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Probing the electronic structure of an active catalyst surface under high-pressure reaction conditions: the oxidation of methanol over copper

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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

1. Introduction

In the past few years *in situ* techniques have attained great importance in the field of heterogeneous catalysis [1]. 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 [9]:

$$CH_3OH \rightarrow CH_2O + H_2 \quad \text{(dehydrogenation)} \qquad (1)$$

$$2CH_3OH + O_2 \rightarrow 2CH_2O + 2H_2O \quad \text{(oxidative dehydrogenation)} \qquad (2)$$

Formaldehyde decomposes partly on the hot catalyst surface in carbon monoxide and hydrogen [7]

$$CH_2O \rightleftharpoons CO + H_2 \qquad (3)$$

$$CH_3OH + \tfrac{3}{2}O_2 \rightarrow CO_2 + 2H_2O \quad \text{(total oxidation)} \qquad (4)$$

NEXAFS (near-edge X-ray absorption fine structure) spectroscopy in the energy range $250\ \text{eV} \leqslant h\nu \leqslant 1000\ \text{eV}$ applied in the total electron yield mode represents an established, surface sensitive method to investigate the electronic structure of solid state surfaces [2]. The formation of copper suboxides Cu_xO ($2.2 \leqslant x \leqslant 2.7$) was found *ex situ* in UHV after pretreatment with various CH_3OH/O_2 mixtures [4]. 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 [5]. Therefore, an *in situ* investigation, which allows the pressure and coverage gap to be overcome, is required to investigate the catalytically active surface. A new *in situ* was introduced [3]. 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 [6] the formation of Cu_2O and CuO was investigated by detecting *in situ* NEXAFS spectra at the 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.

2. Experimental

The experiments are performed in a new constructed reactor cell [3,6,7]. The used UHV system consists of two stainless-steel chambers. The reactor chamber is mounted via a double flange to an UHV chamber, which is adapted

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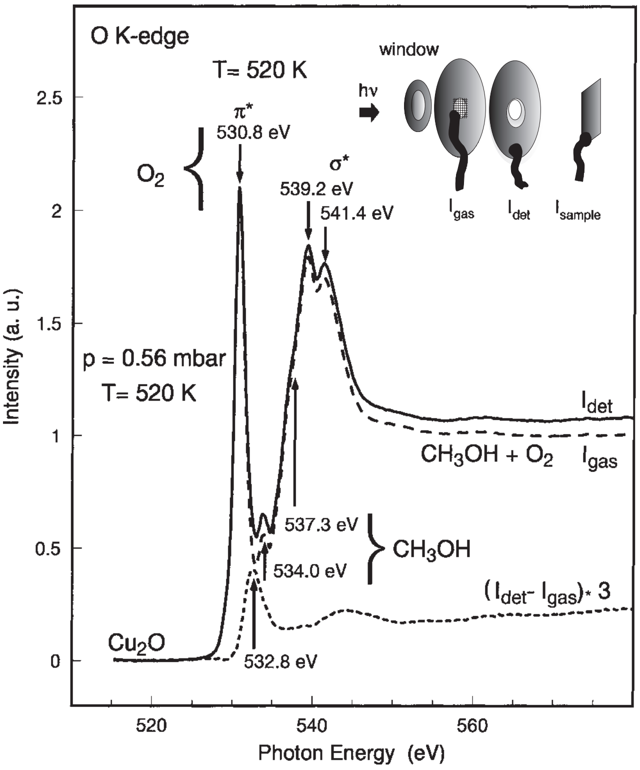

Figure 1. Subtraction of the gas phase from collection plate signal. The pre-edge intensity of both spectra is subtracted. The spectra are normalised to the same intensity of the π^* resonance of molecular oxygen at 531.0 eV [17]. The difference spectra represent the X-ray absorption spectra of the copper catalyst. Under the given conditions it is Cu_2O. The inset shows a schematic drawing of the used detectors mounted in the reaction cell.

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 figure 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 figure 1. The spectra are normalised at the π^* resonance of molecular oxygen at 530.8 eV, after substraction of the pre-edge background [17]. This normalisation makes 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 [22]. 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 [23,24]. 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 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 setup could be reduced to below 10% conversion.

Experiments are carried out at the beamline PM1 [8] 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.

3. Results

The catalytic activity of the copper foil in the *in situ* reactor is demonstrated in figure 2. The yield of carbon dioxide, carbon monoxide, formaldehyde, formaldehyde + carbon monoxide and the conversion of methanol are plotted in figure 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 CO_2 has a maximum around 500 K, whereas the selective oxidation product CH_2O increases continually with the temperature.

Figure 3 shows a plot of a selection of *in situ* NEXAFS spectra of the copper catalyst taken at the oxygen K-edge

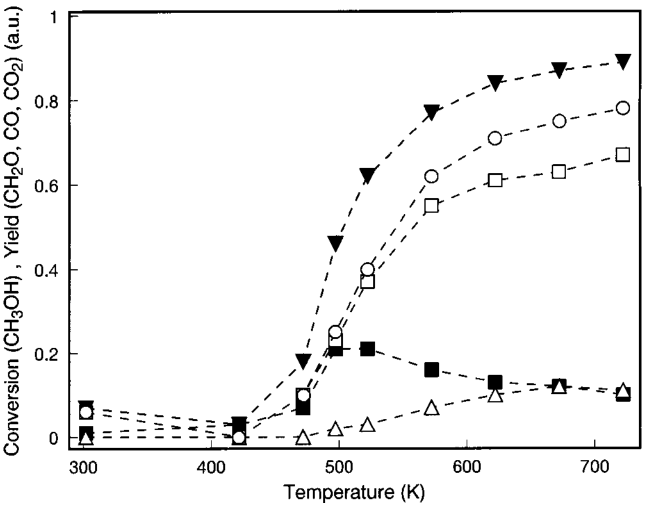

Figure 2. Normalised relative concentration of carbon-containing molecules in the reaction atmosphere of 10 ml/min O_2 + 20 ml/min CH_3OH as a function of catalyst temperature estimated by mass spectra. The yield of carbon dioxide (■), carbon monoxide (△), formaldehyde (□), carbon monoxide + formaldehyde (○) and the conversion of methanol (▼) are plotted in the figure.

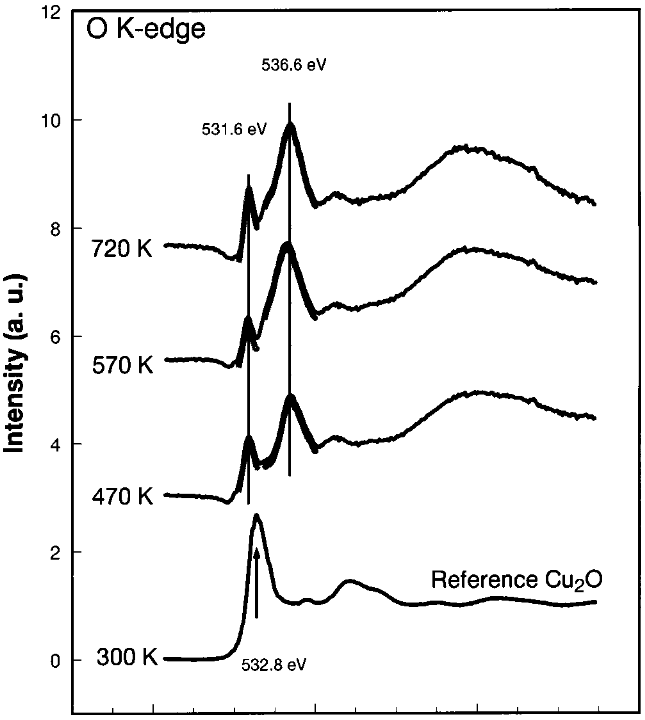

Figure 3. Temperature dependence of *in situ* X-ray absorption spectra of a copper foil at the oxygen K-edge in 10 ml/min O_2 + 20 ml/min CH_3OH at $p = 0.64$ mbar. A reference spectrum of Cu_2O is plotted at the bottom of the figure.

after subtraction of the gas phase signal. A gas flow ratio $CH_3OH/O_2 = 2:1$ is used. The catalyst temperature is increased stepwise from 470 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 and 536.6 eV. For comparison the O K-edge absorption spectrum of Cu_2O is plotted in figure 3. The maximum at 531.6 eV (ox) energically coincidences mostly with the whiteline of Cu_2O at 532.8 eV, assigned to antibonding $O_{2p}Cu_{3d}$ states and even the shape of the feature is similar to the $O_{2p}Cu_{3d}$ state in the Cu_2O reference spectrum [14,15]. The reference spectrum shows additional weak maxima at 539 and 545 eV. These structures are assigned to $O_{2p}Cu_{4sp}$ states [14–16]. The broad peak at 536.6 eV (subox) cannot 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. CH_3OH shows two strong resonances in the X-ray absorption spectrum at the O K-edge at 534.1 and 537.3 eV [25]. 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 CH_3OH 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 CH_3OH are increasing upon increasing temperature, the maximum at 536.6 eV cannot be explained by a gas phase artefact.

Figure 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 both these oxygen species is 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 for a spectroscopical identification of an intermediate in the O and C K-edge spectra. The energy position of the π^* and σ^* resonances of HCO_2/Cu(100) is 535.5 and 545.5 eV, respectively [11]. The energy position of the σ^* resonance of CH_3O/Cu(100) of 539 eV and a low intense feature at 534 eV given by Outka et al. does not fit to the energies we find [11]. These energies do not fit to the energy positions of both species found in this work. Amemiya et al. measured NEXAFS spectra of CH_3O/Cu(111) [18]. They found features at 531.5, 536.5 and 538.5 eV. The features at 531.5 and 536.5 eV coincidence with the copper(I) oxide-like and the novel suboxide species found in this work, respectively. The shape of the spectrum in [18] is different and we do not find a feature at 538.5 eV in this work. In contrast, an independent behaviour of both species cannot be explained by one intermediate, because the consumption of the active phase causes reduced intensities of the π^* and σ^* resonances.

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 figure 3 are fitted by a Gauss profile at 536.6 eV. The O K-edge spectra of a copper catalyst surface presented in [13] that were detected under similar conditions are dominated by an asymmetric maximum at 535.6 eV. To fit these spectra it is nessecary to use two Gauss profiles at 535.6 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 4(a) the correlation for the ox peak with the production of CO_2 is presented. The error bars of the normalised integrated intensities given in figure 4 (a) and (b) 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 4(b) reveals the opposite behaviour to the correlation of figure 4(a). 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 figure 4 (a) and (b) exhibit significant 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, exhibits a depth of information of more than 10 nm (an accurate determination is difficult due to the presence of the gas phase). The species ox and subox exist thus not only at the surface but also below it in the surface-near bulk, as already mentioned with the change of the spectral shape of the subox species in figure 3.

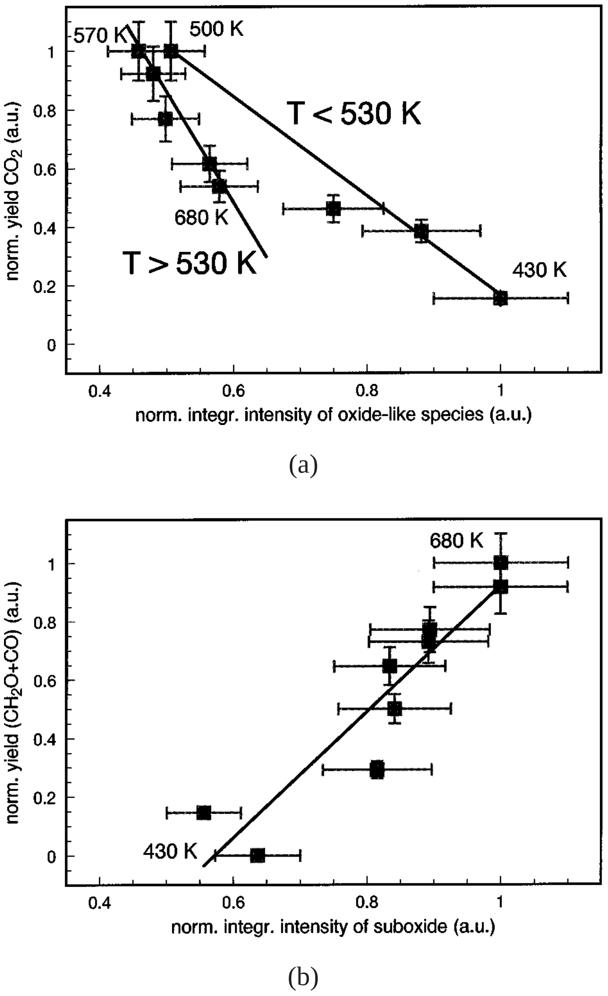

Figure 4. (a) The normalised yield of carbon dioxide is plotted as a function of the normalised integrated intensity of the copper(I) oxide like species that is detected in O K-NEXAFS spectra of a copper foil in 10 ml/min O_2 + 20 ml/min CH_3OH at $p = 0.64$ mbar. (b) The normalised yield of formaldehyde is plotted as a function of the normalised integrated intensity of the suboxide detected in O K-NEXAFS spectra of a copper foil in 10 ml/min O_2 + 20 ml/min CH_3OH at $p = 0.64$ mbar. Since formaldehyde decomposes to carbon monoxide, CO has to be considered as a product of partial oxidation.

4. 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 [19] lists 17 structures of the copper–oxygen system. All of them have in common a structural

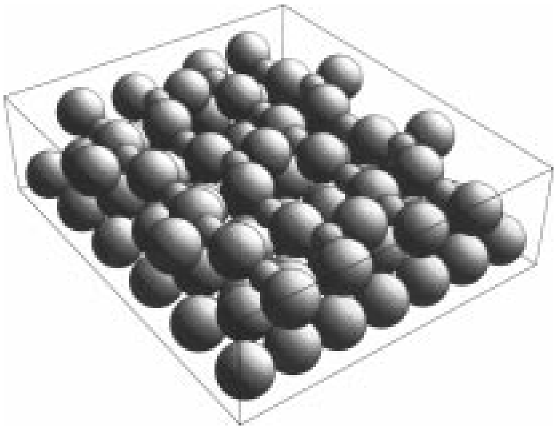

Figure 5. Structural model of the Cu(110) + O system [20]. The structure represents a c(6 × 2)-4O superlattice, which is very similar to the atomic arrangement in the (211) plane of Cu_2O. The system shown in the figure was obtained by exposing the Cu at 573 K to 10 000 L of oxygen [20].

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 [20] shown in figure 5. The structure representing a c(6 × 2)-4O superlattice is very similar to the atomic arrangement in the (211) plane of Cu_2O.

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 [6,7,16] 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 subsurface copper–oxygen mixed systems [21]. 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 [12] 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 4(b) 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 4(a).

At temperatures between 470 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 4(a). At this stage methanol prevents the closure of the coverage of copper metal with the ox phase and such allows two types of copper patches to be exposed to the gas phase. One is covered with the ox phase and the other with the subox phase. The presence of methanol thus not only moderates 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 increase without any experimental discrimination. Between 500 and 530 K the growth of the ox phase becomes fastest. Above 530 K its consumption by total oxidation wins and the CO_2

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 figure 4 (a) and (b) 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 4(a) 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 three-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.

5. 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 [5] 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 becomes 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, respecively, 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 metastabile 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 one to identify the relevance of observed species in the heterogeneous catalytic process. Therefore, this method allows insight, which cannot be reached with other methods.

References

[1] R. Burch, ed., *In Situ Methods in Catalysis*, Catal. Today 9 (1991).
[2] J. Stöhr, *NEXAFS Spectroscopy*, Springer Series in Surface Science, Vol. 25 (Springer, Berlin, 1992).
[3] A. Knop-Gericke, M. Hävecker, T. Neisius and T. Schedel-Niedrig, Nucl. Instrum. Methods A 406 (1998) 311.
[4] T. Neisius, Ph.D. thesis, Technical University of Berlin (1997).
[5] H. Werner, D. Herein, G. Schulz, U. Wild and R. Schlögl, Catal. Lett. 49 (1997) 109.
[6] M. Hävecker, A. Knop-Gericke, T. Schedel-Niedrig and R. Schlögl, Angew. Chem. 110 (1998) 2049; Angew. Chem. Int. Ed. Engl. 37 (1998) 1939.
[7] M. Hävecker, A. Knop-Gericke and T. Schedel-Niedrig, Appl. Surf. Sci. 142 (1999) 438.
[8] H. Petersen, Opt. Commun. 40 (1982) 402.
[9] E. Jones and G. Fowlie, J. Appl. Chem. 3 (1953) 206.
[10] *Ullmann, Encyclopedia of Industrial Chemistry*, Vol. 11 (Verlag Chemie, Weinheim, 1982) p. 687.
[11] D.A. Outka, R.J. Madix and J. Stöhr, Surf. Sci. 164 (1985) 235.
[12] M. Mavrikakis, B. Hammer and J.K. Nørskov, Phys. Rev. Lett. 81 (1998) 2819.
[13] T. Schedel-Niedrig, A. Knop-Gericke, M. Hävecker and R. Schlögl, submitted.
[14] T. Schedel-Niedrig, X. Bao, M. Muhler and R. Schlögl, Ber. Bunsenges. Phys. Chem. 101 (1997) 994.
[15] F. de Groot, M. Grioni, J. Fuggle, J. Ghijsen, G. Sawatzky and H. Petersen, Phys. Rev. B 40 (1989) 5715.
[16] T. Neisius, I. Böttger, E. Kitzelmann, D. Demuth, G. Weinberg, T. Schedel-Niedrig and R. Schlögl, Phys. Chem. Chem. Phys., accepted.
[17] Y. Ma, C.T. Chen, G. Meigs, K. Randall and F. Sette, Phys. Rev. A 44 (1991) 1848.
[18] K. Amemiya, Y. Kitajima, Y. Yonamoto, S. Terada, H. Tsukabayashi, T. Yokoyama and T. Ohta, Phys. Rev. B 59 (1999) 2307.
[19] P.R. Watson, M.A. van Hove and K. Hermann, SSD database NIST database 42, v. 3.0.
[20] W. Liu, K.C. Wong and K.A.R. Mitchell, Surf. Sci. 339 (1995) 151.
[21] R. Schmid, Metall. Mater. Trans. 14 (1983) 473.
[22] G. Ertl, Surf. Sci. 6 (1967) 208.
[23] R.D. Leapman, L.A. Grunes and P.L. Fejes, Phys. Rev. B 26 (1982) 614.
[24] M. Grioni, J.F. van Acker, M.T. Czyzyk and J.C. Fuggle, Phys. Rev. B 45 (1992) 330.
[25] I. Ishii and A.P. Hitchcock, J. Electron. Spectrosc. 46 (1988) 55.