]. Therefore, an in-situ investigation, which allows to overcome the pressure- and coverage gap, is required to investigate the catalytically active surface. A new in situ was

introduced [4]. This method allows the detection of surface sensitive X-ray absorption spectra in the total electron yield mode within the soft X-ray range of 250-1000 eV under reaction conditions. In Ref. [7] the formation of Cu_2O and CuO was investigated by detecting in-situ NEXAFS spectra at the $\text{Cu L}_{2,3}$ -edges during heating of a copper foil at 600 K in 0.05 and 0.1 mbar oxygen atmosphere, respectively. In the present communication the electronic structure of the copper catalyst surface and the composition of the gas phase are detected simultaneously under steady state methanol oxidation reaction conditions. The aim of this work is to find correlations between the electronic structure of the catalyst surface and the conversion of the catalytic reaction.

Experimental

The experiments are performed in a new constructed reactor cell [4,7,8]. The used UHV-system consists out of two stainless steel chambers. The reactor chamber is mounted via a double flange to an UHV-chamber, which is adapted to a 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 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 foil after crossing 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 catalyst surface-related XA spectra using the total electron yield method. The sample current induced by relaxations processes in the copper catalyst is measured too. The catalyst related signals of the collection plate and the sample current contain an important amount of the gas phase signal. The way to extract the absorption spectrum of the catalyst is demonstrated in Fig.1. The spectra are normalised at the π^* -resonance of molecular oxygen at 530.8 eV, after subtraction of the pre edge background [18]. This normalisation is making use of the assumption that there are no species on the surface having structures at the energy of 530.8 eV. This assumption is reasonable, since molecular oxygen is not expected on the copper surface at temperatures above 300 K [23]. A normalisation with respect to higher energetic structures (CH_3OH) would not consider peaks and edge jumps at lower energies and therefore they are represented in a wrong way. The difference of sample current or collection plate signal, I_{det} , and the collection grid signal, I_{gas} , reveals a surface sensitive spectrum of the catalyst. The resulting spectrum measured in a gas feed of 10 ml/min. O_2 + 20 ml/min CH_3OH at 0.52 mbar and at 520 K agrees very well with the known spectrum of Cu_2O [24, 25]. Especially no additional features are observed. The error bars given in this work present the total error. Other errors (noise, beam instabilities, fluctuations of the signal caused by changes of pressure) can be neglected. The spectra presented in this work are not smoothed and are not treated in order to

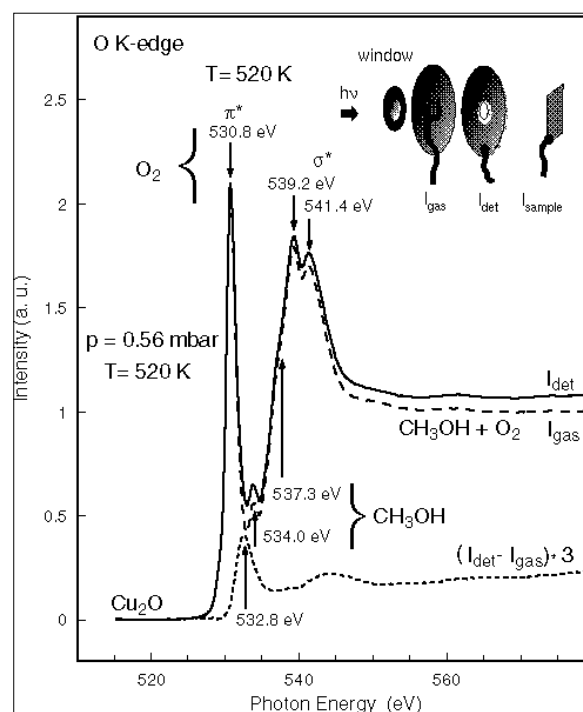


Fig.1: Subtraction of the gas phase from collection plate signal. The pre edge intensity of both spectra is subtracted. The spectra are normalized to the same intensity of the π^* resonance of molecular oxygen at 531.0 eV [18]. The difference spectra represent the X-ray absorption spectra of the copper catalyst. Under the given conditions it is Cu_2O . The inset shows a schematic drawing of the used detectors mounted in the reaction cell.

improve the quality of the data. The detected electron currents are compatible or even higher (a few nanoamperes) compared to signals detected in classical surface sensitive UHV-investigations of adsorbates, because the spectra were recorded in the total electron yield mode, in contrast to the often used partial electron yield mode. The loss of intensity by absorption of photons in the polyimide window and in the gas phase is compensated by a multiplication effect for emitted electrons by ionisation of gas phase molecules.

The copper foil is heated up to 770 K. The measurements are carried out under flow-through conditions. A gas flow of 20 ml/min methanol and 10 ml/min oxygen is regulated by mass flow controllers. The total pressure in the reactor is about 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 [9] and at the Berliner Synchrotron Radiation Facility BESSY I. The spectral resolution of 1.6 eV is determined by the π^* -resonance of molecular oxygen at 530.8 eV. The photon energy is calibrated by the π^* -resonance of molecular oxygen with an accuracy of ± 0.2 eV.

Results

The catalytic activity of the copper foil in the in-situ reactor is demonstrated in Fig.2. The yield of carbon dioxide (■), carbon monoxide (Δ), formaldehyde (□), formaldehyde + carbon monoxide (O) and the conversion of methanol (▼) are plotted in Fig. 2 as a function of the catalyst temperature estimated from mass spectra. The conversion of methanol starts at 470 K. It increases up to 85% at 720 K. The yield of CO₂ has a maximum around 500 K, whereas the selective oxidation product CH₂O increases continually with the temperature.

Fig.3 shows a plot of a selection of in-situ NEXAFS spectra of the copper catalyst taken at the oxygen K-edge after subtraction of the gas phase signal. A gas-flow ratio CH₃OH/O₂ = 2 :1 is used. The catalyst temperature is increased stepwise from 470 K to 720 K. After temperature stabilisation, an O K-NEXAFS spectrum is detected and, afterwards, the temperature is increased.

The spectra are characterised by two maxima at 531.6 eV and 536.6 eV. For comparison the O K-edge absorption spectrum of Cu₂O is plotted in Fig. 3. The maximum at 531.6 eV (ox) energetically coincides mostly with the whiteline of Cu₂O at 532.8 eV, assigned to antibonding O2pCu3d states and even the shape of the feature is similar to the O2pCu3d state in the Cu₂O reference spectrum [15,16]. The reference spectrum shows additional weak maxima at 539 eV and 545 eV. These structures are assigned to O2pCu4sp states [15,16,17]. The broad peak at 536.6 eV (subox) can not be attributed to the known copper oxides. This feature is due to an atomic oxygen species characterising a novel suboxide species since only one broad resonance is observed. CH₃OH shows two strong resonances in the X-ray absorption spectrum at the O K-edge at 534.1 and 537.3 eV [26]. The detection of a minimum or a shoulder between the two peaks depends on the used spectral resolution. The error of the absolute energy calibration, which was done by the use of the gas phase spectrum measured simultaneously, is ±0.2 eV. Therefore the observed maximum at 536.6 eV is not due to any gas phase species. At high temperatures (T > 570 K) the amount of CH₃OH in the gas phase decreases below 20%, because of the high methanol conversion. As far as the intensity of the suboxide species and the conversion of CH₃OH are increasing upon increasing temperature, the maximum at 536.6 eV can not be explained by a gas phase artefact.

Fig. 3 shows a decrease of the integrated intensity of the oxidic feature up to 570 K. At higher temperatures the intensity of the oxidic structure increases. On the other hand, the integrated intensity of the suboxide species increases with temperature. The catalytic function of these both oxygen species are identified by investigating the correlations of these species and the products of catalytic oxidation of methanol.

In the literature, the function of intermediate species like methoxy and formate is discussed in the selective oxidation of methanol over copper surfaces. We did not find any hint

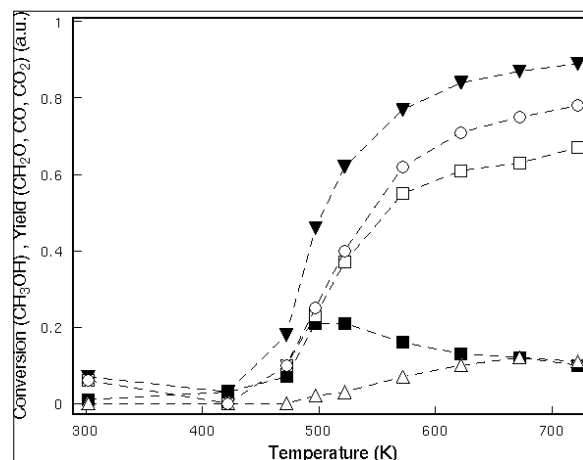


Fig.2: Normalised relative concentration of carbon containing molecules in the reaction atmosphere of 10 ml/min O₂ + 20 ml/min CH₃OH as a function of catalyst temperature estimated by mass spectra. The yield of carbon dioxide (■), carbon monoxide (Δ), formaldehyde (□), carbon monoxide + formaldehyde (O) and the conversion of methanol (▼) are plotted in the figure.

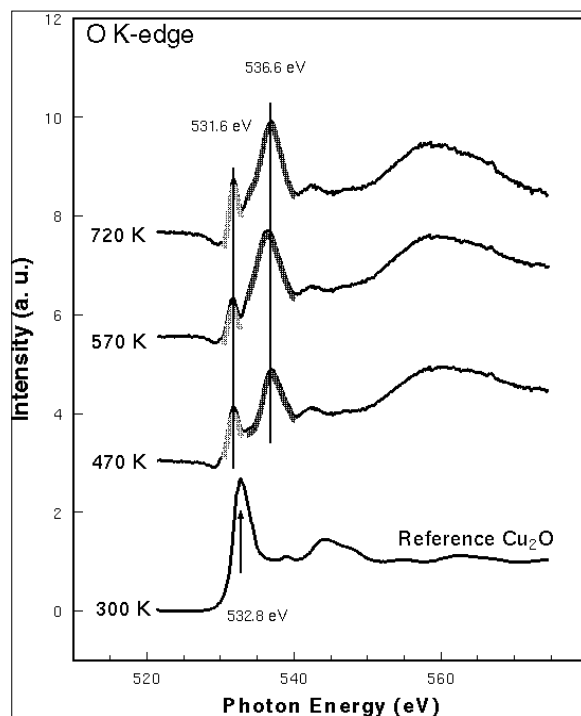


Fig.3: Temperature dependence of in-situ X-ray absorption spectra of a copper foil at the oxygen K-edge in 10 ml/min. O₂ + 20ml/min. CH₃OH at p=0.64 mbar. A reference spectrum of Cu₂O is plotted at the bottom of the figure.

for a spectroscopical identification of an intermediate in the O K-edge and C K-edge spectra. The energy position of the π*- and σ*-resonances of HCO₂/Cu(100) is 535.5 eV and 545.5 eV, respectively [12]. The energy position of the σ*-resonance of CH₃O/Cu(100) of 539 eV and a low intensity feature at 534 eV given by Outka et al does not fit to the

energies we find [12]. These energies do not fit to the energy positions of both species found in this work. Amemiya et al. measured NEXAFS spectra of $\text{CH}_3\text{O}/\text{Cu}(111)$ [19]. They found features at 531.5 eV, 536.5 eV and 538.5 eV. The features at 531.5 eV and 536.5 eV coincidences with the copper(I) oxide-like- and the novel suboxide species found in this work, respectively. The shape of the spectrum in Ref. [19] is different and we do not find a feature at 538.5 eV in this work. On the contrary, an independent behaviour of both species can not be explained by one intermediate, because the consumption of the active phase causes a reduced intensity of the π^* - and σ^* -resonance.

The energy position of the suboxide feature in the O K-NEXAFS spectra of the copper catalyst surface is not constant. The spectra presented in fig.3 are fitted by a gauss-profile at 536.6 eV. The O K-edge spectra of a copper catalyst surface presented in [14] were detected under similar conditions are dominated by an asymmetric maximum at 535.6 eV. To fit these spectra it is necessary to use two Gauss-profiles at 535.6 eV and 537.7 eV. Therefore we propose, the binding energies of these O 1s electrons describe a distribution of locations. This distribution reflects different concentrations and locations of defects in the copper lattice. From the measured gas phase concentrations and suitable integrations of the spectral intensities under the ox and subox peaks a correlation between spectral and catalytic properties is obtained. The error for the determination of the spectral weights is conservatively assumed to be 10% accounting for the uncertainties in the background subtraction and in the large error caused by the subtraction of the gas phase signal (see Figure 1).

In Figure 4a the correlation for the ox peak with the production of CO_2 is presented. The error bars of the normalised integrated intensities given in Figures 4a and 4b indicate the relative error after normalisation with respect to the photon flux, background subtraction and after subtraction of gas phase signal. It occurs that the ox peak describes the species which oxidises methanol to CO_2 as its yield correlates with the consumption of the ox species. The correlation reveals two regimes with strongly different slopes. This reflects the observation that the ox species decreases with increasing temperature up to 570 K (regime of high CO_2 yield) and increases in abundance at higher temperature with a different proportional CO_2 (see Figure 3) increase.

The correlation between the spectral weight of the subox species and the yield of formaldehyde presented in Figure 4b reveals the opposite behaviour to the correlation of Figure 4a. Under steady state conditions the subox species increases in abundance with the yield in the partial oxidation product. This observation and the fact that no organic species is residing on the surface lead to the conclusion that the formation of the subox species is the rate-limiting step in the kinetics of the partial oxidation reaction channel. This implies that the partial oxidation of methanol is an overall fast reaction which is supported by the high yield achieved in a reactor allowing only very short contact times.

The correlations in Figures 4a and b exhibit significant

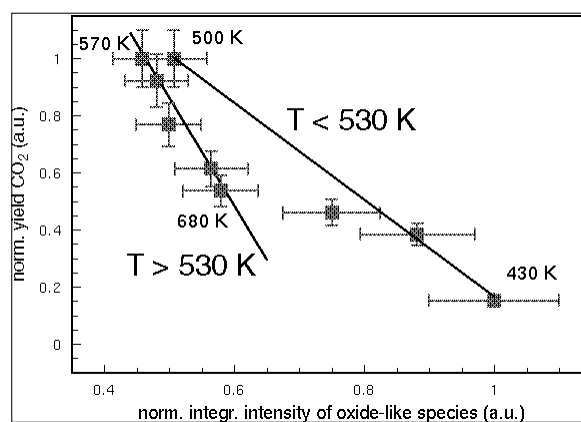


Fig.4a: The normalised yield of carbon dioxide is plotted as a function of the normalised integrated intensity of the copper(I) oxide like species, that is detected in O K-NEXAFS spectra of a copper foil under reaction conditions, shown in Fig.3.

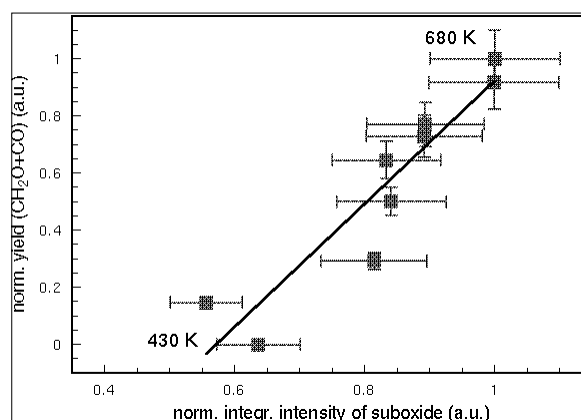


Fig.4b: The normalised yield of formaldehyde is plotted as a function of the normalised integrated intensity of the suboxide detected in O K-NEXAFS spectra of a copper foil under reaction conditions shown in Fig.3. Since formaldehyde decomposes to carbon monoxide, CO has to be considered as a product of partial oxidation.

intercepts with the abscissa. This reflects the different depth of information levels of the two techniques. Catalysis is extremely surface-sensitive. The total yield XAS data on the other hand exhibit a depth of information of more than 10 nm (an accurate determination is difficult due to the thus not only at the surface but also below it in the surface-near bulk, presence of the gas phase). The species ox and subox exist as already mentioned with the change of the spectral shape of the subox species in Figure 3.

Discussion

The clear correlation between the yields of the two reaction pathways total and partial oxidation and the spectral weights of two features in the XAS spectra of the working catalyst established in Figure 4 represents a rare case of an experimentally determined structure-function relationship in heterogeneous catalysis which calls for a more complete

interpretation.

The complex interplay of several processes will be considered separately for the interaction of oxygen with copper and then for the consequences of the presence of methanol. This strategy is taken as the copper-oxygen interaction has been studied extensively in the surface science literature and also in our previous XAS experiments. The surface crystallographic database [20] lists 17 structures of the copper oxygen system. All of them have in common a structural motif which is a copper-oxygen tetrahedron. The oxygen is interacting strongly with the copper atoms as can be derived from the structural model of the Cu (110) + O system [21] shown in Figure 5. The structure representing a $c(6 \times 2)-4O$ superlattice is very similar to the atomic arrangement in the (211) plane of Cu_2O .

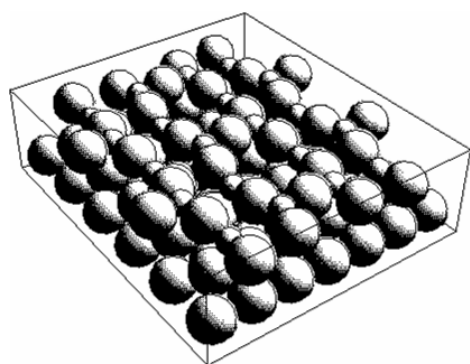


Fig.5: Structural model of the Cu(110) + O system [21]. The structure represents $c(6 \times 2)-4O$ superlattice, which is very similar to the atomic arrangement in the (211) plane of Cu_2O . The system shown in the figure was obtained by exposing the Cu at 573 K to 10000 L of oxygen [21].

The system shown in Figure 5 was obtained by exposing the Cu at 573 K to 10.000 L of oxygen representing conditions comparable to those prevailing in our experiments. The structure in Figure 5 may represent the ox phase in our experiments. This phase is the beginning formation of an oxide starting with a two-dimensional growth of an oxide-like species. The shift in the white line maxima between bulk Cu_2O and the ox phase may be accounted for by the presence of a still metallic substrate in the ox phase. From previous experiments [7,8,17] we know that the ox phase develops into bulk oxide upon sufficient exposure to gas phase oxygen. The chemical bonding of oxygen in the ox phase and in the bulk oxide are similar. It is characterised by a significant rehybridisation between oxygen 2p states and copper d states. For the catalytic function this means facile access to the free electron reservoir of the catalyst which should characterise a strongly oxidising species. This is in line with the total oxidation activity ascribed to these

species.

At the “high” partial pressures used here a further reaction of copper and oxygen is put into action. Oxygen atoms can penetrate through the surface and form sub-surface copper oxygen mixed systems [22]. This process causes defects in the copper lattice, supports the diffusion of copper atoms at low temperatures and favourably contributes to overcome the kinetic barrier of three dimensional oxide growth at low temperatures after complete coverage of the initial metallic surface by the ox phase. The spectroscopic signature of this process is the appearance of the subox signal in the XAS spectra. Its position between the white line of the oxide and the corresponding sigma resonance indicates a qualitatively different chemical bonding for the oxygen in the subox phase than in the ox phase. This can be understood by considering the defective structure resulting from the motion of oxygen atoms through the copper lattice. In the vicinity of oxygen atoms significant distortions of the copper lattice will occur at the surface and in the bulk. Such distortions are known from recent theoretical considerations [13] to greatly affect the metal d-state electronic structure. Hence it is plausible to deduce that the XAS signature of subox stands for oxygen atoms which are only weakly interacting with the distorted copper d-band system. Such a species cannot exist in equilibrium structures and requires observation under in-situ reaction conditions where a significant surface abundance of distorted copper metal sites does exist. For the catalytic function the non-availability of the copper d states for the subox oxygen means that this species is less or not at all oxidising. This species should thus exert only its Brønsted/Lewis basic chemical function arising from the strong electron localisation at the oxygen centre. This would point to a dehydrogenating function with no transfer of the oxygen to carbon atoms as this process requires the exchange of electrons with the catalyst.

In this way the correlation of Figure 4b is well explained. The creation of the basic oxygen located at copper metal defect sites seems to be the rate-limiting step for the partial oxidation leading to the positive slope in this graph. At this point it cannot be excluded that the formation of the copper defects is the relevant elementary step and that oxygen species are activated at these sites which react so quickly with the methanol that their surface abundance is too low for spectroscopic identification. For the total oxidation the availability of free surface sites seems to be involved in the rate-limiting process which leads to the inverse slope in the graph of Figure 4a.

At temperatures between 470 K and 570 K where the copper oxygen interaction leads only to two-dimensional compounds the presence of methanol affects the growth process of the ox phase. This can be seen in the CO_2 evolution of Figure 2 and in the decrease of the ox signal in XAS as seen in Figures 3 and 4a. At this stage methanol prevents the closure of the coverage of copper metal with the ox phase and allows such to expose two types of copper patches to the gas phase. One is covered with the ox phase and the other with the subox phase. The presence of methanol is thus not only moderating the oxidising power of

the oxygen partial pressure over copper; its presence creates at steady state the existence of two chemically different types of surfaces.

The reaction involves two pairs of processes namely the formation of the ox phase and its consumption by the total oxidation and the formation of the subox phase and its action as partial oxidation agent. The increase of temperature at steady state gas feed increases all four processes with, however, different increments. This leads to the complex behaviour seen in Figure 2. Below 500 K all rates are increasing without any experimental discrimination. Between 500 K and 530 K the growth of the ox phase becomes fastest. Above 530 K its consumption by total oxidation wins and the CO₂ production continuously falls. Above 500 K also the partial oxidation yield increases until it reaches saturation which is caused by overloading the number of active sites in the in-situ reactor with methanol.

The inverse slopes of the graphs in Figures 4a and 4b as well as the different temporal evolutions of the yield curves for partial and total oxidation clearly proof the existence of two parallel reaction pathways with two different active site types which we can associate with the subox and ox species identified by XAS.

The changeover in slopes of Figure 4a in the low yield regime which is at temperatures above 600 K (see Figure 2) is caused by an increase in the intensity of the spectral weight of the ox species which is inactive for catalysis. This indicates the beginning of the formation of the 3-dimensional oxide phase. With increasing temperature the formation of subox becomes increasingly faster which is beneficial at the oxide-free patches of the surface for the partial oxidation reaction. At the ox covered patches the formation of bulk oxide is supported by increased mobility of copper migrating to the oxide-metal interface and/or by the oxygen atoms becoming available below the initially formed ox phase.

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Conclusions

In the present study nothing can be said about the dynamic nature of the creation of the two types of surfaces which could be inferred from the oscillatory behaviour of the methanol oxidation process [6] nor can anything be deduced about possible structure sensitivity effects for the oxide and metal surface types.

The experiments have revealed that under practical reaction conditions the oxidation of methanol is kinetically controlled by the interaction of oxygen with the copper catalyst and not by any step involving the presence of chemisorbed methanol. The two reaction pathways of total and partial oxidation can be associated with two oxygen species bound to copper via predominantly d-states (ox) and s-p states (subox). This control of the copper – oxygen interaction is achieved by the action of geometric defects in the copper created by the high-pressure action of oxygen atoms. The catalyst become selective only under the high pressure action of one reactant and the active phase is an intermediate in the oxidation of copper. Under reaction conditions this process cannot be fully suppressed causing a finite selectivity towards total oxidation.

It remains to be seen if under a given oxygen to organic species molar ratio the resulting surface ratio covered with oxide and the subox species can be affected by promoters for which structure-sensitivity of the formation of ox and subox respectively would be a suitable basis.

In situ XAS in the soft X-ray range is a surface sensitive method, that enables the spectroscopic detection of metastable species under reaction conditions. The copper suboxide species is not detectable by ex situ investigations. The simultaneous investigation of the catalytic activity and the electronic structure of the surface allows to identify the relevance of observed species in the heterogeneous catalytic process. Therefore this method allows insight, which can not with other methods.

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