Keywords: amides · atropisomerism · molecular devices · molecular dynamics

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High-Pressure Soft X-Ray Absorption Spectroscopy: A Contribution to Overcoming the "Pressure Gap" in the Study of Heterogeneous Catalytic Processes

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Thomas Schedel-Niedrig,* and Robert Schlögl

*Dedicated to Professor Sir John Meurig Thomas
on the occasion of his 65th birthday*

X-ray absorption spectroscopy (XAS) is an important tool in the study of gas–solid reactions and their products.[1] In the past few years in situ techniques have attained great importance in the field of heterogeneous catalysis.[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. To allow any relevant interpretation, an in situ measurement requires the simultaneous detection of spectroscopic data together with the conversion from the gas phase. Silver, copper, or molybdenum catalysts are used in technical processes for the conversion of methanol into formaldehyde.[3] These are well-suited to the study of the principles of chemical reactions on various surfaces due to the apparent clarity of the possible courses of reaction.[4] The oxidation of methanol on pure silver has shown, for example, that catalytic reactions under model conditions in ultra high vacuum (UHV) can take a different course to those under practicle conditions.[5–7] Three different types of atomic oxygen were identified by surface science studies of silver that was subjected to oxygen under pressure in a manner that is used in practice;[5, 8–10] their positions are shown in Figure 1. The critical oxygen pressure at which qualitative differences to the UHV model conditions in the surface chemistry of the Ag–O system were observed was 0.1 mbar. The only differences observed up to an oxygen partial pressure of 1000 mbar were in the reaction kinetics of the formation processes involved. With increasing temperature, atomic oxygen is initially formed on the surface (O_α). At a critical level of pressure and temperature, it then migrates under the surface to occupy interstitial sites in the silver crystal (O_β).[11] On increasing the temperature still further, a new form of oxygen is formed from the O_β species and, parallel to this, directly from the gas phase. The new form is incorporated into the top atomic layer of the crystal (O_γ) and interacts strongly with the silver centers. This state differs from that of a metal oxide—silver oxide is no longer thermodynamically stable at temperatures of formation above 600 K—both in structure and in that its existence is strictly limited to a single atomic layer. [5, 8–10]

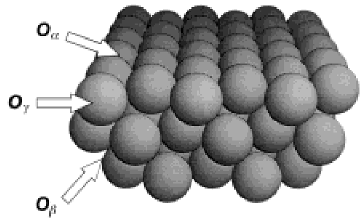

Figure 1. Schematic depiction of the Ag(111) surface treated with oxygen. The atomic oxygen species O_α, O_γ, and O_β were characterized by surface-sensitive spectroscopic techniques.[5–13] The chemisorbed O_α species and the O_γ species bonded in the surface layer are responsible for the oxide hydrogenation and the dehydrogenation of methanol.[12, 13] The O_β species acts as a reservoir for both surface species during the catalytic oxidation of methanol.

The oxidation of a methanol molecule can either occur by dehydrogenation with loss of one hydrogen molecule and the formation of formaldehyde [Eq. (1)], or by oxide hydrogenation or total oxidation with loss of hydrogen and simultaneous uptake of oxygen to give water and formaldehyde or water and carbon dioxide [Eqs. (2) and (3)].

$$CH_3OH \xrightarrow[Ag]{O_\gamma} CH_2O + H_2 \tag{1}$$

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$$CH_3OH+1/2\,O_2 \xrightarrow[Ag]{O_\alpha} CH_2O+H_2O \qquad (2)$$

$$CH_3OH+3/2\,O_2 \xrightarrow[Ag]{O_\alpha} CO_2+2\,H_2O \qquad (3)$$

Kinetic measurements have revealed that above the critical pressure of about 1 mbar both reaction pathways are followed, and thus at least two different types of oxygen must be present.[12, 13] Under UHV conditions, however, only reaction (2) is observed.[14] This correlates with the results described above which show the atomic adsorbed oxygen (O_α) and the special atomic oxygen built into the surface layer (O_γ) to be catalytically active centers.[12, 15]

In contrast to the case of silver, for copper the atomic chemisorbed oxygen is thermodynamically metastable with respect to the transition to the oxide state under the conditions of the selective oxidation of methanol. One consequence of this is that different non-oxidic oxygen species are difficult to detect in conventional UHV studies, even if the surface is previously subjected to an O_2/CH_3OH gas mixture at high temperature.[16] According to ex situ UHV studies, copper(I) oxide was primarily formed.[16] As this species can only catalyze the total oxidation of methanol [reaction (3)], it cannot be the active phase sought.[15] In situ studies under reaction conditions close to those found in practice are thus imperative to spectroscopically characterize the selective catalytically active phase.[17, 18]

In Figure 2 the oxygen K absorption near edges of copper(I) oxide, Cu_2O (Ib), and copper(II) oxide, CuO (Ic) as well as the corresponding copper $L_{2,3}$ absorption near-edge spectra of Cu_2O (IIb), CuO (IIc), and polycrystalline metallic copper (IIa) are shown.[9, 10, 19, 20] The copper $L_{2,3}$ absorption spectrum of the pure metal shows the typical steplike form of the absorption edge with some fine structure that is characteristic for the formal oxidation state 0 (Cu^0, $d^{10}s^1$ configuration).[27–29] The in situ X-ray absorption spectra measured during the reaction of polycrystalline copper with oxygen at 600 K are also presented in Figure 2. These indicate the formation of Cu_2O (d) and CuO (e) at a total O_2 pressure of 0.05 and 0.10 mbar, respectively, at the surface and in the area near the surface. The considerably different products 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.[17]

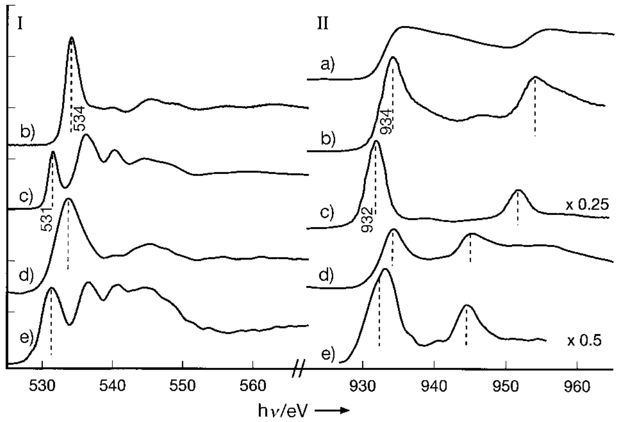

Figure 2. I) Oxygen K-absorption near-edge spectra of Cu_2O (b) and CuO (c); II) copper $L_{2,3}$-absorption near-edge spectra of metallic copper (a), Cu_2O (b), and CuO (c). The spectra Ib, c and IIa–c were recorded under ultra high vacuum in the surface-sensitive electron-yield mode (information depth about 60 Å). The in situ spectra Id, e and IId, e were recorded at $T = 600$ K and a total O_2 pressure of $p = 0.05$ and 0.10 mbar, respectively. The in situ copper $L_{2,3}$-absorption near-edge spectra IId, e were obtained using the second-order light of the monochromator and subsequently shifted by 466 eV to higher photon energy. This is why the difference in energy between the copper L_3- and copper L_2-edges is a factor of 2 smaller than in the spectra IIa–c which were measured using the first-order light of the monochromator.

Measurements performed on the oxygen K 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 ca. 3000 L[35]). Subsequent reduction occurs after about 190 min. This reduced phase is characterized by the formation of an oxygen–copper compound on the surface or in the region near the surface. This compound does not correspond with either of the usual oxides and is characterized by a covalent O2p–Cu4sp bonding contribution in the oxygen K-edge spectra. In contrast, the copper $L_{2,3}$-edge spectra of this phase show the steplike form of the absorption edge typical for metallic copper (see Figure 2IIa).[27] According to ex situ studies on this system, however, Cu_2O is formed on the transition to UHV with simultaneous cooling to room temperature.[16, 17] This means that it is only possible to observe the special oxygen–copper phase under in situ 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. The significance of this special phase in practice for the partial oxidation was proven by analysis of the oscillatory behavior of the $Cu/O/CH_3OH$ system.[15]

A direct measurement of the conversion of pure methanol under comparatively high pressure (0.2 mbar) on polycrystalline copper pretreated with oxygen was first determined by the spectral proportion of CO[36] in the X-ray absorption spectrum of the gas phase. The copper catalyst was loaded with bulk oxygen (O_β) by an oxygen pretreatment followed by reduction in methanol. Under the reaction conditions the bulk oxygen diffuses to the surface and takes part in the oxidation reaction. Figure 3 shows the conversion of methanol as a function of reaction time. In the plot the percent spectral proportions of methanol and carbon monoxide determined from the gas-phase X-ray absorption spectra are compared with the gas-phase proportions measured simultaneously by quadrupole mass spectroscopy.[37] The initial conversion frequency of about 0.3 methanol molecules per second and per copper surface atom lies in the range of known values for heterogeneous catalytic reactions of small molecules (between 0.01 and 100 molecules per second and per active surface atom).[38–40]

Parallel to the gas phase spectra, X-ray absorption spectra of the active copper catalyst surface were recorded during the reaction with 0.2 mbar of methanol. Figure 4 shows the spectra of the oxygen K- (I) and the copper $L_{2,3}$-absorption near edges (II) during the conversion of methanol at catalyst temperatures of 520 K (a) and 600 K (b). As is the case with

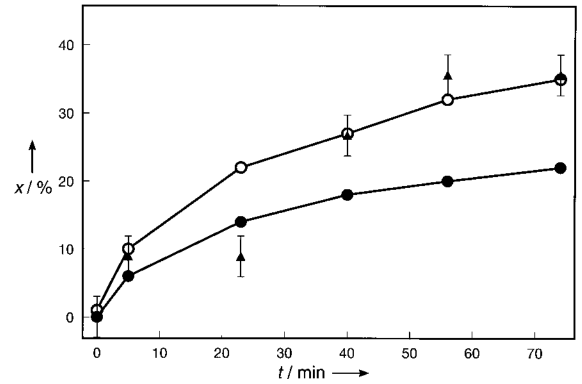

Figure 3. The catalytic conversion of pure methanol into formaldehyde on polycrystalline copper was followed in situ for the first time in a batch reactor by observing the spectral proportion of CO in the gas phase spectrum.[17] The copper catalyst was loaded with bulk oxygen (O_β) by pretreatment with oxygen at 620 K (1 mbar O_2, 30 min) and subsequent reduction in methanol ($p \approx 5 \times 10^{-6}$ mbar, $T = 600$ K, 90 min).[15] The diagram shows the conversion of methanol (○) into formaldehyde (▲; multiplied by 8.4) and carbon monoxide (●) at a total pressure of 0.2 mbar and a catalyst temperature of $T = 520$ K as a function of the reaction time t [min]. The proportions of the gaseous products were determined independently by XAS (CH_3OH, CO) and mass spectroscopy (H_2CO).

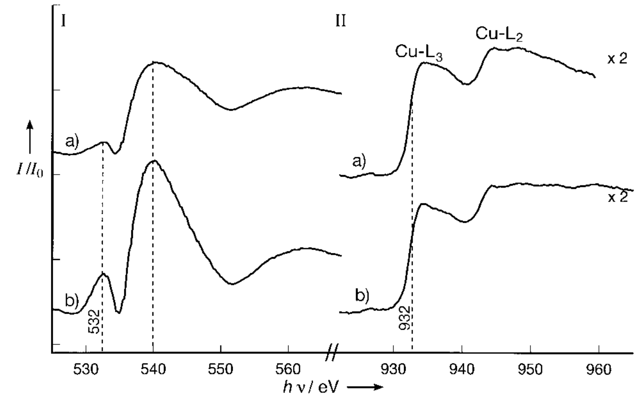

Figure 4. I) In situ oxygen K-absorption near-edge spectra measured during the conversion of methanol at catalyst temperatures of 520 K (a) and 600 K (b); II) the corresponding copper $L_{2,3}$-edge spectra. The spectra of the pure oxides CuO and Cu_2O are depicted in Figure 2. The line profiles of the oxygen K-edge spectra of the active copper catalyst are quite different from those of known copper oxides (see Figure 2) A broad peak appears in the spectra at 540 eV which can be attributed to the selective catalytically active oxygen state. The copper L-absorption near-edge spectra were recorded with monochromated second-order X-rays (see the legend to Figure 2).

the pure copper oxides, high covalent oxygen–copper bonding contributions are also observed in the oxygen K edge spectra of the catalyst in the active state with participation of mainly O2p–Cu4sp states (at 540 eV) and, to a lesser extent, of O2p–Cu3d states (532 eV) (see Figure 4I a, b). However, the spectral shapes of the oxygen K edge spectra of the active copper catalyst are completely different from those of the known copper oxides (see Figure 2II d, e). In contrast, good agreement is observed with the oxygen K-edge spectrum of the adsorbed atomic O_α species of the silver catalyst, which would indicate the same type of bonding interaction between copper and oxygen.[9, 10] The copper $L_{2,3}$-edge spectra have an absorption step with a form typical of metallic copper compounds (see Figure 2II a). This indicates a "catalytically active" state which is significantly different from those of the well-known copper oxides and, in analogy to the O_α–Ag(111) phase, has an oxygen–copper interaction with participation of mainly O2p–Cu4sp states.[9, 10]

A comparison of the spectra of the catalyst surface with those of the gas phase shows that the formaldehyde molecules formed under the chosen reaction conditions decompose on the copper surface with the participation of covalently bonded oxygen to predominantly give CO and H_2. If the active surface was a known copper oxide, carbon dioxide and not carbon monoxide would be the main product formed.

Thus, for the first time it has proved possible to study a catalytically active phase under reaction conditions by absorption spectroscopy not at the high-energy copper K edge, but rather at the chemically more informative oxygen K and copper $L_{2,3}$ edges. In particular, it was ascertained that the catalytically active phase is metallic and contains an atomic form of oxygen, the chemical bonding of which differs significantly from those in conventional oxides. It was not possible to identify the presence of covalently bonded oxygen in the active state during the reaction in previous in situ XAS studies at the high-energy copper K-edge.[41, 42] Measurements performed on stoichiometric O_2/CH_3OH gas mixtures at 0.5 mbar (not detailed here) confirm that after most of the methanol has reacted, unused oxygen in the gas phase reacts with the surface to give Cu_2O. The catalyst is then no longer selective and effects complete oxidation.

The novel Cu/O phase discovered by high-pressure in situ analysis can be described as copper suboxide. However, the high surface sensitivity of this method excludes any reasonable bulk analytical characterization in the sense of an overall stoichiometric formula. The structures of different copper suboxides on surfaces[43] and in small particles[44] are well known. The selective active state for the application of copper as a partial oxidation catalyst was thus made analytically accessible for the first time. Considering the surface states of the pure metal (weakly active, rearranging) and copper(I) oxide (highly active, totally oxidizing), it is possible to understand the reason for the nonlinear behavior of the reaction system.[15] Our experiment is a contribution to experimentally overcoming the "pressure gap" in catalytic science. The commissioning of the new synchrotron radiation source BESSY II will enable us to increase the upper pressure limit at which useful spectra can be obtained by at least one order of magnitude. We thus expect to gain considerable knowledge on the local electronic structure of catalytically active surfaces in the operational state.

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[18] As could be shown in surface-sensitive ex situ photoemission and X-ray absorption studies on copper samples under reaction conditions, these differ from the known copper oxides with regard to spectral shape and intensity of the signals, which would indicate the presence of a copper suboxide phase.

[19] The spectra were recorded by the surface-sensitive electron-yield method (ca. 60 Å depth of information) with monochromated synchrotron radiation from the BESSY synchrotron in Berlin on the PM-1 monochromator.

[20] X-ray absorption is a process in which a core electron is promoted to an excited electronic state that is related to the original level by the dipole selection rules ($\Delta L = \pm 1$).[21, 22] For the oxygen K-edges ($L = 0$) this means that only oxygen p states ($L = 1$) are accessible. The resulting spectrum can be interpreted to a first approximation as depicting the oxygen p projected unoccupied density of states.[21] As X-ray absorption is a local process on the absorbing atom, this means a very high sensitivity of the X-ray absorption near-edge structures (XANES or NEXAFS) to the local bond to the neighboring atoms and thus permits detailed statements to be made on the chemical nature of the bond.[21, 22]

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[23] In a purely ionic model the oxygen anion (O^{2-}) would have the electronic configuration $O1s^2 2s^2 2p^6$ and a ($1s \rightarrow 2p$) dipole transition caused by X-ray absorption would not be possible. The covalent interaction lowers the number of occupied states with O2p character, so that the height of the O1s signal at the absorption edge can be assigned to the degree of covalency. It is known that transition metal oxides are not purely ionic compounds, but have high covalent bonding contributions in the total bonding interaction,[24] and that for heavy transition metal oxides the covalent O2p–metal d bonding contribution relative to the covalent O2p–metal sp bonding contribution tends to decrease when compared with lighter elements.[25, 26]

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[28] In the spectra of CuO and Cu_2O, and indeed in all $L_{2,3}$-edges of copper(II) compounds (Cu^{II} with formal d^9 configuration), a large part of the intensity of the near-edge region is concentrated in the sharp, strongest feature ("white line", $Cu2p_{1/2,3/2} \rightarrow Cu3d$ dipole transition) at about 932 (CuO) and about 934 eV (Cu_2O).

[29] The "white-line" signal in the spectrum of CuO is about five times larger than the edge jump in metallic copper, whereas in the edge spectrum of Cu_2O it is about 2.5 times larger. These differences in the copper L-edge spectra occur in all corresponding spectra of Cu^I and Cu^{II} compounds, and can therefore be employed as reliable indicators of the copper valency.[30] The oxygen K-edge spectra of the two oxides can be divided into two regions. The first region immediately at the absorption threshold is assigned to the covalent bonding contribution of oxygen 2p states with copper 3d states. This assignment agrees with molecular-orbital and band-structure calculations.[30–33] The second region, which stretches from 5 to 20 eV above the absorption threshold, is assigned to the covalent bonding contribution of the oxygen p states with copper 4sp states. The occurrence of covalent oxygen p bonding contributions in a broad energy range confirms the high proportion of covalent interactions in the oxides and is typical for all transition metal oxides.[25, 34]

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[35] 1 Langmuir (symbol L) corresponds to 1×10^{-6} s Torr = 1.33×10^{-6} s mbar.

[36] The formaldehyde molecule formed in the oxidation of methanol decomposes on the surface to give CO and H_2 if it is not pumped away from the hot catalyst surface and cooled quickly.[3]

[37] There is good agreement between the methanol proportions as determined by XAS and mass spectroscopy, whereas the amount of CO determined by mass spectroscopy increases with respect to that measured by XAS after about 20 min due to the decomposition of formaldehyde and methanol on the filament of the mass spectrometer.

[38] J. M. Thomas, W. J. Thomas, *Principles and Practice of Heterogeneous Catalysis*, VCH, Weinheim, **1997**, chap. 1.

[39] The conversion frequency was calculated under the assumption that every atom at the copper surface is an active center. In a batch reactor (volume ca. 4 L) at room temperature and a pressure of 0.2 mbar there are about 2×10^{19} methanol molecules (calculated from the equation of state for gases). After 70 min 30% are converted by the copper catalyst (surface 2.5 cm^2, i.e. 2.5 $cm^2 \times 2 \times 10^{15}$ atoms per cm^2). With the definition of conversion frequency as the number of converted molecules per unit time and per active center, a conversion frequency of 0.3 methanol molecules per second and per copper surface atom is obtained. This is a lower limit for the conversion frequency, as not every surface atom is active and morphological changes at the surface during the actual conversion are not considered.

[40] The reaction of methanol on preoxidized copper was carried out in a batch reactor at different temperatures. The conversion frequencies calculated are strongly dependent on the catalyst temperature. At 750 K, for example, the conversion frequency is 1.3 molecules per second and per surface copper atom. The active copper suboxide phase was detected to be present over a prolonged period (120 min) irrespective of the catalyst temperature; a total reduction of the catalyst, which would thus have meant the destruction of the suboxide phase, was not observed. This can be explained by the redelivery of covalently bonded oxygen by the diffusion of oxygen from the metal interior (O_β) to the surface.

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