Partial methanol oxidation over copper: Active sites observed by means of *in situ* X-ray absorption spectroscopy

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Polycrystalline copper is investigated by a new surface sensitive *in situ* X-ray absorption spectroscopy method at the oxygen K-edge and copper $L_{2,3}$-edges under, for the first time, dynamic steady-state methanol-oxidation reaction conditions close to those used in practice. It is found that the selective oxidation of methanol to formaldehyde is catalyzed by a copper suboxide phase with a stoichiometry of $Cu_{(x \geqslant 10)}O$. The product gas-phase composition is monitored simultaneously during the gas/solid reaction by using X-ray absorption and conventional mass spectroscopy. Novel atomic oxygen species are observed at the copper surface and sub-/near-surface region under reaction conditions characterized by a chemical bonding that is significantly different from copper (sub) oxides found in the *ex situ* spectroscopic analysis which contain oxygen atoms interacting strongly with copper 3d states. The abundance of the novel oxygen species is quantitatively correlated with the catalyst activity for the selective oxidation of methanol to formaldehyde. Conclusions are reached about the chemical composition of the active sites for the selective and total oxidation, respectively.

1. Introduction

In situ investigations of heterogeneous catalysts under realistic reaction conditions are necessary since the surface and bulk structures of catalysts can be very different from those found post mortem or *ex situ*. An *in situ* study requires, for any relevant interpretation, the simultaneous detection of spectroscopic data together with the recording of the conversion from the gas phase. The active oxygen species at a copper surface is thermodynamically metastable towards the transition into a (sub-) oxide state. Although treatment under reaction conditions has been performed in the preparation chambers of photoemission and X-ray absorption experimentally, *ex situ* spectroscopic analysis under ultra-high vacuum (UHV) conditions was found to be hampered by the formation of stable oxides, Cu_2O, and, $Cu_{(x \geqslant 2.5)}O$.[1,2] The substoichiometric phase of $Cu_{(x \geqslant 2.5)}O$ revealed a similar electronic structure to that of the copper(I) oxide phase. Both phases cause the total oxidation of methanol to carbon dioxide and water and, hence, cannot be the active phase of the partial methanol oxidation to formaldehyde.[3] To search for the species causing the partial oxidation of methanol we devised an *in situ* X-ray absorption experiment allowing spectroscopic characterization of oxygen and copper bonding states during catalytic action.

A new total-electron yield (TEY) detector system was constructed for *in situ* X-ray absorption spectroscopy (XAS) studies in the soft X-ray range of $250 \leqslant h\nu/\text{eV} \leqslant 1000$ at conditions close to those used in practice (up to 20 mbar total pressure and up to 1000 K reaction temperature).[4] The reactor cell is equipped with a TEY detector system in order to collect simultaneously XA spectra of the gas phase and the solid sample. Furthermore, the investigations can be performed under either static or dynamical reaction conditions.

In situ XA spectra measured during the reaction of polycrystalline copper with oxygen at 600 K have shown that the formation of Cu_2O and CuO occurred at the (near-) surface region at a total O_2 pressure of 0.05 and 0.10 mbar, respectively.[4] The considerably different oxides obtained under reaction conditions which are only minimally different illustrate the high sensitivity of the system with respect to the exterior reaction conditions and confirm the specificity of the new surface-sensitive *in situ* XAS measurement technique. Surface-sensitive measurements performed at the oxygen K-edge and the copper $L_{2,3}$-edges during the reduction of polycrystalline copper(II) oxide with methanol (total pressure 5×10^{-6} mbar) at 600 K indicate the formation of Cu_2O after about 10 min (total methanol dose ∼3000 L; 1 L = 1.33×10^{-6} mbar s (=1×10^{-6} Torr s)). Subsequent reduction occurs after about 190 min. The reduced phase is characterized by the formation of an oxygen–copper phase at the surface and sub/near-surface region very different from the copper(I) and copper(II) oxide phases.[4] The oxygen of this suboxide does not correspond to either Cu_2O or CuO and is characterized by a dominant covalent O 2p–Cu 4sp bonding contribution in the oxygen K-edge spectra. In contrast, the copper $L_{2,3}$-edge spectra of the suboxide phase show the steplike shape of the absorption edge typical for metallic copper.[4] According to *ex situ* studies on this system, however, Cu_2O is formed on the transition to UHV with simultaneous cooling to room temperature.[1,2,4] This means that it is only possible to observe the special copper suboxide phase under reaction conditions during the treatment with methanol, as it is metastable and segregates into pure metal and copper(I) oxide on cooling and removal of the volatile components.[3] The significance of the suboxide phase in practice for the partial oxidation was indicated by an analysis of the oscillatory behaviour of the $Cu/O/CH_3OH$ system.[5]

In hydrocarbon oxidation processes thermodynamics favours the ultimate formation of carbon dioxide and water (total oxidation: see Table 1, eqn. (1) and (2)). Therefore, all products of partial oxidation are derived by kinetic control of

Table 1 Reaction enthalpies for gaseous reactants at 300 K (standard conditions)[10,11]

Reaction		ΔH_r/kJ mol^{-1}
(1) $CH_3OH + 3/2\ O_2 \leftrightarrow CO_2 + 2H_2O$	Total oxidation	−674
(2) $CH_2O + O_2 \leftrightarrow CO_2 + H_2O$	Total oxidation	−519.4
(3) $CH_3OH + \frac{1}{2}O_2 \leftrightarrow CH_2O + H_2O$	Oxidative dehydrogenation	−156.6
(4) $CH_3OH \leftrightarrow CH_2O + H_2$	Dehydrogenation	+85.3
(5) $CH_2O \leftrightarrow CO + H_2$	Decomposition	+12.5

the reaction. All oxidation processes are strongly exothermic and efficient heat removal must be ensured to control the temperature and prevent over-oxidation, the appearance of hot spots and catalyst damage.[6] Thus, oxidation of hydrocarbon molecules proceeds as a multistep process, consisting of consecutive abstractions of hydrogen atoms and addition of oxygen atoms. If conditions exist for the abstraction of a hydrogen atom to be followed by abstraction of the second hydrogen atom and desorption of water, a new C bond to oxygen can be formed. Such reactions are known as oxidative dehydrogenation (see Table 1, eqn. (3)). The first steps in the oxidative dehydrogenation are endothermal dehydrogenation reactions (see Table 1, eqn. (4)). The role of pre-adsorbed oxygen is also of significance since no detectable reaction between methanol and the copper surface has been observed by means of surface science. The ability of copper[7,8] and silver[9] to adsorb methanol dissociatively was found to be greatly enhanced by the presence of adsorbed oxygen species (O–*). This is called "oxygen-induced adsorption" by Madix.[7] Oxygen atoms adsorbed on Ag surfaces are identified as strong Brønsted bases (proton acceptors) acting as nucleophilic species. The adsorbed oxygen species is thus able to activate heterolytically both O–H bonds necessary for the creation of the methoxy species, and C–H bonds, leading to compounds with double bonds between carbon and oxygen. The endothermicity of the dehydrogenation is overcompensated by the heat of H_2O formation as demonstrated for the formation of formaldehyde from methanol in Table 1.[9]

This paper decribes now a detailed study of the spectral features of the reacting catalyst under a variety of reaction conditions. Further, it gives an assignment of the various spectral features observed and describes a model of the active sites for the two pathways of oxidation catalysis by copper.

2. Experimental details

The experiments were carried out at the beamline HE-TGM1 at the Berliner Synchrotron Radiation source BESSY-I with an electron beam energy of 0.8 GeV. A toroidal grating monochromator equipped with two gratings (1100 mm^{-1} and 1500 mm^{-1}) was used;[12] it was operated at a resolution of 1.6 eV at the O K-edge determined by the full width at half maximum of the O K-absorption edge π^* resonance of molecular oxygen. The photon energy was calibrated to an accuracy of ± 0.3 eV by reference to the O K-edge π^* resonance at 530.8 eV of molecular oxygen. The XAS studies were performed with the 1100 mm^{-1} grating in the photon energy range of $250 \leqslant h\nu/\text{eV} \leqslant 1000$. Measurements were carried out on polycrystalline copper surfaces (Goodfellow, 99.95%) which were cleaned in the reactor chamber by exposure to a He–H$_2$ (98% : 2%) gas mixture at 10 mbar at 600 K. This process was repeated until no carbon and oxygen contamination could be detected by XAS. Oxygen with purity of 99.998% was supplied by Linde and methanol (p.a.) was supplied by Merck.

The Cu L$_{2,3}$-edge spectra were measured by using the second-order light of the monochromator in order to enhance the experimental energy resolution. The spectra were divided by the I_0 signal collected with the (TEY) collection grid. For

details concerning the reactor see ref. 4. The raw XAS data of the Cu L$_{2,3}$-edge are treated as follows: In order to avoid problems with artifacts arising from carbon, nitrogen and oxygen spectral features mainly from the X-ray window and, additionally, from the optical components of the beamline, the spectra accumulated with the TEY collecting plate (signal I_2) and with the sample current (signal I_3) in the reactor are divided by the signal I_1 of the TEY collection grid measured under vacuum or inert gas-phase conditions. The X-ray absorption edge jumps are subsequently normalized after background subtraction. The photon energy is calibrated using the references CuO, Cu$_2$O, the clean copper metal as well as O$_2$, CO, and CO$_2$ gases. The energy values are defined as taking the lowest, sharp and strongest Cu 2p → Cu 3d transition at 931.3 and 933.7 eV, respectively, of the oxides from the *in situ* prepared copper oxide reference XAS data and the energy position of the Cu metal absorption edge (inflection point: 932.5 eV).

The oxygen K-edge spectra are treated in the following way. The spectra are divided by a signal detected under vacuum or inert gas-phase condition in order to deduce the ratio I/I_0. After background subtraction the edge jumps of the spectra are normalized. The photon energy is calibrated using molecular oxygen by taking the value of the lowest, sharp and strongest energy O 1s → π^* resonance at 530.8 eV of molecular oxygen.

The gas-phase spectra accumulated with the TEY collection grid, I_1, are divided by the signal I_0 of the TEY collection grid which is subsequently detected in the reactor under UHV conditions. The sharpest π^*-transitions of the CO and CO$_2$ gas-phase spectra of the carbon K-edge at 287.3 and 290.7 eV serve as energy calibration points. The mentioned TEY signals of the grid, the collector plate, and the sample were measured simultaneously and independently from each other.

A gas station is mounted on the reactor in order to flood the reactor (volume of ∼4 l; batch reactor mode) with reactants such as O$_2$, He, Ar, CH$_3$OH or, alternatively, to produce a gas flow by using gas flow controllers (flow reactor mode). A wide-range pressure detector equipped with a Bayard–Alpert ion gauge head and a cold anode is used to control the total gas pressure in the reactor. The turbomolecular pumping unit can be separated from the reactor *via* a gate valve during the batch or flow reaction studies.

3. Results

3.1 Conversion experiments

Studies on catalytically active copper catalyst surfaces by means of *in situ* XAS spectroscopy are not restricted to static reaction conditions (batch mode) but are also possible under dynamic reaction conditions (flow mode) close to those used in practice. The dynamic steady-state methanol-oxidation reaction over copper allows detection of the gas-phase products during the gas/copper surface reaction where a defined gas mixture flows over the catalyst surface. Typical gas flow rates are within the range 30 to 40 ml min^{-1}, the catalyst surface exposed was about 1 cm^2 of non-porous metal. One advantage of the flow mode over the batch mode is that one can rapidly change the gas-phase composition in order to

study the change in the turnover frequency (TOF) and selectivity at constant catalyst temperature without exchanging the whole gas volume in the reactor. A change in the gas-phase composition was detected by means of MS and XAS after 30 s on average. The conversion values of methanol and oxygen are calculated by subtraction of the educt molecule concentration and its concentration after reaction and subsequent division by the educt molecule concentration. Yield data of carbon-containing species are obtained from the concentration of a product molecule divided by the educt concentration of methanol molecules.

The catalytic behaviour of copper metal under conditions of only wall-reactions which simulate the kinetic boundary conditions of the XAS reactor, is revealed in a reference experiment described in Fig. 1. A copper tubing spiral (id 2 mm) was heated externally and used as a tubular reactor for a temperature-programmed reaction (TPR) experiment at atmospheric pressure. Fig. 1 shows the second ramp after an initial ramp intended to clean the wall of the tubing. Between 500 and 550 K a "pre-activity" can be seen. The start of activity is the evolution of carbon dioxide and this is followed by evolution of formaldehyde. This split reactivity is seen as an indication of the co-existence of a small amount of highly reactive sites and a large amount of moderately reactive sites. Both are present in their oxidized and hence inactive form and need pre-reduction under evolution of carbon dioxide before the selective oxidation activity starts. No CO was detected in the temperature regime of the experiment, which is an indication of the absence of after-reactions in the empty tube and which classifies the eventual detection of CO from the XAS reactor as an artefact. The reactor experiments showed that the maximum activity for methanol oxidation is reached at a stoichometric $1:1$ composition of oxygen and methanol. The maximum yield for formaldehyde is, however, reached under more reducing conditions closer to the $3:1$ stoichiometry of the XAS experiments. In principle, it has been found that the selectivity of the methanol-to-formaldehyde reaction increases with decreasing oxygen concentrations in the educt gas composition at a constant methanol conversion.[3,5]

A typical gas-phase XA spectrum of the carbon K-edge detected under dynamic reaction conditions with the TEY collection grid is shown in Fig. 2(a). In order to deconvolute the gas-phase spectrum into its constituent gas-phase components, the gas-phase spectra of pure methanol, (b), carbon monoxide, (c), carbon dioxide, (d), and formaldehyde, (e), were measured for reference and for calibration in the reactor and are shown in the figure as dots. The gas-phase spectrum of the carbon K-edge obtained under dynamic reaction conditions
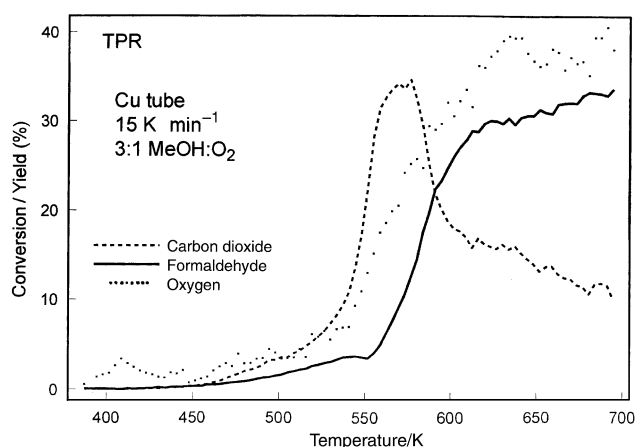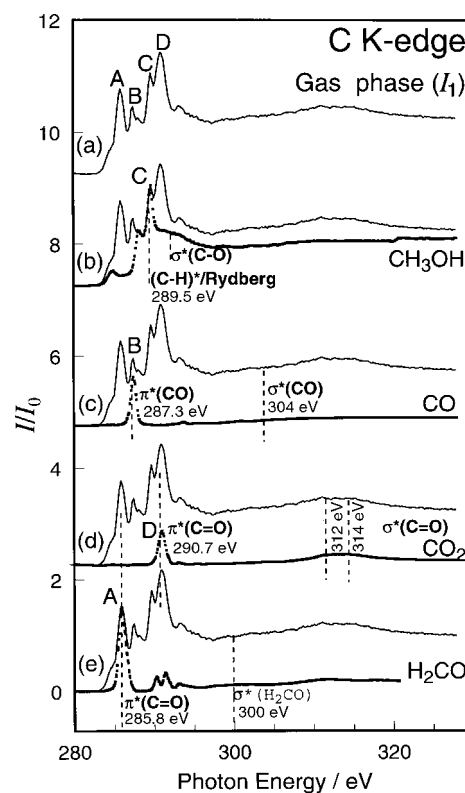
Fig. 2 (a) Gas-phase XA spectrum of the carbon K-edge detected under steady-state dynamic reaction conditions (reactor pressure: 0.6 mbar) with the TEY collection grid. In order to deconvolute the gas-phase spectrum into its constituent gas-phase components, the gas phase spectra of pure methanol, (b), of carbon monoxide, (c), of carbon dioxide, (d), and formaldehyde, (e), are also measured in the reactor at a pressure of 0.2 mbar. Spectrum (a) is superimposed over the reference data in (b)–(e).

consists of methanol, carbon monoxide, carbon dioxide and formaldehyde. The separation of the complex gas-phase spectrum into its components is possible due to the existence of non-overlapping and characteristic features in each component spectrum. The sharp, strong feature A at 285.8 eV corresponds to the $C1s \rightarrow \pi^*(C=O)$ transition of formaldehyde,[13] while the peak B at 287.3 eV is primarily assigned to the π^*-resonance of carbon monoxide.[14] The features C and D at 289.5 and 290.7 eV, respectively, arise from the transition of a C 1s electron into the unoccupied $(C-H)^*$/Rydberg-state of methanol[15] and into the unoccupied $\pi^*(C=O)$-orbital of carbon dioxide,[16] respectively.

The relative contributions of the distinct gas-phase species are obtained by determining the spectral proportion of each gas-phase species to the total gas-phase spectrum (a) that is reflected in its absorption edge height. The corresponding gas-phase spectrum at the oxygen K-edges exhibits, additionally, the contributions from molecular oxygen and from water to the total gas phase (not shown) and, thus, is more difficult to deconvolute into its constituent gas-phase components. Therefore, the simultaneously detected mass spectrometer data are used here to determine the oxygen and water proportions in the total gas phase.

The steady-state oxidation of methanol during the exposure of polycrystalline copper to a methanol–oxygen gas-flow for at least 30 min at each desired temperature is monitored by determining the contributions of formaldehyde, carbon monoxide, carbon dioxide and methanol molecules in the gas phase by means of gas-phase XAS- and MS-analysis. Additionally, the contributions of water and oxygen molecules in the gas flux are detected with MS. Carbon monoxide molecules are formed by partial decomposition of the created

Fig. 1 TPR spectroscopy of copper tubing spiral (id 2 mm) under methanol and oxygen (3 : 1) at atmospheric pressure. The conversion of oxygen (···) is given together with the yield of carbon dioxide (– – –) and formaldehyde (——) as a function of temperature.

formaldehyde molecules in consecutive reactions to CO and H_2 (see Table 1, eqn. (5)).[17]

It is found, by means of *in situ* XAS under varying oxygen concentrations (4 to 20 ml min^{-1} O_2 and 40 ml min^{-1} methanol), that the selectivity towards formaldehyde increases with decreasing oxygen proportion in the gas flow at a constant methanol conversion of about 90%.[3] Therefore, the results of the formaldehyde formation presented here are obtained under conditions of ($CH_3OH : O_2$ 3 : 1) at a total pressure of 0.6 mbar. This low pressure was chosen to optimize the detection of the surface species in the very intense gas-phase oxygen K-edge spectrum.

Fig. 3 shows the steady-state methanol conversion at catalyst temperatures in the range 300–730 K under dynamic reaction conditions obtained by XAS and MS gas-phase analysis, respectively. MS and XAS data are collected simultaneously during the steady-state methanol conversion reaction. The figure shows the conversion of methanol and oxygen to formaldehyde, carbon monoxide, carbon dioxide, and water at a total pressure of ∼0.6 mbar as a function of the catalyst temperature (as indicated on the abscissa). The sum of the relative concentrations of the carbon-containing products, formaldehyde, CH_2O, carbon monoxide, CO, and dioxide, CO_2, is equal to the relative concentration of the converted methanol, CH_3OH (carbon balance).

It is found, irrespective of the method used (XAS or MS) that about 55(5)% of the methanol molecules (*i.e.* ∼22 ml min^{-1} of 40 ml min^{-1}) and also 55(5)% of the oxygen molecules (*i.e.* ∼7 ml min^{-1} of 13 ml min^{-1}) are converted within the methanol–oxygen flux at a catalyst temperature of 730 K. The value in parentheses is the estimated uncertainty in the determination of the relative proportion. Turn-over-frequencies of 0.15 ($\pm$0.02) and 0.28 ($\pm$0.03) methanol molecules per second and per surface copper atom are determined for 570 and 730 K catalyst temperature, respectively, by analysis of the MS and XAS data which are in the range of heterogeneously catalyzed conversion reactions of small molecules.[18]

The main reaction channels of dehydrogenation (Table 1, eqn. 4), oxidative dehydrogenation (Table 1, eqn. 3), total oxidation (Table 1, eqn. (1) and (2)) and formaldehyde decomposition (Table 1, eqn. 5) can be followed with the simultaneous detection of formaldehyde, carbon monoxide, and carbon dioxide as shown in Fig. 3. At about 490 K catalyst tem-

perature, it is observed that the methanol oxidation reaction starts and the major product is carbon dioxide, as shown in Fig. 1. This should be also valid for the data given in Fig. 3, since the absolute error in the formaldehyde detection at this temperature is higher than for CO_2.

At 570 K catalyst temperature, one observes, with XAS gas analysis, that the conversion of methanol and oxygen is enhanced to ∼30% (∼12 ml min^{-1}) and ∼50% (∼6.5 ml min^{-1}), respectively, and carbon dioxide, carbon monoxide, formaldehyde, and water are the products. A stoichiometric ratio of the converted methanol and oxygen gas proportions of about 1.9 : 1 is detected which might indicate that the oxidative dehydrogenation of methanol is the main reaction channel.
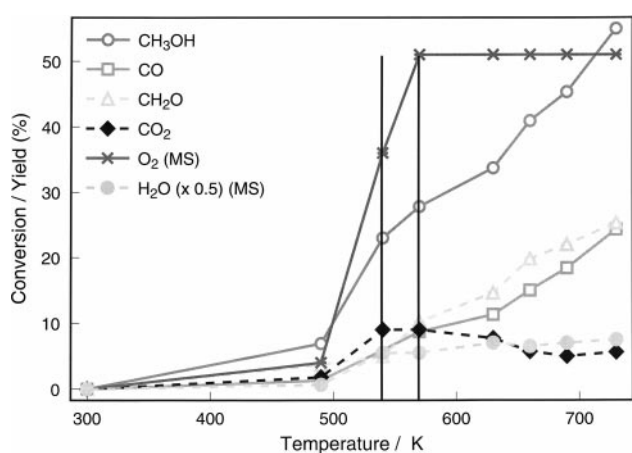
It is noted that the methanol conversion at 570 K is somewhat higher and, additionally, that the relative proportions of formaldehyde and carbon dioxide are higher, by comparing with the corresponding MS data (not shown). Furthermore, carbon monoxide is detected by XAS in the product gas flow. The enhanced relative CO_2 proportion detected by MS can be due to a subsequent total oxidation of carbon monoxide and methanol, at the filament of the quadrupole mass spectrometer, to carbon dioxide and water. This shows that gasphase XAS is, after suitable calibration, a more reliable tool for *in situ* conversion analysis than MS which exhibits problems with artefact reactions at its hot filament.

The increase in the catalyst temperature from 570 to 730 K leads to an increase in methanol conversion within the methanol–oxygen gas flow. The methanol conversion changes from ∼30% (∼12 ml min^{-1}) at 570 K to ∼50% (∼20 ml min^{-1}) at 730 K while the corresponding oxygen conversion remains almost constant at 50% (∼6.5 ml min^{-1}). This points to an enhancement of the dehydrogenation reaction rate at higher temperatures where the oxygen molecules will not be converted. Simultaneously, it is observed that the relative volume proportion of formaldehyde increases from 10% to 25% (the relative carbon monoxide proportion increases continuously from 10% at 570 K to a maximum of 25% at 730 K, indicative of enhanced formaldehyde decomposition at the hot surfaces of the reactor) while the monitored relative volume proportion of carbon dioxide in the product gas flux decreases continuously from ∼10% to ∼5%. The relative volume proportion of water in the product gas flux determined by MS analysis remains almost constant at ∼15%.
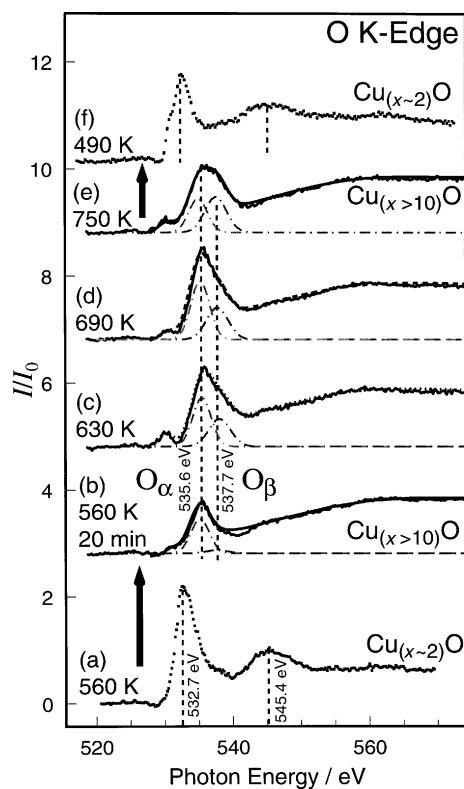
Thus, it is found that, upon increasing the catalyst temperature above 570 K, the selectivity of the total methanol oxidation reaction rate decreases while, simultaneously, the selectivity of the partial methanol oxidation rates increases drastically. Furthermore, the increased relative volume proportion of formaldehyde is not correlated with an appropriate increment in the relative volume proportion of water in the product gas stream, which may indicate that both partial oxidation routes, the oxidative dehydrogenation and, additionally, the dehydrogenation reaction, are catalyzed over copper at catalysts temperatures above 570 K.

Fig. 3 Catalytic oxidation of methanol to formaldehyde on polycrystalline copper was followed *in situ* in a flow reactor by means of XAS and MS. The copper catalyst was exposed to a methanol–oxygen-gas flux (volume ratio ∼3 : 1; total flux: ∼53 ml min^{-1}) at different catalyst temperatures under steady-state reaction conditions. The diagram shows the conversion of methanol (○) and oxygen (×) and the yield of formaldehyde (△), carbon monoxide (□), carbon dioxide (◆), and water (●) at a total pressure of ∼0.6 mbar as a function of the catalyst temperature (as indicated on the abscissa).

3.2 Surface spectroscopy

The oxygen K- and copper $L_{2,3}$-edge XAS data of the catalyst (sub/near-) surface region at various temperatures are shown in Fig. 4 and 5, respectively. These spectra have been collected under the same reaction conditions, either simultaneously (at the oxygen K-edge) or subsequently (at the carbon K- and copper $L_{2,3}$-edges) as the data shown in Fig. 3. At low temperatures up to about 560 K, XA spectra typical of copper(I) oxide are detected (Fig. 4(a) and (f) and Fig. 5(a)). It is seen that the spectral shapes of the XAS edges shown in Fig. 4(b) and Fig. 5(b) change drastically at a catalyst temperature of 560 K under steady-state reaction conditions, indicative of a

Fig. 4 The oxygen K-edge XAS data of the catalyst surface and sub/near-surface region are shown for different catalyst temperatures as indicated. The copper catalyst is exposed to a methanol–oxygen-gas flux (volume ratio $\sim 3:1$; total flux: ~ 53 ml min^{-1}) at different catalyst temperatures under steady-state reaction conditions. The intensities of both oxygen species, O_α and O_β, are determined by fitting each species with Gaussian broadened Lorentzians as shown in (b)–(e).
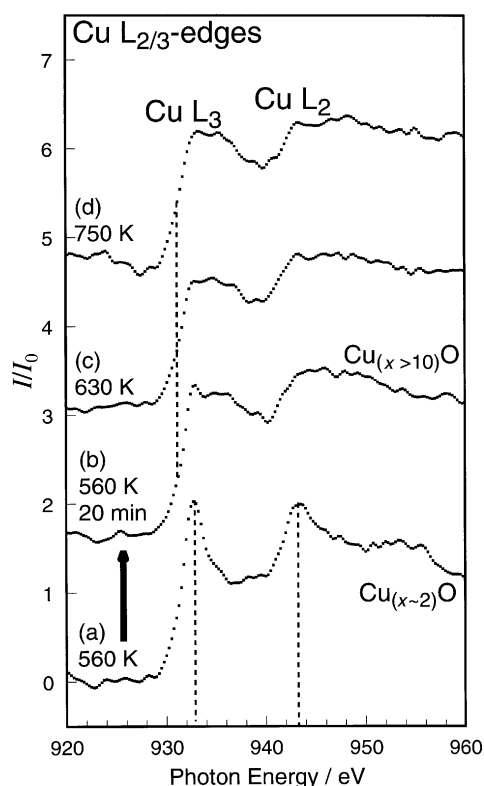
Fig. 5 The copper $L_{2,3}$-edge XAS data of the catalyst surface and sub/near-surface region are shown for different catalyst temperatures as indicated. The copper catalyst is exposed to a methanol–oxygen-gas flux (volume ratio $\sim 3:1$; total flux: ~ 53 ml min^{-1}) at different catalyst temperatures under steady-state reaction conditions. The spectra were recorded by using the second-order light of the monochromator and were subsequently shifted by 467 eV.

copper(I)-to-copper suboxide phase transition within a few tens of minutes. Only a small contribution of Cu_2O can be observed at 560 K in Fig. 5(b) due to the presence of a low-intensity peak at about 933 eV, disappearing at 630 K. The copper-to-oxygen stoichiometric ratio also changes drastically from $2:1$ for Cu_2O to about $10:1$ for the novel suboxide phase, $Cu_{(x \geqslant 10)}O$. The stoichiometric ratio was determined by the corresponding absorption edge heights detected at the O K- and Cu $L_{2,3}$-edges, which were weighted by the photoionization cross section[19] and by the number of core electrons.

Generally, it was found that this critical phase transition temperature, T_{CT}, strongly depends on the oxygen proportions in the gas mixture and increases with increasing oxygen concentration.[3] The phase transformation is found to be reversible, which can be seen in the copper(I) oxide-like spectrum of Fig. 4 detected after lowering the catalyst temperature from 750 to 490 K. This strongly indicates that the copper(I) oxide is the thermodynamically stable phase at temperatures below T_{CT} that is also found after quenching the reaction, *i.e.* *ex situ* (see ref. 1, 2 and 4). It remains an open question whether the suboxide phase represents a thermodynamically stable or metastable phase under the conditions of selective oxidation. Thus, this observation strongly indicates that, at low temperatures, the solid state chemistry of copper and oxygen plays the dominant role and not the catalytic reaction. The phase transformation under reaction conditions leads, contrary to expectation, not to pure Cu and CO_2 but to a phase with residual oxygen which is not stated in the known phase diagrams of the Cu–O system.[20] It is important to state that the spectroscopic observations fit very well with the reactor experiment of Fig. 2. At very comparable temperatures the reduction of copper oxides to the partial oxidation catalyst is observed by either CO_2 evolution or spectral changes at the Cu and O absorption edges.

The spectral shape of the O K-edge spectrum of copper(I) oxide (see Fig. 4(a) and (f)) agrees well with the corresponding *ex situ* and *in situ* data for Cu_2O.[1–4,21–23] The Cu_2O-oxygen K-edge spectrum can be divided into two regions.[24,25] The strongest peak at ~ 533 eV, is assigned to the bonding contributions of O 2p states with Cu 3d states, and is due to a transition of an O 1s electron into unoccupied anti-bonding O 2p Cu 3d states. The broad feature at higher energies is attributed to the convolution of O 2p states with Cu 4sp states. The oxygen K-XANES spectra of the $Cu_{(x \geqslant 10)}O$ phase (Fig. 4(b)–(e)) show a strong feature at about 536 eV indicative of a covalent O 2p Cu 4sp bonding interaction between atomic oxygen species, and the copper surface. Furthermore, the appearance of a small feature at 532 eV preceding the strong 536 eV peak points to the presence of small proportions of oxygen from the oxide characterized by a bonding interaction between the O 2p and Cu 3d states. It will be shown below that the small feature is indeed arising from a second species and not an intrinsic weak component of the spectrum of the main oxygen species.

At temperatures above the critical temperature T_{CT}, the bonding interaction between oxygen and copper is lowered from O 2p Cu 3d/Cu 4sp observed for the oxide phase to only O 2p Cu 4sp found for the suboxide phase, $Cu_{(x \geqslant 10)}O$. This can be viewed as a consequence of a decrease in the splitting between antibonding and bonding O 2p Cu 3d states so that the antibonding states are closely located below the Fermi level.

The suboxide phase of $Cu_{(x \geqslant 10)}O$ is characterized by oxygen atoms located at the surface and near-surface region, O_α. Additionally, oxygen atoms, $O_{(oxi)}$, from the oxide phase, Cu_2O, are also found in the region of detection. The suboxide oxygen species O_α is not directly consumed in the course of the methanol oxidation but represents a steady-state oxide proportion present under the methanol oxidation reaction conditions.

The copper $L_{2,3}$-XANES spectra (Fig. 5(b)–(d)) exhibit a typical metal-like absorption edge shape[24] at temperatures above T_{CT}, while below T_{CT}, the copper L-edges show a strong feature directly at the threshold due to a transition of copper 2p electrons into unoccupied Cu 3d states characteristic of the copper(I) oxide phase.[24]

Thus, the copper catalyst (near-) surface region exhibits, at temperatures above T_{CT}, a novel copper suboxide phase of $Cu_{(x \geq 10)}O$ characterized by atomic oxygen species, O_α, and, additionally oxygen species, $O_{(oxi)}$, from a copper oxide while the copper $L_{2,3}$-edges show a spectral shape typical of copper metal. The abundance of the copper oxide can be too low to cause a discernible pre-edge feature. Alternatively, the spectral differences between authentic Cu_2O and low-abundance oxide species (see Fig. 4) indicate a bonding situation giving rise to only weak pre-edge features. Only higher spectral resolution data could resolve this question.

At temperatures below T_{CT}, the copper spectrum reveals the presence of the copper(I) oxide phase. This strongly indicates that, under the selected steady-state reaction conditions, the copper(I) oxide phase decomposes at T_{CT} into a catalytically relevant form of oxygen bound to copper metal *via* only s–p state interactions that represents the novel suboxide phase, $Cu_{(x \geq 10)}O$, and, additionally, into a small fraction forming an oxide phase.

As shown in the conversion data of Fig. 3, the critical temperature, T_{CT}, of about 560 K is correlated to an increase in the methanol conversion. Up to this temperature it is found that methanol is mainly oxidized to carbon dioxide and water (*i.e.* reduction of the copper(I) oxide phase occurs) and, to a lesser extent, also to formaldehyde. It is interesting to note that the critical temperature strongly depends on the methanol-to-oxygen ratio, *i.e.* if the oxygen proportion becomes higher the critical temperature is shifted to higher values and *vice versa*.[3]

The oxygen K-edge spectra show broadening of the strongest 536 eV peak towards higher photon energy with increasing catalyst temperatures, indicating that an additional feature occurs at about 538 eV (as marked in Fig. 4) under steady-state reaction conditions at high catalyst temperature. The new 538 eV feature cannot be observed at lower catalyst temperatures and, thus, might be correlated with the dehydrogenation reaction channel which opens up at temperatures above 600 K. This additional feature appears close to the energy at which the sub/near-surface related oxygen is found under pure methanol reduction conditions (see ref. 21 and 23). Thus, the oxygen species can be attributed to atomic oxygen species, O_β, dissolved in the surface-near bulk regions of copper.

The edge jump of the oxygen spectrum remains almost constant with increasing working temperature of the catalysts. This suggests that the second species is formed at the expense of the surface atomic oxygen species. The increasing temperature provides the activation energy for the process of surface-to-bulk migration of oxygen atoms. This process is related to a displacement of copper atoms as oxygen atoms are much larger than copper atoms. The required restructuring creates an energetic barrier for the dissolution of oxygen atoms.

The bulk-dissolved oxygen atoms remain in their atomic state and do not oxidize the copper, as seen by the spectral shapes in Fig. 4 and 5. Also the oxide pre-edge feature is not correlated with the abundance of the bulk-dissolved oxygen. The reason for the existence of this thermodynamically metastable situation with respect to the formation of copper oxide is again the activation barrier for the atomic displacement of copper atoms in the bulk. The density of copper oxide is lower than that of bulk copper, thus requiring the creation of empty space within the close-packed structure of metallic copper. The necessary mobility of copper atoms is likely to be not

present at these low temperatures compared to the melting point of 1360 K. This could be the origin of the kinetic stabilization of the copper plus oxygen solid solution against precipitation of copper oxide.

The finite mobility of oxygen which allowed its dissolution will also enable its segregation back to the surface. The extent to which this occurs is not only given by the thermodynamic boundary conditions but also by the presence of reducible species at the surface (methoxy, formate, hydrogen) which reduce the chemical potential of oxygen at the interface below the dissociation pressure of the solid solution (chemically induced segregation). When an oxygen atom reaches the surface it can either react with the adspecies and desorb as CO/CO_2 or it can form an oxide species. At the surface the activation barrier for restructuring is lower than in the bulk and, thus, in the spectra of Fig. 4, the formation of oxide species can be seen with increasing temperature.

The benefit of a real *in situ* experiment is the possibility to correlate the catalytic behaviour quantitatively with the spectral features. Such a correlation reinforces the assumption that the observed spectral features are relevant for the catalytic action. In Fig. 6 the correlation between the partial oxidation activity and the integrated intensity under the non-oxidic oxygen species, O_α, O_β, is shown. The possible discrimination between oxidative dehydrogenation and dehydrogenation and between surface- and subsurface oxygen is not considered due to the small number of data points available.

The correlation holds well for the two quantities, revealing that the non-oxidic oxygen is indeed connected with the catalytic action. The sign of the correlation is, however, unexpected, as with increasing conversion the steady-state coverage of the involved species should decline and not increase. This means that the oxygen detected in Fig. 4 cannot be the species directly involved in the partial oxidation of methanol.

The search for adsorbed intermediates which was unsuccessful at the oxygen K-edge, where also no indication of molecular oxygen was found, was also unsuccessful at the carbon K-edge. Surface science studies[7,26–30] suggested that adsorbed methoxy or less stable species like formate or dioxymethyl species should populate the reacting surface. With a detection limit of below 0.1 monolayers it was impossi-
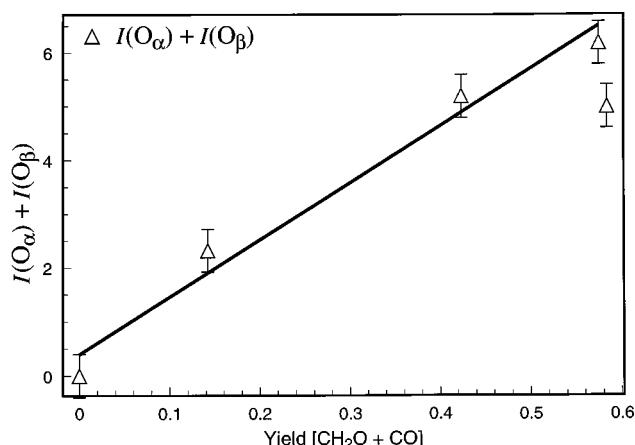
Fig. 6 The abundance of the two oxygen species, O_α and O_β, appearing only at temperatures above T_{CT} at 536 and 538 eV, is correlated with the catalytic action of the copper as a partial oxidation catalyst. The intensities of the oxygen species, $I(O_\alpha)$ and $I(O_\beta)$ are plotted together with the relative gas-phase proportions of H_2CO and CO. The figure presents the sum of the oxygen intensities $[I(O_\alpha) + I(O_\beta)]$ as a function of the sum of the gas-phase concentrations of formaldehyde and carbon monoxide (called yield) at different catalyst temperatures in the range of 560 to 750 K. It is assumed here that the formaldehyde molecules decompose partially at the hot catalyst surface to CO and H_2.[17]

ble to find any of these species using the carbon K-edge spectra which only showed gas-phase species.

The *in situ* surface analysis reveals that the reacting surface is essentially free of detectable amounts of chemisorbed intermediates during steady-state operation. The reaction intermediates found in static surface science studies are thus either spectator species or do not exist as long-lived species under reaction conditions. This points to an overall fast reaction kinetics with steady-state surface coverage well below 0.1 monolayers. The oxygen species detected in the spectra of Fig. 4 are thus part of the solid catalyst and can be viewed as a marker for the active sites of the partial methanol oxidation.
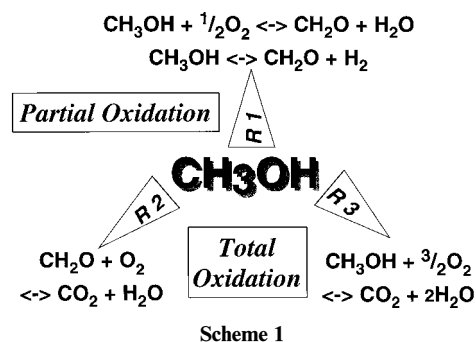
The abundance of the two oxygen species, O_α and O_β, appearing only at temperatures above T_{CT} at 536 and 538 eV, is correlated with the catalytic action of the copper as a partial oxidation catalyst. Therefore, the intensities of both oxygen species, $I(O_\alpha)$ and $I(O_\beta)$, are determined by fitting each species with Gaussian broadened Lorentzians as shown in Fig. 4(b)–(e) and are plotted together with the relative gas phase proportions of H_2CO and CO. Fig. 6 presents the sum of the oxygen intensities $[I(O_\alpha) + I(O_\beta)]$ as a function of the sum of the gas-phase concentrations of formaldehyde and carbon monoxide (called yield) at different catalyst temperatures in the range 540 to 750 K. It is assumed here that the formaldehyde molecules decompose partially at the hot catalyst surface to CO and H_2.[17] It is found that the quantitative abundances of the selectively acting oxygen species, O_α and O_β detected under steady-state reaction conditions are proportional to the product gas-phase concentration of formaldehyde and carbon monoxide. This strongly indicates that these two oxygen species are unequivocally correlated with the operation of the copper surface and near-surface region as partial oxidation catalyst. The same proportionality is found if the conversion of methanol is considered. On the other hand, the rate constant of the methanol oxidation reveals also a temperature-dependence. This temperature dependent change in the yield of the reaction has not been deconvoluted from the original data set since calculated activation energies were found to be always too small for the methanol oxidation within the Arrhenius approach. This points to a diffusion-controlled process where the rate of reduction or oxidation of the copper catalyst can be more appropriately described within a shrinking core or nucleation model.

4. Discussion

First, it was demonstrated that it is possible to investigate a catalytic reaction with a surface-sensitive electron spectroscopic technique under realistic reaction conditions. It was further shown that these realistic reaction conditions involve surface processes as well as the participation of surface/subsurface processes.

The good correspondence of the phase-transformation temperature between the reactor experiment (Fig. 1) and the *in situ* study (Fig. 4 and 5) is a strong indication for the relevance of the study as well as the correlation of spectral intensities with catalytic activity (Fig. 6). Also, the chemical fingerprint of a preceding reduction of a copper oxide to metal and carbon dioxide which was detected in the reactor study and in the *in situ* conversion experiment in the same way supports the view that surface spectroscopy detects the really relevant electronic features of the working catalyst.

The multiplicity of reaction pathways described in Table 1 calls for the discrimination of parallel and consecutive reaction pathways. In the case of parallel reactions, several chemically inequivalent types of active sites should be identified by spectroscopy. For the simplified reaction network shown in Scheme 1 two inequivalent sites for total and partial oxidation are required. The temperature dependence of the CO_2 production in Fig. 3 reveals that at low temperatures the reaction

$$CH_3OH + \tfrac{1}{2}O_2 \longleftrightarrow CH_2O + H_2O$$
$$CH_3OH \longleftrightarrow CH_2O + H_2$$

Partial Oxidation — R1

CH₃OH

R2 — *Total Oxidation* — R3

$$CH_2O + O_2 \longleftrightarrow CO_2 + H_2O \qquad CH_3OH + \tfrac{3}{2}O_2 \longleftrightarrow CO_2 + 2H_2O$$

Scheme 1

channel R3 is dominant and at higher temperature the R1 channel. The reaction channel R2, the consecutive total oxidation of formaldehyde, is not dominant under all conditions of this study. The well-known water-gas shift reaction ($CO + H_2O \leftrightarrow CO_2 + H_2$) was not observed under the applied reaction conditions although a catalyst based on copper–zinc oxide, promoted by Cr, Co, Al, and Ni, is used at low temperatures of about 500 K for this reaction.[31,32]

The two inequivalent sites can be associated with the oxidic type oxygen characterized by an O 2p–Cu 3d in addition to an O 2p–Cu 4sp bonding interaction and with the atomic type oxygen associated with only an O 2p–Cu 4sp bonding interaction. Such an assignment is supported by the documented reactivity of copper oxide with methanol to CO_2 and water (see Fig. 3) and by the relative proportions of the two oxygen species in relation to the selectivity between partial and total oxidation seen in in Fig. 3.

More difficult is the discrimination between oxidative dehydrogenation and dehydrogenation which would also require different sites characterized by oxygen species which are more oxidizing or nucleophilic with respect to methanol[7,26–30] or more basic which translates into weaker and stronger bonds to copper. As it was not possible to detect any oxygen directly involved in the turnover of methanol it is impossible to identify the existence of the two types of oxygen species for the two channels of partial oxidation. On the other hand, the oxygen conversion remains almost constant across much of the high temperature range under study, which can be viewed as an indirect hint towards an increase in the yield of the dehydrogenation reaction channel. Thus, the second oxygen species, O_β, can be associated with the dehydrogenation reaction channel, since its intensity increases with increasing catalyst temperature.

The positive correlation of the abundance of the two non-oxidic species with the catalytic activity shows that both of these species cannot be involved in the direct conversion of methanol, *i.e.* they cannot be the oxidizing agents for the hydrogen atoms to be subtracted from the methanol.

The formal dehydrogenation reaction (Table 1) does not require stoichiometric amounts of oxygen and will occur on a site involving strongly bound oxygen with high local electron density to act as a base in the C–H activation of the methanol molecule. The oxygen-to-copper bond must be such that deprotonation to hydrogen occurs rather than the preferred formation of a water molecule. The balance between formaldehyde and water in Fig. 3 strongly implies that such a reaction exists above 570 K. In full analogy to silver as dehydrogenation catalyst for methanol,[33] where such a strongly bound species was identified, the species segregating from the bulk to the surface could account for such sites.

The oxygen required for oxidative dehydrogenation should activate the methanol C–H bond by its nucleophilic character and should thus be more weakly bound to copper. The surface atomic species could account, in principle, for such a function. As their abundance is, however, positively correlated with the conversion of methanol to formaldehyde, this straightforward assignment is not correct. The atomic oxygen detected is part

of an active centre for oxidative dehydrogenation but the oxygen residing long enough at the surface to be detectable by the XAS method is not the nucleophilic species required for the methanol conversion. The oxygen species detected can, however, well enhance the sticking coefficient of either methanol or oxygen at this particular site. It is well known on silver[34,35] as well as on copper[27–30] that pre-adsorbed oxygen is essential to obtain significant sticking coefficients for adsorbates on the otherwise rather inert clean coin metal surfaces. The function of the oxygen detected in XAS and positively correlated to the partial oxidation reaction is thus clearly the enhancement of the sticking coefficients of the reactants methanol and oxygen for a fast Langmuir–Hinshelwood reaction which itself leads to no detectable stationary-state coverage of the active sites. In addition, the atomic oxygen O_β can provide the sites for dehydrogenation where no stochiometric oxygen consumption is involved.

These atomic oxygen species form the sub-oxide $Cu_{(x \geqslant 10)}O$ which is metallic in character and which is formed only *in situ* in the simultaneous presence of oxygen and methanol. Its lower temperature of existence is fixed by the partial pressure ratio of oxygen and reducing agents. This critical temperature marks clearly the lowest catalytically useful temperature of copper as a partial oxidation catalyst. Below this temperature the surface is covered by an oxide film. The oxygen in this film is chemically substantially different from the atomic oxygen species above the phase transformation temperature, as was shown in Fig. 4 and 5. Its strong contribution of O 2p–Cu 3d hybrid interactions to the bonding[22,25] renders its chemical character electrophilic. The oxidic oxygen is highly reactive towards methanol and its reaction products. The activity of splitting all C–H bonds in organic molecules is too high for formaldehyde to be a substantial reaction intermediate. Thus, the reactivity of copper oxide is only directed towards total oxidation.

The presence of oxygen atoms above the phase transformation temperature causes the existence of a small but detectable amount of copper oxide, as detected in the data of Fig. 4. Its presence seem unavoidable and is correlated with the finite reaction probability of oxygen atoms to dissolve sub-surface and, thus, to escape the reaction with reducing agents at the surface. The thermodynamically driven segregation of dissolved oxygen occurs as the preferred reaction channel of oxide formation is kinetically blocked in the bulk. At the surface, however, this reaction channel is open and leads to a continuous re-formation of the oxide, which reacts with methanol to give CO_2 and water. The involvement of the sub-surface region limits thus the selectivity of the partial oxidation to a value below 100% at all temperatures.

For kinetic considerations the following conclusions arise from the findings described. At least two different active sites for total and partial oxidation were clearly identified, corroborating the reaction network in Scheme 1. The conversion of methanol is fast on the timescale of the present experiments. This is the reason for the good correlation between the kinetic behaviour of the reactor under atmospheric pressure flow conditions and the differential reactor of a flat metal surface under low-pressure flow conditions. It can be speculated from the agreement of the features of Fig. 2 and 3 that the rate-determining steps of the reaction are not amongst the elementary steps of the methanol conversion but rather amongst the formation/regeneration of the catalyst active sites. That these processes are probed by the present *in situ* XAS measurements is evidenced by the correlation shown in Fig. 6. The reaction rates are enhanced by the presence of strongly bound oxygen atoms which affect the sticking coefficients of the reactants (and products). Such data from clean single crystal faces can thus not be used for kinetic models. Further, only a fraction of the copper metal surface is catalytically active. An estimate for this fraction can be the abundance of oxygen atoms above the

phase transformation temperature amounting to 10% of all surface atoms. The TOF of the reaction is thus at least an order of magnitude faster than the values given above. Estimations of the fractional abundance of electrophilic (oxidic) and nucleophilic or basic (atomic) oxygen from the XAS data are difficult without knowing spectral cross-sections for the differently bound species. From the functional discussion it appears that the electrophilic oxygen is less abundant than the nucleophilic oxygen. Assuming roughly equal specific activities of these sites such a distribution is in line with the reaction data in Fig. 2.

Finally, it is noted that the present *in situ* experiments are still inadequate to identify the chemical nature of reaction intermediates of the oxidizing species as well as of the organic components. An experimentally founded reaction scenario has thus to await further efforts in *in situ* spectroscopy. The present experiments identify, however, novel bonding states of atomic oxygen at and in copper metal. These states are involved in the formation of active sites and exist only under high-pressure reaction conditions as evidenced by comparison of the present results with earlier *ex situ* low-pressure studies.[1,2,4] For the constitution of the active sites it appears that they all contain oxygen and copper. The chemical interactions between copper and oxygen atoms can be substantially different from each other and also from those of conventional oxides. The atomic sizes of copper and oxygen imply that the copper structure in the environment of the oxygen species will be distorted from the regular metal structure. The effects of such distortions[36] can well contribute to the identification of active sites from simple chemisorption sites on clean copper surfaces. In the present experiments the spectral resolution is inadequate to search for such effects which should, however, be identifiable *in situ* with more advanced synchrotron light sources as they become available *e.g.* at BESSY-II. where we will continue these measurements.

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