Catalytic Methanol Oxidation over Copper: Observation of Reaction-Induced Nanoscale Restructuring by Means of In Situ Time-Resolved X-ray Absorption Spectroscopy

Ingolf Böttger, Thomas Schedel-Niedrig,* Olaf Timpe, Rainer Gottschall, Michael Hävecker, Thorsten Ressler, and Robert Schlögl[a]

Abstract: The catalytically active copper phase for the partial oxidation of methanol is studied by means of time-resolved extended X-ray absorption fine structure (EXAFS) spectroscopy combined with the detection of the catalytic turnover. It is found that the active form of the copper is a strained nanocrystalline form of the metal. The metal is no longer made up from large crystallites but contains a defect structure in which oxygen is already intercalated.

Keywords: copper · heterogeneous catalysis · oxidation · X-ray absorption

Introduction

The phase diagram of the copper–oxygen system shows that gaseous O_2 can be dissolved in liquid copper leading to segregation to give the well-known bulk oxide deposit Cu_2O and CuO phases during the crystallization of copper.[1] The solubility of O_2 and Cu_2O in solid metallic copper is about 0.002–0.007 wt % O_2 and 0.02–0.06 wt % Cu_2O at 870 K.[2, 3] Typically 0.001–0.02 wt % O were determined in molten copper by means of solid-state electrolyte sensors.[4] On the other hand, it was proposed that the solubility of oxygen in solid copper is so small that it would have a totally negligible effect on the thermodynamic properties of copper.[5]

The formation of copper suboxide was observed indirectly by thermogravimetry due to the delayed reduction kinetics of Cu_2O during the exposure to a gas flow of methanol and oxygen within the temperature range of 585 to 735 K.[6] On the other hand, the existence of different copper suboxides on surfaces[7] and in small particles[8] is well documented. For example, the suboxide formation on a Cu(100) surface reveals that adsorption states of oxygen exist with predominant ionic character for the unreconstructed surface and with nonnegligible covalent contributions for the reconstructed surface.[7]

Using the new surface-sensitive in situ X-ray absorption spectroscopy (XAS) technique[9] has revealed that a novel copper suboxide phase of $Cu_{(x\approx 10)}O$ is formed at the surface and near-surface region which is unequivocally attributed to the selective active phase in the heterogeneously catalyzed oxidation reaction of methanol–formaldehyde [Eqs. (1) and (2)].[10–12]

$$CH_3OH + \tfrac{1}{2}O_2 \rightarrow CH_2O + H_2O;\ \text{oxidative dehydrogenation} \quad (1)$$

$$CH_3OH \rightarrow CH_2O + H_2;\ \text{dehydrogenation} \quad (2)$$

The suboxide phase is electronically significantly different from the well-known copper oxide phases but is only accessible for in situ detection under particular reaction conditions.[10] This phase consists of covalently bonded atomic oxygen species without participation of the Cu d-states which form the main bonding contribution in the copper oxides. The high surface sensitivity of the X-ray absorption spectroscopy technique applied in the electron-yield mode excludes any reliable bulk analytical characterization.[10, 11] At temperatures *below* a critical temperature or after quenching the gas/solid state reaction (ex situ), the formation of a thermodynamically stable oxide phase was observed in agreement with the phase diagram that is only active in the total oxidation of methanol [Eq. (3)].[6, 12–14]

$$CH_3OH + 1\tfrac{1}{2}O_2 \rightarrow CO_2 + 2H_2O;\ \text{total oxidation} \quad (3)$$

To complement the detection of unconventional suboxides at the surface we have performed in situ time-resolved extended X-ray absorption fine structure (EXAFS) experiments. Such data are independent from the long-range ordering requirement of powder X-ray diffraction. In addition, the time-resolved dispersive X-ray absorption fine structure (DXAFS) mode allows one to detect small changes in the local chemical environment as a function of the time-

[a] Dr. T. Schedel-Niedrig, I. Böttger, Dr. O. Timpe, Dr. R. Gottschall, M. Hävecker, Dr. T. Ressler, Prof. Dr. R. Schlögl
Fritz-Haber-Institut der Max-Planck-Gesellschaft
Faradayweg 4–6, 14195 Berlin (Germany)
Fax: (+49) 30-84134401
E-mail: thomas@fritz-haber-institut.mpg.de

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modulated gas phase composition of the reacting atmosphere. This "chemical lock-in" technique provides unambiguous evidence that only those bulk structural properties are studied which are correlated with the surface reaction. The dispersive X-ray absorption spectroscopy measurements were performed at the European Synchrotron Radiation Facility (ESRF) with parallel detection of the *whole EXAFS spectrum* by using energy-dispersive highly focusing X-ray optics.[15–19] A time-resolved ($\leq 100\,\mu s$) study of solid-state samples like powder pellets or foils gives "real time" information on the bulk solid state transformation taking place during the change of the gas phase from oxidative to reductive which is controlled by the methanol-to-oxygen ratio. This information is combined with that obtained by the simultaneous detection of the catalytic activity by monitoring the gas phase composition with a mass spectrometer.

The key question is whether a homogeneous copper suboxide phase exists in the bulk phase under the conditions for the partial oxidation of methanol, or whether the copper bulk phase exhibits an inhomogeneous solid solution of pure copper and oxide. In addition, it is of great relevance to detect any correlation between surface catalytic reactivity and the bulk structural properties of the catalyst.

Results

It has been found[12, 20, 21] that the selectivity of the methanol-to-formaldehyde reaction [Eqs. (1) and (2)] increases with decreasing oxygen concentration in the gas flow at constant methanol conversion. The Cu catalysts are treated under a flow of methanol and synthetic air at different temperatures ($570\,K < T < 670\,K$).[22] The oxygen-to-methanol ratio (O_2:CH_3OH) is changed during the accumulation of the absorption spectra from O_2:$CH_3OH = 1$:2 to O_2:$CH_3OH = 0$:2 in order to investigate the catalytic conversion of methanol.[23] The corresponding "real time" modification of the catalyst is detected by time-resolved EXAFS at the copper *K*-edge under a flow of methanol ($12.8\,mL\,min^{-1}$) with various admixtures of synthetic air in the gas stream controlling the conversion of methanol.

Cu(poly) and supported Cu particles

Copper *K*-edge EXAFS spectra typical of metallic copper are shown in Figure 1 for a polycrystalline copper foil catalyst (Figure 1, right) and for a supported copper particles catalyst (Figure 1, left): three-dimensional (3D) plots of time-resolved normalized X-ray absorption spectra are given at the top of Figure 1.[24] The data are recorded in situ during the exposure to a methanol–oxygen gas stream at $T = 670$ K. The corresponding radial distribution functions (RDFs) are shown on the bottom of Figure 1. The insets show typical EXAFS functions $\chi(k)$ (k range: 3.8–9.4 $Å^{-1}$) of selected absorption spectra obtained after substracting the absorption of a "free" Cu atom (cubic spline fit) and the subsequent multiplication by k^2 in order to enhance the small amplitudes at high k values.[26] It is observed that the metal phase does not change as no oxidation of the copper bulk phase takes place not even after the exposure to a gas mixture of O_2:$CH_3OH = 1$:2.[29]

Abstract in German: *Die zeit-aufgelöste ausgedehnte Feinstruktur der Röntgenabsorptionskante (EXAFS) wurde zur Untersuchung der katalytisch aktiven Kupferphase bei der Partialoxidation von Methanol analysiert und mit Messungen des katalytischen Umsatzes kombiniert. Es konnte gezeigt werden, daß die aktive Kupferphase sich als eine verzerrte nanokristalline Form des Metall darstellen läßt, die nicht mehr aus großen Nanokristalliten aufgebaut ist, sondern eine Defektstruktur besitzt, in der Sauerstoff intercaliert ist.*

Metal-to-oxide transition

In order to show the potential of the time-resolved EXAFS method, the metal-to-oxide solid state transition is investigated of the supported copper catalyst system during the oxidation at 670 K. A 3D plot of the RDFs (not phase-shift corrected) is shown in Figure 2. At the beginning of the experiment, the supported copper particles are exposed to an oxygen-methanol gas flow of O_2:$CH_3OH = 0.32$:2 (frame 0 to 14: 0 s to 67 s) and subsequently to a pure methanol gas flow (frame 15 to 64: 72 s to 307 s). Radial distribution functions typical of metallic copper are observed. Afterwards, at time $t = 312$ s (frame 65), the catalyst is exposed only to a flow of synthetic air without methanol. A discernible change in the near-edge structure of the absorption spectrum is detected at $t = 432$ s (frame 90), that is after 120 s, and good agreement is found with a copper(I) oxide EXAFS reference spectrum at time $t = 576$ s (frame 120), that is after 260 s. The corresponding RDFs also change drastically. It is observed that the intensity of the metal RDF (maximum at about 2.2 Å; not phase-shift corrected) decreases while, simultaneously, a new RDF at about 1.9 Å attributable to bulk copper(I) oxide grows. At time $t = 1000$ s (frame 210), that is after 700 s, the beginning of a bulk copper(I) oxide-to-copper(II) oxide phase transition is observed due to the change of the X-ray absorption near-edge structures (XANES). The transition to copper(II) oxide is completed at $t = 1080$ s (frame 225), that is after 780 s. It is found that the complete oxidation of supported metal copper particles to copper(I) oxide takes place within 260 s (≈ 4.3 minutes) at a reaction temperature of 670 K, while the copper(I)-to-copper(II) oxide phase transition takes place within 520 s (≈ 8.6 minutes).

Catalytic turnover

The catalytic turnover of methanol obtained by using the mass spectrometer signal (given in arbitray units) is shown in Figure 3 (solid line) under varying gas-phase conditions in order to correlate the catalytical activity of copper with the local response of the copper catalyst found by means of EXAFS. Thus, Figure 3a shows the alteration of the normalized RDF maximum positions (dots)[30] under increasing oxygen partial pressure in the gas mixture corresponding to an increase of the turn-over of methanol with time (abscissa axis). The reversibility of the change in the RDF position is documented in Figure 3b. It should be mentioned that these time-resolved experiments were performed under varying

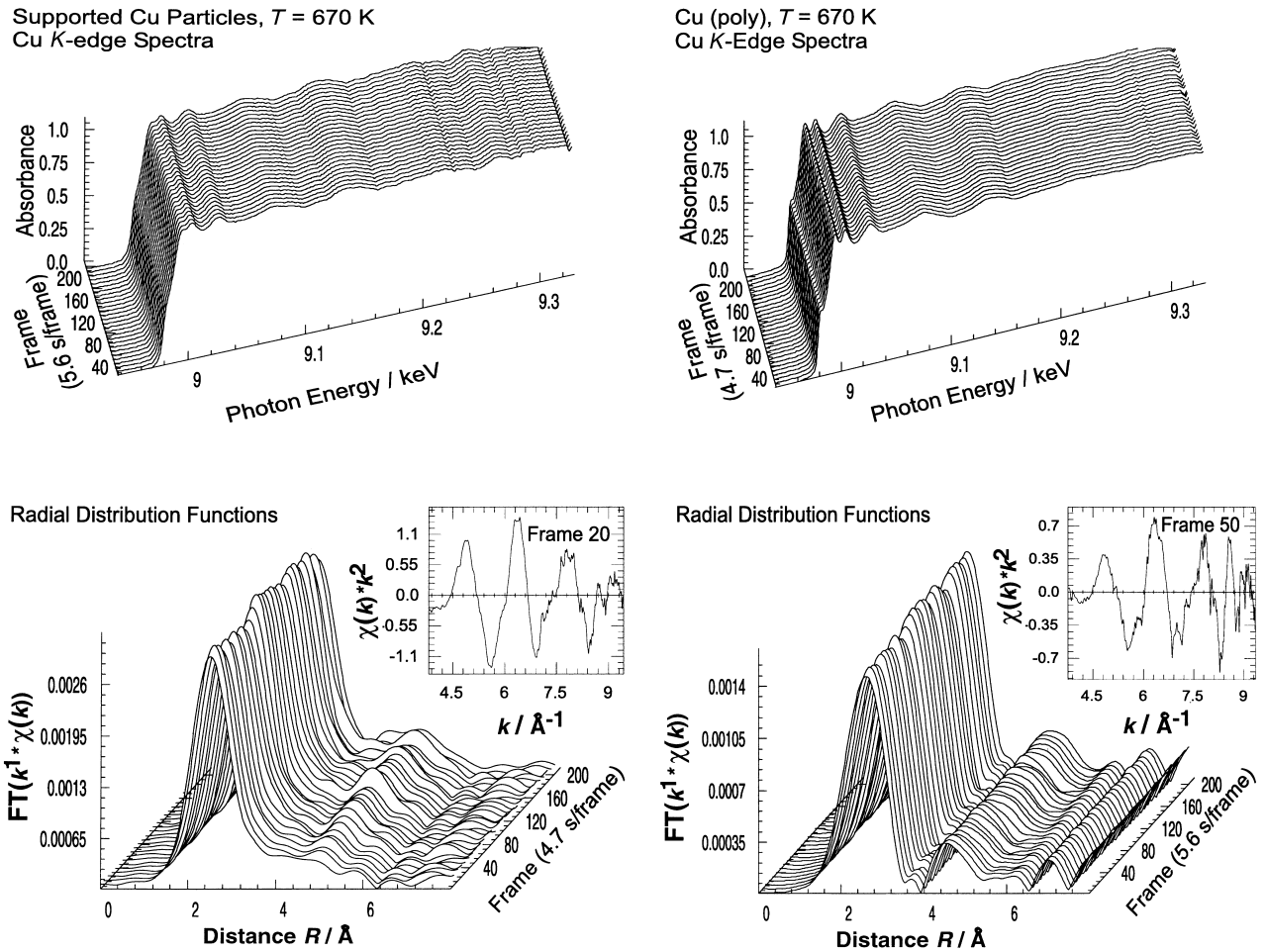

Figure 1. Copper *K*-edge EXAFS spectra typical of copper metal are shown for the polycrystalline copper foil (right) and for supported copper particles (left); top: 3D plots of time-resolved normalized X-ray absorption spectra. The data are recorded in situ during the exposure to a methanol–oxygen gas stream at $T = 670$ K, that is under methanol turnover conditions. The time between each spectrum is 4.7 s and 5.6 s, respectively. Bottom: The corresponding radial distribution functions (RDFs: Fourier-transformed X-ray absorption fine structure $\chi(k)k^1$; phase-shift- and amplitude-corrected; theoretical phase shifts are taken from ref. [25]). The metal phase does not change since no oxidation of the copper metal phase takes place even after exposure to a mixture of O_2:$CH_3OH = 1$:2. Inset: EXAFS function $\chi(k)k^2$ of an absorption spectrum.

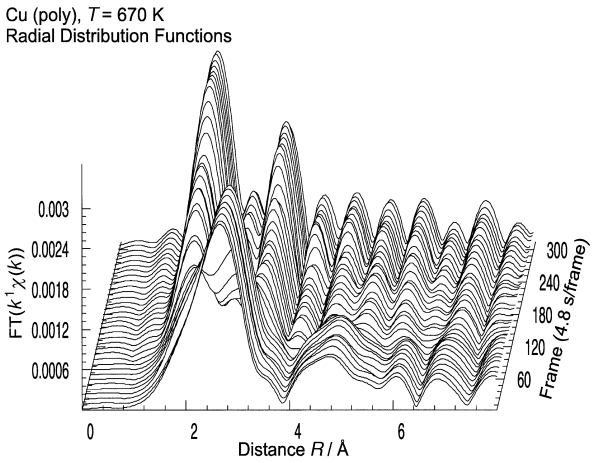

Figure 2. A three-dimensional plot of RDFs (not phase-shift-corrected) for a metal-to-oxide phase transition of supported copper particles at 670 K. Radial distribution functions typical of the copper metal are observed during the exposure to an oxygen–methanol of O_2:$CH_3OH =$ 0.32:2 (frame 0 to 14: 0 s to 67 s) and to a pure methanol gas flow (frame 15 to 64: 72 s to 307 s), respectively. Afterwards, the catalyst is exposed at the time $t = 312$ s (frame 65) to a flow of synthetic air. The metal-to-copper(I) oxide phase transition occurred within 260 s, while the copper(I) oxide-to-copper(II) oxide phase transition is completed after 520 s.

compositions of the gas mixture for several times in the temperature range of 570 to 670 K in order to reproduce the observed effects.

The RDF maximum positions shown as dots in Figure 3 are found to be correlated to the catalytic turnover of methanol in the temperature range of 570 to 670 K. Thus, the apparent nearest neighbor Cu–Cu coordination shell distance (RDF maximum position) decreases with increasing turnover of methanol. This effect is reversed by exposing the catalysts to a gas flow with decreasing oxygen contributions, that is with decreasing conversion of methanol (phases 4–1).[31] Additionally, the corresponding amplitudes of the RDF reveal higher intensities during the treatment in pure methanol and are lower in intensity by exposing the catalysts to a gas flow with increasing contributions of oxygen. The apparent RDF maximum position found under pure methanol reduction treatment corresponds to the bulk metal reference value of 2.57 ± 0.02 Å, while an averaged decrease of the RDFs maximum position of about 0.03 ± 0.01 Å is observed during the exposure to an oxygen–methanol gas flow, that is under partial methanol oxidation conditions. Furthermore, it is found that the corresponding coordination numbers are

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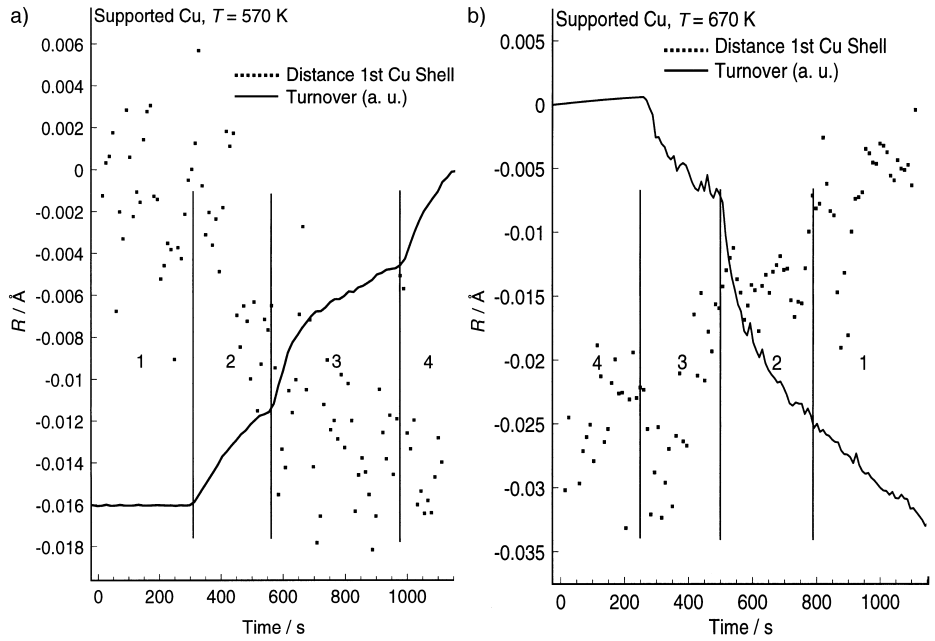

Figure 3. The development of the RDF maximum positions (dots) of the supported copper particle catalyst is shown in relation to the RDF maximum position of bulk copper metal of 2.57 ± 0.02 Å (set to zero at the ordinate axis) under a) increasing oxygen proportions to the gas mixture, that is at an increase of the turnover of methanol with time (abscissa axis) and b) at a decrease of the methanol turnover; phase 1: O_2:$CH_3OH = 0$:2; phase 2: O_2:$CH_3OH = 0.32$:2; phase 3: O_2:$CH_3OH = 0.64$:2; phase 4: O_2:$CH_3OH = 1$:2.

somewhat smaller (9.5 ± 1) than the copper reference value of 12, indicative of the formation of small particles in the course of the methanol oxidation reaction.[32]

The presence of oxygen in copper becomes most apparent as an overall reduction of the RDF maximum positions (as shown in Figure 3) and their corresponding amplitudes during the methanol/oxygen treatment, while these RDF maximum positions and amplitudes reveal their characteristic value for pure metal during the reduction treatment in pure methanol. The oxygen-induced small alterations under isothermal conditions are reproducibly observed several times in the given temperature range of 570 to 670 K after changing the oxygen partial pressure in the gas flow.[33] Unfortunately, the effect is not manifested significantly on the Cu *K*-edge position (1st inflection point) nor on the position and/or amplitude of the first low-energy peak in the XANES, indicating that the presence of oxygen under these conditions has little effect on the electronic structure of the metal, as probed by X-ray absorption. The observed variations can clearly not be attributed to a metal-to-oxide phase transition since the EXAFS and XANES spectra remain typical of copper metal under conditions for the partial oxidation of methanol.

Discussion

It is well known from the literature that particles smaller than about 200 Å have a large fraction of surface atoms and accordingly their RDFs will show a reduction in the coordination numbers compared to the bulk values.[34–37] A recent EXAFS study has shown that the atomic motion in small Cu particles is very anharmonic, resulting in a non-Gaussian pair distribution function.[35, 36] Since the surface atoms move in a more anharmonic potential than the bulk atoms, and furthermore, the fraction of surface atoms increases with decreasing particle size, the pair distribution function becomes more and more asymmetric when going to smaller particles. For Cu, the change in the average nearest-neighbor Cu–Cu bond length relative to the Cu bulk value upon decreasing the particle size from the bulk metal to a 17-Å-large particle is about 0.03 Å at 587 K,[34, 35] which agrees well with the extracted variation of the RDF maximum position found in the copper catalysts sample. Furthermore, an EXAFS study of supported, 10-Å-large Pt particles detected at various temperatures indicates that an apparent bond length contraction with increasing temperature is manifest in the data as a retardation in the phase of the first neighbor oscillation.[37]

The data given in Figure 3 clearly indicate that the small structural changes observed for copper in the catalytic working state cannot be related to changes in the crystalline phase of copper. This is in agreement with observations recorded with X-ray diffraction under similar conditions to those in the present experiments. It is thus suggested that the active copper is not composed of large mosaic crystals but rather of small nanocrystalline units. Such units (ca. 2 nm) would create a large internal surface. A significant amount of oxygen atoms can be stored on its internal surfaces creating structures which are well-known from LEED and STM studies of external copper–oxygen adsorbate systems. The EXAFS spectra recorded under the reaction conditions reveal the modifications of the mean positions of copper atoms at the internal interface. With increasing abundance of intercalated oxygen atoms the mean displacement of copper atom positions increases as the catalytic activity increases.

The time scale of solid-state transformations that occur as a consequence of the immediate response of the active copper to the oxygen partial presure in the gas phase indicates that the intercalated oxygen species are mobile and can easily diffuse, most likely along the internal surface. The surface-sensitive in situ XANES experiments[10–12] have revealed that the catalytic activity of copper is related to the abundance of an oxygen species which is only bonded through s–p valence states and which does not interact with the copper d states, as is characteristic for normal copper oxides. This catalytically relevant oxygen species may well be identical with oxygen atoms diffusing from the inner surface onto the outer surface. This would explain the correlation described in Figure 3. The

EXAFS spectrum reveals a distortion of the copper lattice created by a nanostructuring of the solid and the intercalation of oxygen into the internal interface. This bulk-dissolved oxygen is mobile and segregates to the surface where it either reacts with copper to give an oxide, or creates the active site for oxidative dehydrogenation of methanol. The segregating oxygen is not directly the oxidizing species as the rate of methanol conversion is much faster than the segregation kinetics. It remains to be clarified whether the weakly bound oxygen atom is essential for the active site or whether the distortion of the copper atoms around a segregating oxygen atom become activated for catalysis. It has been documented and rationalized[38, 39] that local geometric distortions in a flat surface can be sites of catalytic activity.

The fact that the nanocrystalline copper interface is three-dimensional in the active catalyst and not two-dimensional as at the external surface allows the detection of its existence by a "bulk-sensitive" method. As the EXAFS method is sensitive to the mean local geometric structure it is more sensitive to such a subtle change in structure than powder X-ray diffraction. In the latter technique the described structure would contribute to modifications of the lineshape of the diffracted intensity which is broadened already by the particle size. In recent in situ experiments such a phenomenon has been detected as displayed in Figure 4. The change in position

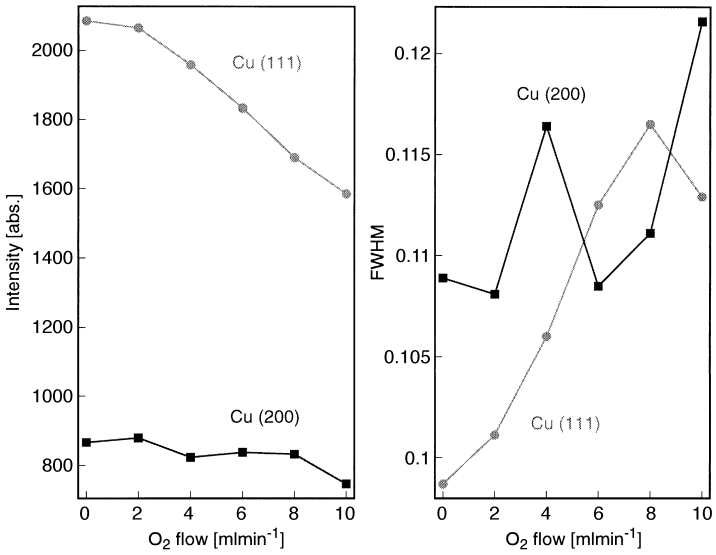

Figure 4. In situ X-ray diffraction of the copper catalysts exposed to a flow of methanol (16 mL min^{-1}) and oxygen (0 to 10 mL min^{-1}) at 625 K. The intensities of both the (111)- and (200)-Cu reflections (left) as well as the variation of the full-width at half maximum (FWHM) of both reflections (right) are given as a function of the oxygen gas flow concentration.

and shape of the copper (111) reflection occurs reversibly upon changing the gas phase from only reducing to catalytic, that is when adding oxygen to the system. This experiment, which has been carried out under a wide range of conditions, complements the in situ EXAFS observations. The width of the XRD profile in Figure 4 is well compatible with a 2 nm average crystallite size and classifies active copper as a nanocrystalline material. The functional correlation of nanocrystallinity and catalytic activity can explain the "magical" industrial practice of activating metallic copper catalysts by careful oxidative pretreatment. The subsequent slow reduction in the reaction gas atmosphere preserves the defects produced by a topochemical oxidation of the bulk copper.

Conclusion

In conclusion, catalytically active copper is a strained nanocrystalline form of the metal. Its transformation into a metastable state allows the bulk solid to respond in its defect structure instantaneously to changes in the chemical composition of the gas phase. The active catalyst can be considered to be a copper solid in its early transition phase towards an oxide structure. The metal is no longer made up from large crystallites, and contains a defect structure in which oxygen is already intercalated. The driving force for this self-organization is the oxidizing potential of the gas-phase oxygen, which is just sufficient to stabilize the initial stage of the bulk transformation of the metal into the oxide by the multiple crackling core-and shell scenario. The working catalyst is thus a thermodynamically destabilized state as compared to a mixture of highly crystalline copper metal and a segregated binary oxide which is always observed in ex situ phase analysis of used copper catalysts. Figure 5 gives a schematic representation of the active state and reveals why the long-range ordering of this state is barely distinguishable from normal copper.

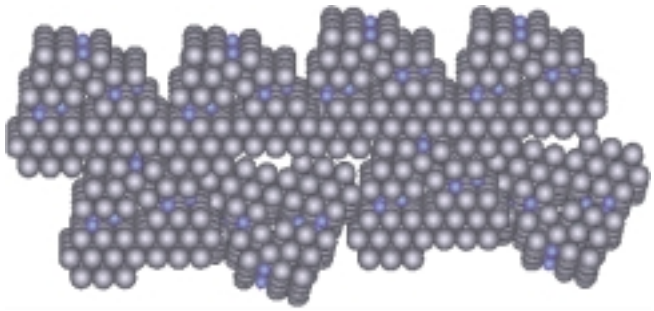

Figure 5. Model of the copper catalyst for the partial oxidation of methanol. The copper catalyst consists of nanocrystals in which the oxygen atoms are intercalated at the large internal surface of the defect structure. The catalyst material can be considered as a copper solid in its initial oxidation state.

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[1] *Gmelins Handbuch der anorganischen Chemie:* Kupfer, Verlag Chemie, Weinheim, Teil B, **1958**, *24; Gmelins Handbuch der anorganischen Chemie:* Kupfer, Verlag Chemie, Weinheim, Teil D, **1963**, *26*.
[2] A. Phillips, E. N. Skinner, *Am. Inst. Min. Met. Eng. Techn Publ.* **1941**, *1280*, 1.
[3] F. R. Rhines, C. H. Mathewson, *Trans. Am. Inst. Min. Met. Eng. Inst. Metals Divis* **1934**, *11*, 337.
[4] E. A. Enofev, F. N. Streltsov, A. N. Solovov, O. F. Velichkina, A. Tabanakov, *Zavod. Lab.* **1988**, 54.

0947-6539/00/0610-1874 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 10

[5] N. H. Santander, O. Kubaschewski, "The Thermodynamics of the Cu–O System", *High Temp. High Pressures* **1975**, *7*, 573.
[6] H. Werner, D. Herein, G. Schulz, U. Wild, R. Schlögl, *Catal. Lett.* **1997**, *49*, 109.
[7] T. Lederer, D. Arvanitis, G. Comelli, L. Tröger, K. Baberschke, *Phys. Rev. B* **1993**, *48*, 15390.
[8] J. Urban, H. Sack-Kongehl, K. Weiss, *Catal. Lett.* **1997**, *49*, 101.
[9] A. Knop-Gericke, M. Hävecker, T. Neisius, T. Schedel-Niedrig, *Nucl. Instr. Meth. A* **1998**, *406*, 311.
[10] M. Hävecker, A. Knop-Gericke, T. Schedel-Niedrig, R. Schlögl, *Angew. Chem.* **1998**, *110*, 2049; *Angew. Chem. Int. Ed.* **1998**, *37*, 1939.
[11] A. Knop-Gericke, M. Hävecker, T. Schedel-Niedrig, *Appl. Surf. Sci.* **1999**, *142*, 438.
[12] M. Hävecker, A. Knop-Gericke, T. Schedel-Niedrig, R. Schlögl, *Catal. Lett.* in press.
[13] I. Böttger, T. Schedel-Niedrig, T. Neisius, E. Kitzelmann, G. Weinberg, D. Demuth, R. Schlögl, *Phys. Chem. Chem. Phys.* in press.
[14] T. Neisius, PhD Thesis, Technische Universität Berlin, **1997**.
[15] M. Hagelstein, C. Ferrero, U. Hatje, T. Ressler, W. Metz, *J. Synchrotron Rad.* **1995**, *2*, 174.
[16] T. Ressler, M. Hagelstein, U. Hatje, W. Metz, *J. Phys. Chem. B* **1997**, *101*, 6680.
[17] T. Ressler, M. Hagelstein, U. Hatje, W. Metz, *J. Phys. IV France* **1997**, *7*, 731.
[18] *ESRF Beamline Handbook,* **1995**, p. 123.
[19] The synchrotron X-ray beam is generated by a low-K undulator and the provided synchrotron radiation photon energy ranges from 5 to 25 k eV.[15] The upstream optics consists of two X-ray focusing cooled mirrors. Both have three different stripes (Rh and Pt coating and a bare strip) allowing different cutoffs without changing the overall geometry of the beamline. The energy-dispersive optics consist of a cooled dynamically bent silicon crystal which is cut with a specific contour and held by a four point bender. The spectrometer consists of a Θ-2Θ goniometer with the monochromator on the Θ axis and an optical bench supporting the sample and the position-sensitive detector which is rotated around 2Θ. A fan of X-rays is detected by a position-sensitive device. Indirect X-ray detection was acheived by means of a fast phosphor lens-coupling optic and a 2D cryogenic CCD detector. The monochromator is operated at a resolution of $\Delta E/E = 2 \times 10^{-4}$. A typical flux of 10^{12} photons per second at the sample and a time resolution below 100 μs can be reached.
[20] J. Find, PhD Thesis, Technische Universität Berlin, **1998**.
[21] J. Wölk, R. Gottschal, G. Mestl, R. Schlögl, unpublished results.
[22] A special designed reactor equipped with gas-flow controllers and a mass spectrometer as product gas monitor is used. A Cu catalyst (14.7 wt% copper) as well as thin polycrystalline copper foils (3 μm thick, 99.98 + %, Goodfellow) are used. The supported catalyst was prepared by using copper carbonate (malachite) supported on carbon and was pressed to a self-supported ≈1-mm-thick pellet. Scanning electron microscopy (SEM) images of the calcinated (heated in air at 400 K for 2 h) and subsequently reduced supported copper catalyst (heated in methanol atmosphere at 670 K overnight) show that the copper spreading on the carbon support cluster decreases after the reduction treatment; this is attributable to a lower surface free energy of small spherical metal particles.
[23] The sample is installed in the flow-through reactor cell where the temperature of the reactor and the sample can be measured independently. For comparison, the oxidation of the Cu foil under synthetic air (20 vol.% oxygen) at various temperatures is also studied. The temperature of the reactor and the flow of the gases are controlled remotely during the data acquisition. The default concentrations of oxygen (synthetic air) and methanol are 5.5 and 11.0 vol%, respectively, in the gas stream (total gas flow: 45 mL min^{-1}). In order to modify the oxygen contribution in the gas stream, the flow of synthetic air was changed.
[24] The I_0 signals through air or graphite are used as the background absorption signals for the Cu(poly) catalyst or the carbon-supported catalyst, respectively. The energy calibration of the EXAFS spectra within a series is performed by means of reference spectra for Cu(poly) foil oxidized in air at the same temperature to CuO which are measured before and after an EXAFS series, and additionally, by means of a reference CuO EXAFS spectrum. The first three peaks at the threshold of the copper *K*-absorption edge at 8.9980 keV, 9.0128 keV, and 9.0517 keV, respectively, and, additionally, the minimum between the second and third peak of the reference spectra are used as energy calibration points.
[25] A. G. McKale, B. W. Veal, A. P. Paulikas, S. K. Chan, G. S. Knapp, *J. Am. Chem. Soc.* **1988**, *110*, 3763.
[26] The EXAFS function $\chi(k)$ (available k range at the Cu *K*-edge: 3.82–9.37 Å^{-1}) of an absorption spectrum is obtained after subtraction of the absorption of a "free" Cu atom (cubic spline fit; 6 splines). Subsequently, the EXAFS functions are multiplied by k^2 in order to enhance the small amplitudes at high k values. The Fourier transformation of the EXAFS function $\chi(k)$ is performed in the k range of 3.78–9.34 Å^{-1} by using a Bessel window (size 4); the backtransformation range is 1.30–2.95 Å. A one-shell fit of the nearest Cu–Cu neighbor radial distribution function (RDF; Fourier-transformed $\chi(k)$) was performed in the r-space by using a constant Debye–Waller factor σ^2 of 0.0195 (also: $S_o^2 = 1$; fit range: 1.04–3.15 Å). The Debye–Waller factor is calculated by means of a one-shell fit of the first Cu–Cu RDF of a metallic Cu(poly) reference spectrum (treated in a methanol gas flow at 670 K). The coordination number of the first Cu–Cu radial distribution function of 12 as well as the metallic nearest-neighbor Cu–Cu distance of 2.55266 Å are held constant during the fit. The phase and amplitude corrections for metallic copper are calculated by using the curved-wave scattering-matrix formalism of J. J. Rehr and co-workers[27, 28] which are used afterwards for the one shell fits.
[27] J. J. Rehr, R. C. Albers, *Phys. Rev. B* **1990**, *41*, 8139.
[28] J. J. Rehr, R. C. Albers, S. I. Zabinsky, *Phys. Rev. Lett.* **1992**, *69*, 3397.
[29] The nearest-neighbor Cu–Cu bond length and the corresponding first-shell coordination number of polycrystalline copper metal and supported copper metal particles treated under a pure methanol flow at 670 K are determined by using a one-shell fit of the first RDF with a constant Debye–Waller factor σ^2 of 0.0195. The Debye–Waller factor was calculated by means of a one-shell fit of the nearest-neighbor Cu–Cu RDF of a Cu(poly) metal reference spectrum (treated in a methanol flow at 670 K). The coordination number of 12 of the first Cu–Cu RDF as well as the nearest-neighbor metal Cu–Cu distance of 2.553 Å are held constant during the fit procedure. The phase and amplitude correction are calculated by using the curved-wave scattering-matrix formalism of J. J. Rehr et al.[27, 28] Coordination numbers in the range of 10.8 ± 1.0 to 12.4 ± 1.0 and nearest-neighbour bond lengths of 2.55 ± 0.02 Å are obtained for the polycrystalline copper bulk sample, indicative of densely packed face-centered cubic copper metal. The coordination numbers of 7.4 ± 1.0 to 8.9 ± 1.0 of the particles are found to be somewhat smaller, while the nearest-neighbor Cu–Cu bond length of 2.55 ± 0.02 Å is found to be the same as in the copper foil.
[30] The alterations are given relative to the RDF maximum position of bulk copper metal of 2.57 ± 0.02 Å ($570 \leq T \leq 670$ K) set to zero at the ordinate axis in the figure.
[31] One-shell fits of the nearest-neighbor Cu–Cu RDF are performed in r-space for both systems by using the FEFF7 computer code of J. J. Rehr et al.[27, 28] The fit-results support the observed variation of the Cu–Cu bond length as a function of the methanol turnover and show a reversible change of the apparent nearest-neighbor Cu–Cu bond length. It is found that the Cu–Cu bond length is reversibly varied if the other fit parameters are held constant ($S_o^2 = 1$, $\sigma^2 = 0.0195$, the phase and amplitude corrections are theoretically calculated).[27, 28]
[32] A constant RDF maximum position is found over a long-time period of about 1600 s (27 minutes) within the statistical variation under steady-state reaction conditions (i. e. at constant methanol turnover), which strongly indicates that external effects related to the X-ray source for example, can be excluded.
[33] In the course of a temperature increase from 573 to 673 K, the thermal expansion of the first Cu–Cu coordination shell distance in the bulk metal is 0.0046 Å (from 2.5852 to 2.5898 Å; derived by means of XRD analysis), which is about a factor of 6 smaller than the observed change of the RDFs maximum position of 0.03 ± 0.01 Å. This strongly indicates that a methanol turnover (i. e. an oxygen) induced bulk lattice distortion is observed in the catalyst systems that cannot be explained only by the thermal lattice expansion or contraction caused

by a possible temperature change in the course of the methanol oxidation reaction.
[34] M. Lenglet, K. Kartouni, J. Machefert, J. M. Claude, P. Steinmetz, E. Beauprez, J. Heinrich, N. Celati, *Mater. Res. Bull.* **1995**, *30*, 393.
[35] B. S. Clausen, H. Topsøe, *J. Catal.* **1993**, *141*, 368.
[36] B. S. Clausen, L. Gråbæk, G. Steffenesen, P. L. Hansen, H. Topsøe, *Catalysis Today* **1994**, *21*, 49.
[37] E. C. Marques, D. R. Sandstrom, F. w. Lytle, R.B Greegor, *J. Chem. Phys.* **1982**, *77*, 1027.
[38] M. Mavrikakis, B. Hammer, J. K. Nørskov, *Phys. Rev. Lett.* **1998**, *81*, 2819.
[39] F. Besenbacher, I. Chorkendorff, B. S. Clausen, B. Hammer, A. M. Molenbroek, J. K. Nørskov, *Science* **1998**, *279*, 1913.

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