High-Pressure Low-Energy XAS: A New Tool for Probing Reacting Surfaces of Heterogeneous Catalysts

A. Knop-Gericke, M. Hävecker, Th. Schedel-Niedrig, R. Schlögl[*]

Department of Inorganic Chemistry, Fritz-Haber-Institute of the MPG, Faradayweg 4-6, 14195 Berlin, Germany
BESSY, Albert-Einstein-Straße 15, 12489 Berlin, Germany

[*] Corresponding author: e-mail acsek@fhi-berlin.mpg.de, phone +49 30 8413 440, fax +49 30 8413 4401

Abstract

An instrumentation is presented allowing to study the X-ray absorption edge spectra of light elements (z =3-15) in the surface-sensitive Auger yield detection at elevated pressures (mbar range). Heterogeneous catalysts can be studied for their surface electronic structure under working conditions in a flow-through reactor mode.

An example of methanol oxidation to formaldehyde over copper metal is studied in detail. A new form of weakly bonded atomic oxygen was found which only exists under reaction conditions. Its existence is linked to defect sites on the Cu. Several mechanistic predictions from earlier low pressure studies could be verified with this in situ experiment.

Introduction

It has been recognised since long [1] that the investigation of geometric and electronic structural details of heterogeneous catalysts should be done under working conditions. This means not only that the gas phase, the pressure and the temperature of the analytical experiment should match the respective conditions of the kinetic experiment (or the "practical" reaction conditions) but also that the performance of the catalytic material under study must be monitored and compared to the performance under the practical conditions. Such experiments are referred to as "in situ".

In recent years an increasing number of high-pressure experiments on heterogeneous catalytic systems has been performed[2] with relatively few of them being in situ in the sense of the above definition. Only few techniques lend themselves to such investigations. Photons in the VUV range (100 eV – 1000 eV) are suitable probes for the electronic structure of reacting surfaces. Their interaction with solid matter leads to photoabsorption processes which can be detected by the Auger electrons created by the relaxation of the core holes. Photons of this energy interact also moderately strong with gas molecules giving rise to the same type of photoabsorption-electron emission processes.

The gas phase absorption limits the useful pressure range of the experiments to about 1 - 10 mbar depending on the nature of the gas phase and the brilliance of the excitation source. This limiting process allows on the other hand to devise an elegant method of on-line gas analysis and allows hence to monitor the catalytic performance exactly real-time and without further analytical instrumentation. As gas phase photoabsorption spectra are characteristic for each type of molecules and spectra of all non-hydrogen atoms in a molecule can be recorded, it will often be possible to analyse mixtures without separation. Limits exist in the detection of trace amounts and in the distinction of large molecules and isomers. For many practical applications with catalytic

High-Pressure Low-Energy XAS: A New Tool for Probing Reacting Surfaces of Heterogeneous Catalysts, A. Knop-Gericke et al., Topics in Catalysis, 2000

2

reactions of small molecules the analytical power is, however, fully adequate.

The detection of the signal from the solid surface is no problem as long as an element is investigated which is not contained in the gas phase. Then the free surface and adsorbates can be analysed by virtue of the surface-sensitivity of the Auger electrons used for detection leading to a depth of information of typically several nm. When all secondary electrons are used for detection the analysis can be made less surface-sensitive probing about 10 nm of the bulk. Typical cases are the investigation of 3 d metal L edges which can be informative about the oxidation state of a working catalyst.

Many investigations require, however, the analysis of carbon, oxygen, nitrogen or sulphur K edge spectra which are also constituents of the gas phase. It is thus necessary to have a procedure which allows the separation of the total signal into a large part of the gas phase and a small signal from the adsorbate/surface. The procedure which is described below uses a combination of several detector signals allowing to normalise out either the solid or the gas phase signal. In this way two sets of raw data are obtained which characterise at the very same moment the solid surface and the gas phase above it. In this way correlation between spectral features and catalytic performance can be obtained. When multiple steady states are obtained in a system, the resulting correlation can be used to undoubtedly establish a stringent connection between surface electronic structural details and their catalytic relevance.

The present paper describes in the following sections the experimentation and data analysis. In a further section the example problem of copper as a catalyst for selective oxidation of methanol to formaldehyde will be introduced. The main section reports on the results of the application of the new in situ method to this problem and puts the results in perspective to other findings in this system. Methodical conclusions indicate application potential and further developments.

The Instrumentation

The instrument consists of two chambers [3], one attaching the reactor to the front end of the synchrotron storage ring and the other serving as reactor. The reactor is separated from the UHV of the storage ring by a polyimide window array which is sufficiently transparent to low-energy X-rays[3] and allows to raise the pressure in the reactor up to 20 mbar, the maximum useful operation pressure at the BESSY I synchrotron used in these experiments.

The reactor can be operated as a batch reactor or in a flow-through mode. The large dead volume necessary to insulate the catalyst sufficiently from the walls and from the window of the chamber leads to a mixed operation mode between plug-flow and continuously stirred tank reactor. The preservation of the thermally labile reaction product formaldehyde in the flow through mode as opposed to a quantitative decomposition of formaldehyde into CO and hydrogen in the batch mode indicates that a significant gas exchange is reached in the flow-through mode.

The sample is heated resistively with the heating wires well shielded from the gas phase by a AlN / BN housing. Blank experiments showed less than 5% conversion of methanol under operation conditions without the copper catalyst in place.

A schematic drawing of the detector arrangement is presented in Figure 1. The synchrotron light beam is monitored in the UHV chamber yielding the I_o signal.
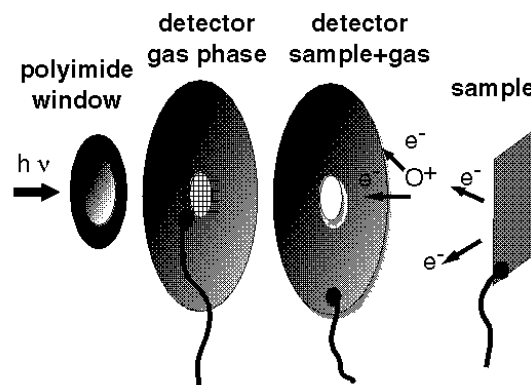

Fig. 1

Figure 1. Array of detectors used in the tank reactor. The detector electrodes are made from carbon-passivated nickel which showed excellent stability in work function and absolute chemical inertness under the reaction conditions employed. The electrodes are set to variable bias potentials via battery boxes and the electron current to ground is recorded by means of precision current meters (Keithley).

After passing through the window the beam is monitored again by a total electron detector in the form of a grid monitoring the absorption of the beam by the window and by the gas phase. A consecutive detector electrode monitors a combined signal from the gas phase and from the solid sample absorptions. Finally, the sample current is monitored which contains an independent but not surface-sensitive information about the sample XAS signal. The array of the detectors is mounted within 10 mm between the window and the sample surface. The sample is mounted on a precision manipulator allowing to position the sample between 5 and 25 mm in front of the detector plate. In this way a reasonable match between the detector dimensions and the mean free path of the Auger electrons at pressures in the millibar range is maintained. The thermal conductivity of the sample which can be heated to 1000 K is the limiting factor for the proximity of the sample to the detector assembly and to the window which requires high pressure water cooling.

The gas phase is maintained constant in its inlet composition by means of differentially pumped (cold traps, membrane pumps) gas flows regulated with mass flow controllers. Volatile liquids can be dosed by passing He through saturators filled with the respective liquid. The conversion and calibration of the system can be controlled independently from the XAS data by a quadrupole mass spectrometer attached via a calibrated leak to the reactor

High-Pressure Low-Energy XAS: A New Tool for Probing Reacting Surfaces of Heterogeneous Catalysts, A. Knop-Gericke et al., Topics in Catalysis, 2000

3

tank. Calibrations of the mass spectrometer for CO_2, oxygen and methanol allow the control of the gas phase composition before and during catalytic reaction experiments. Further details of the instrumentation can be found in the literature[3,4].

The data analysis

Each scan through the XAS energy range produces four spectra and a data set of the gas phase composition by mass spectrometry. During conversion measurements the gas phase data from the XAS spectra give a more accurate composition, as secondary reactions at the mass spectrometer filament with e.g. highly abundant oxygen are avoided. The sample current is normally not used to derive the signal of the reacting surface. It is inspected as control signal for avoiding spurious artefacts during normalisation.

The data analysis is exemplified in Figure 2. The raw data are calibrated in energy using either the maximum of the π^* resonance of gaseous oxygen (or any other suitable gas component) or the inflection point of the metal L3 edge absorption. Then the signals from the gas phase detector and gas phase plus sample detectors (see Figure 1) are normalised by the I_0 signal. The gas phase signal is subtracted from the gas phase plus sample signal leading to the surface-sensitive sample signal as indicated in Figure 2. This signal is small (about 10%) compared to the gas phase signal. The data treatment is considered as completed if no negative intensity occurs in the sample signal. The example in Figure 2 reveals the growth of Cu_2O on Cu in a gas mixture of oxygen to methanol 1:1. The combined signal is dominated by the spectrum of gaseous oxygen with its sharp π^* resonance at 530.8 eV (calibration point for the energy) and the σ^* resonances at 539.2 eV and 541.4 eV. Structures at 534.0 eV and at 537.3 eV (shoulder) indicate the presence of methanol in insufficient abundance to prevent the oxidation of the metal. The resulting surface spectrum with its characteristic white line at 532.8 eV is clearly [5] resolved from the data analysis procedure.

The selective oxidation of methanol over elemental copper

Pure copper is used as unsupported catalyst for the oxidehydration with air of alcohols to aldehydes. The reaction of methanol to formaldehyde

$$2CH_3OH + O_2 \rightarrow 2\,H_2CO + 2\,H_2O \qquad (1)$$
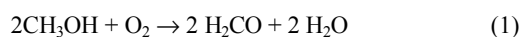
is a good model reaction using a simple substrate. Its conversion vs. temperature profile is very similar to that of the more relevant higher alcohols. The fact that the conversion of methanol runs up to 75 % with over 80% selectivity to formaldehyde and the fact that the reaction is very fast (transport-limited kinetics) render this process suitable for fundamental model studies. Figure 3 shows a typical temperature profile of a flow reaction experiment. The reaction was limited in conversion in order to better control the temperature of the experiment by feeding an excess of methanol over the stoichiometrically required 2:1

ratio. At 550 K a peak of CO_2 evolution marks the removal of the native oxide layer from the copper surface (total
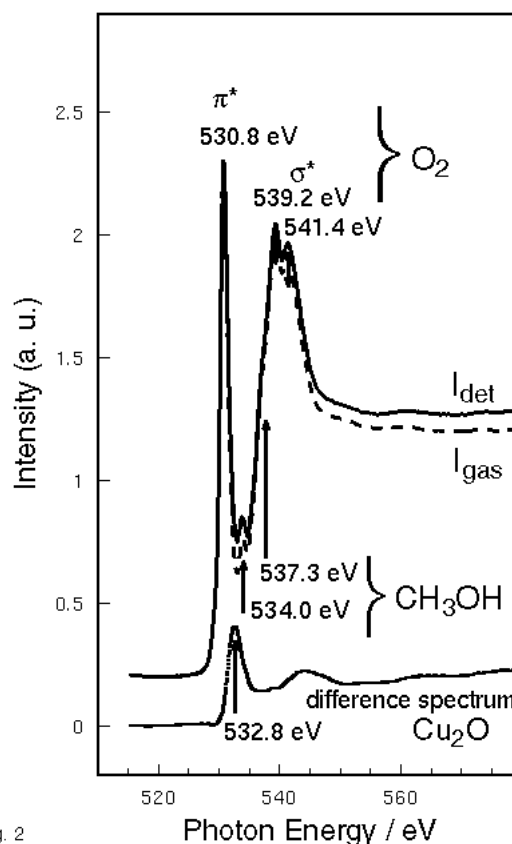
Fig. 2

Figure 2. Example of data reduction from a reaction experiment. The temperature was 520 K, the pressure was 0.52 mbar and the catalyst sample was polycrystalline copper foil. The spectra are normalised for the window transmission and calibrated for the first resonance of the gas phase oxygen signal. The sample is fully oxidised under these conditions leading to no discernible conversion of methanol in these raw data. The data shown are smoothed difference spectra. A FFT smoothing procedure with a small cut-off parameter of the Fourier transform signal is used in order to preserve the spectral shape [32].

oxidation). This layer does not catalyse the formation of formaldehyde which is in agreement to earlier observations [6] stating that copper oxide is not the selectively acting phase in the system. The amount of oxygen required to account for the reactions to formaldehyde and CO_2 is larger than the actually measured oxygen conversion. The deficit becomes smaller with increasing temperature. The copper oxide and eventually dissolved oxygen act as additional supply for oxygen during this temperature-programmed experiment. Under steady state conditions above 623 K this difference vanishes completely without, however, complete loss of the total oxidation pathway. It must be concluded that CO_2 is not only the product of the initial activation of the catalyst which is poisoned at temperatures up to 530 K (Figure 3, onset of CO_2 peak) by the oxide layer, but that an additional pathway transforming gas-phase oxygen into a total oxidising agent exists at steady state conditions.

High-Pressure Low-Energy XAS: A New Tool for Probing Reacting Surfaces of Heterogeneous Catalysts, A. Knop-Gericke et al., Topics in Catalysis, 2000

4

The robust kinetic behaviour allows the use of in situ reactors designed to the needs of spectroscopy and not optimised for the reaction kinetics. The reaction parameters can be varied over a wide range of conversions allowing convenient reaction monitoring and a correlation with spectroscopic data.
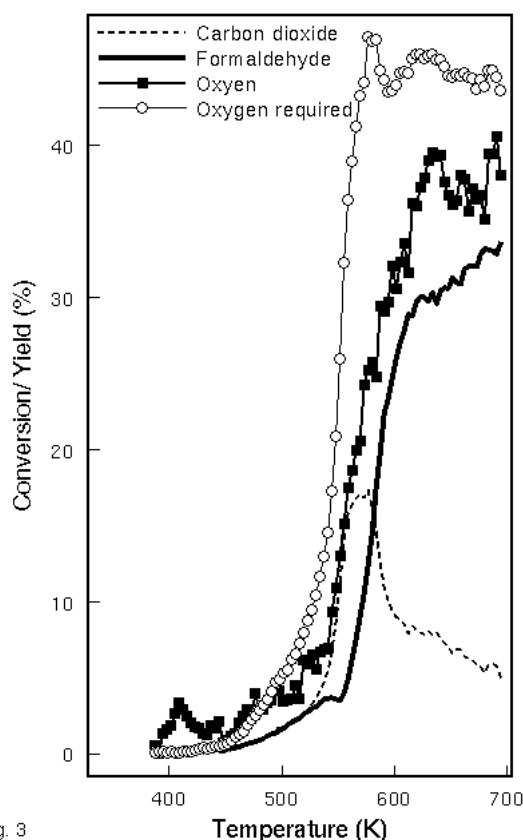

Fig. 3

Figure 3. Temperature profile of the selective oxidation of methanol over a copper tube. The catalyst was an empty copper capillary wound into a spiral of a path length of 100 cm. A ratio of 3:1 methanol to oxygen was used at a temperature ramp of 15 K/min. A gas flow was applied of 60 ml/min diluted in 100ml/min He.

Technical Cu catalysts require an activation procedure in which the metal is pre-oxidised and then reduced under feed at operation temperature. This activation sheds some doubt on the notion that pure elemental copper is the active phase in the system. Post-reaction analysis with either X-ray diffraction or XPS revealed, however, only elemental copper besides a thin layer of oxide ascribed to a transfer artefact. Also in situ X-ray diffraction results [6] indicated the existence of only copper as active phase during selective oxidation of methanol.

The reaction exhibits rate oscillations in a wide range of parameters [6]. This was ascribed in an earlier study on acrolein oxidation to an interchange of the catalyst between an oxide and a metallic state [7]. The frequency of these oscillations is on the order of hours per period in contrast to the rapid rate oscillations described with the methanol oxidation in the second to minute frequency range.

Figure 4 shows temperature-programmed reduction experiments with copper oxides revealing for all compositions below CuO the existence of (metastable) intermediate compositions of copper plus oxygen species.
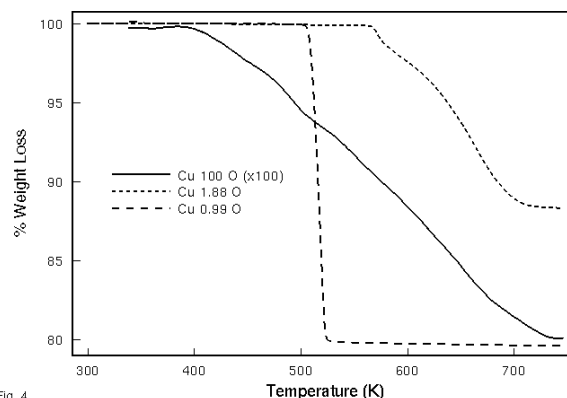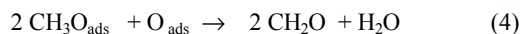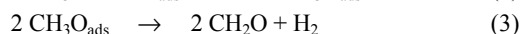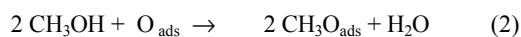

Fig. 4

Figure 4. Weight loss curves of copper oxide species during reduction in 5% methanol in nitrogen. The $Cu_{100}O$ sample was a commercial copper metal tubing used to fabricate the reactor used for the experiment described in Figure 3. The $Cu_{1.88}O$ sample contained an impurity of CuO giving rise to fast initial weight loss. The different onsets are caused by different heatings ramps and different morphology of the samples.

Even nominally pure copper (X-ray diffraction) still contained oxygen which was easily removed by methanol vapour. The formation of sub-oxides seems to be a slow process as during reduction of CuO there is no time to form the sub-species as can be seen from the extremely narrow temperature profile of the reduction. This indicates that the existence of CuO under reaction conditions is highly unlikely whereas all oxides at and below a composition Cu_2O seem to exhibit a (kinetic) stability against reduction in methanol at relevant temperatures. The inhibiting oxide scale determining the conversion vs. temperature profile shown in Figure 3 is thus likely to be Cu_2O.

In an in situ XAFS study of the system at the Cu K edge it was found that a copper particle catalyst supported on graphite exists under reaction conditions in the metallic state. A clear correlation was found between the catalytic activity of the sample and a small apparent reduction in the first nearest neighbour distance. This is interpreted as a breakdown of the normal EXAFS analysis due to the presence of stress/strain which was thought to be the consequence of the dissolution of oxygen in the bulk of the copper [8]. Previous EXAFS studies at the Cu K edge did not observe any effect of adsorbed or dissolved oxygen on the structure of Cu particles [9].

These findings point to the necessity to interrogate the electronic structure of copper during methanol oxidation. Copper sub-oxides [10] with possibly modified electronic bonding characteristics may be candidates for the active phase of the selective oxidising surface. In surface science studies of the reaction it was already concluded that a "partially oxidised" copper surface should be the active state

High-Pressure Low-Energy XAS: A New Tool for Probing Reacting Surfaces of Heterogeneous Catalysts, A. Knop-Gericke et al., Topics in Catalysis, 2000

5

of the catalyst [11]. In this study and in an extension of the work to polycrystalline surfaces [12] a combined reaction mechanism comprising dehydrogenation (3) and oxidehydration (4) was suggested to operate from a methoxy precursor (2):

$$2\,CH_3OH + O_{ads} \rightarrow \quad 2\,CH_3O_{ads} + H_2O \qquad (2)$$
$$2\,CH_3O_{ads} \quad \rightarrow \quad 2\,CH_2O + H_2 \qquad (3)$$
$$2\,CH_3O_{ads} \; + O_{ads} \rightarrow \quad 2\,CH_2O \; + H_2O \qquad (4)$$

In a slow reaction the decomposition path via formate was also found to occur without the presence of adsorbed oxygen (5).

$$2\,CH_3O_{ads} \quad \rightarrow \quad CHO_{2\,ads} + CH_4 + 0.5\,H_2 \qquad (5)$$
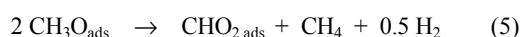
The respective surface species were all identified[12] by photoemission and HREELS at temperatures around 300 K. At higher temperature the molecular beam technique had to be used to detect the reaction products with, however, only limited access to the structure of the reaction intermediates [13]. The oxygen species present on the surface should be "nucleophilic" [11] which indicates a weak bonding to the copper and a structure different from that of an oxide. LEED structural studies under various conditions [14] reveal, however, that the copper oxygen surface structures are all similar to the motif of a copper-oxygen tetrahedron [15] characteristic for copper oxide. A strong copper-oxygen interaction can be expected in all these species. This follows also from the interpretation of photoemission and photoabsorption studies of copper oxides [5,16-18] which all point to strong hybridisation of the oxygen 2p states with copper d-states excluding a strongly "nucleophilic" character of such oxygen species.

The presence of strongly bound methoxy together with pre-adsorbed surface oxygen was identified by STM of Cu (110) [119] and verified by post-reaction XPS analysis [6] on copper foil. The relevance of these methoxy species as reaction intermediates was concluded from the reaction of the two adsorbates at 300 K under the assumption that the product should be formaldehyde at these temperatures [20]. The resulting conclusion that the selective oxidation occurs at the boundaries between oxide islands and surrounding adsorbed methoxy should also be tested under practical conditions. Further important conclusions from the surface science studies [11,12,19,20,21] indicate that completely oxygen-covered surfaces are inactive as no methoxy can be formed (see also discussion of Figures 3,5), that the reaction above 450 K should only proceed via the oxidehydration path (equ. 4) and that partially oxygen covered surfaces are most active in the overall reaction. It was also found that the distribution between several reaction pathways at a given temperature can be strongly time-dependent with the absolute time scales (of many minutes) of the surface science data having little in common with a fast reaction observed at practical reaction conditions.

Results of the in situ XAS

The catalytic performance of a polycrystalline copper foil within the in situ reactor set-up operated in the flow through mode is shown in Figure 5. The overall characteristics of the temperature profile is very similar to that shown for the tubular reactor in Figure 3. The "light off" shape of the conversion profile and the observation of the initial formation of CO_2 allow to conclude that the reaction is oxygen inhibited at lower temperatures. The mismatch in light-off temperatures between the two experiments and the lower CO_2 evolution in the in situ experiment can thus be attributed to a reduced inhibition of the pre-cleaned copper foil as compared to the thicker oxide scale on the copper tubing. The initial activity for selective oxidation was in both experiments at 450 K in excellent agreement with the surface science data [10].
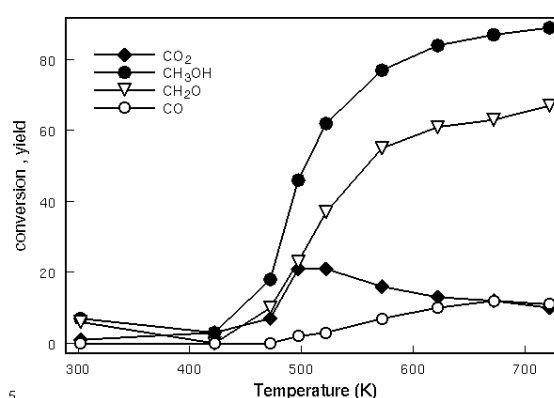
Fig. 5

Figure 5. Conversion vs. temperature profile for methanol oxidation over a copper foil in the in situ reactor. The gas feed was stoichiometric 1:2 oxygen to methanol applied at 0.59 mbar. The symbols mark the experimental data, the lines serve as guide to the eye. The low CO yield from thermal decomposition of formaldehyde is a good indication of the good mixing in the reactor. In the batch mode of this reactor all formaldehyde is decomposed into CO.

The very good selectivity is a consequence of the low overall pressure and the a typical low loading of the catalyst with reactants. The data show, however, that the operation conditions of the copper in the in situ reactor can be well compared to those of a realistic catalyst application. The difference in total pressure of three orders of magnitude between the reaction experiments in Figure 5 and 3 is not affecting the catalytic performance in a qualitative way. The state of the surface in the in situ experiment is thus expected to be representative of that of the practical catalyst. The fact that about 90% of the methanol is consumed in this reactor indicates that its sticking probability is high under the given conditions of simultaneous presence of oxygen and methanol [22].

Rising the temperature in the in situ experiment above the light off temperature leads to increasing decomposition of the product into CO (and hydrogen). This temperature dependence indicates the chemical origin of the

High-Pressure Low-Energy XAS: A New Tool for Probing Reacting Surfaces of Heterogeneous Catalysts, A. Knop-Gericke et al., Topics in Catalysis, 2000

6

decomposition and excludes the notion that gas phase beam damage of the synchrotron light is the cause of this reaction which is also well known under technical conditions [22].

The identification of the reaction products in the gas phase which is illustrated in Figure 6 allows further to exclude a detection artefact by the hot filament of the quadrupole mass spectrometer which would also decompose formaldehyde. In Figure 6 an experimental carbon K edge gas phase spectrum is compared with weighted intensities of the components CO, CO_2, methanol and formaldehyde. It occurs that the π^* resonances of the molecules together with their molecular skeletal anti-bonding states are highly characteristic allowing the non-destructive separation and quantification of this gas mixture which is difficult to analyse by other means such as chromatography or mass spectroscopy.
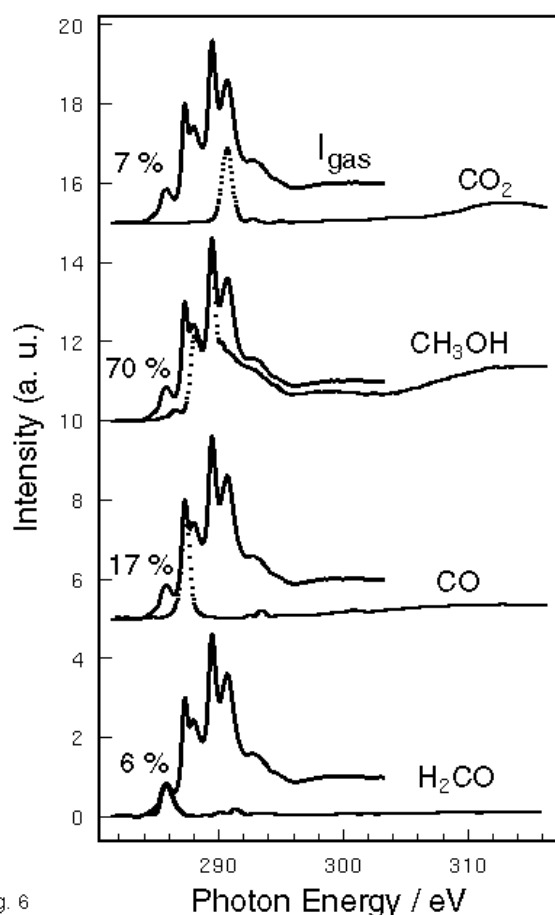
In situ Cu L edge spectra

The copper L edge spectra of the reacting surface are shown in Figure 7. From 300 K up to 540 K the spectrum is typical of Cu_2O with its characteristic white lines seen in the bottom spectrum of Figure 7. At 540 K the copper oxide is decomposed under reaction conditions within ca 20 min leading to a metallic surface. This information holds for the volume probed by these spectra. The inelastic mean free path length was estimated [23] to be 12 nm for this system corresponding to about 30 monolayers of copper oxide.
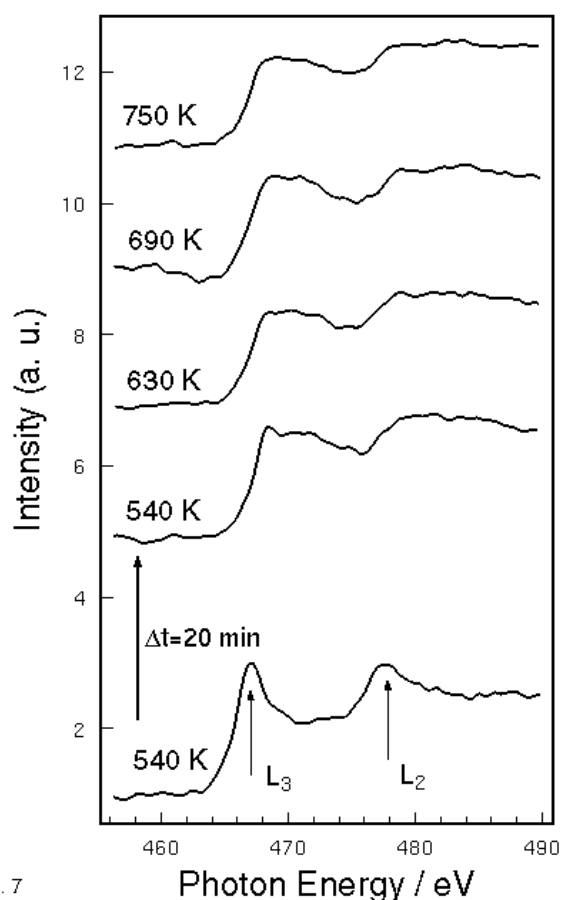

Fig. 6

Figure 6. Gas phase X-ray absorption spectra at the carbon K edge of a reaction mixture methanol :oxygen 2:1 passed at 500 K and at 0.67 mbar over polycrystalline copper. The solid spectrum arises from the reaction mixture, the dotted reference spectra are weighted in their intensities to match the spectrum of the mixture. The reference spectra were obtained from pure components measured without catalyst in the reactor. The percentage contribution from each component is indicated. The energy scale is calibrated by the molecular oxygen peak measured at the oxygen K edge where all molecules exhibit additional characteristic features (not shown). The following photon energies characterise the positions of the main resonances: H_2CO: 286.8 eV; CO: 287.3 eV; CH_3OH: 288.0 eV and 289.4 eV; CO_2: 290.7 eV.

Fig. 7

Figure 7. X-ray absorption spectra at the copper L2,3 edge for a in-situ reaction experiment with copper foil. The gas feed is 2:1 methanol: oxygen and applied at a pressure of 0.59 mbar. The detection is done in the secondary electron yield mode.

From analysing pure copper oxide in the partial electron yield mode which yielded a mean free pathlength of 3 nm and by applying the rule that the depth of information is three times the value for the inelastic mean free pathlength it can be concluded that the surface layer would contribute about 20 % of the intensity of the spectra in Figure 7. This means that a fractional monolayer coverage with oxide affecting the shape of the spectra between 640 K and 690 K which was postulated as active state from surface science experiments (see above) may not be excluded by the analysis of the copper XAS data.

High-Pressure Low-Energy XAS: A New Tool for Probing Reacting Surfaces of Heterogeneous Catalysts, A. Knop-Gericke et al., Topics in Catalysis, 2000

7

In Figure 8 the copper L edge data are shown of a series of isothermal conversion experiments in which the oxidising potential of the gas phase was varied. The slightly lower pressure of 0.4 mbar as compared to the data in Figure 7 significantly improved the data quality allowing to state that the existence of copper oxide ceases at stoichiometric gas phase compositions. All spectra measured in excess of methanol over oxygen exhibit with high quality the metallic edge features corroborating that copper oxide is barely present and has nothing to do with the main reaction pathway of selective oxidation which is dominating at 670 K (see Figures 3 and 5). This conclusion is also in line with the surface science data described above.
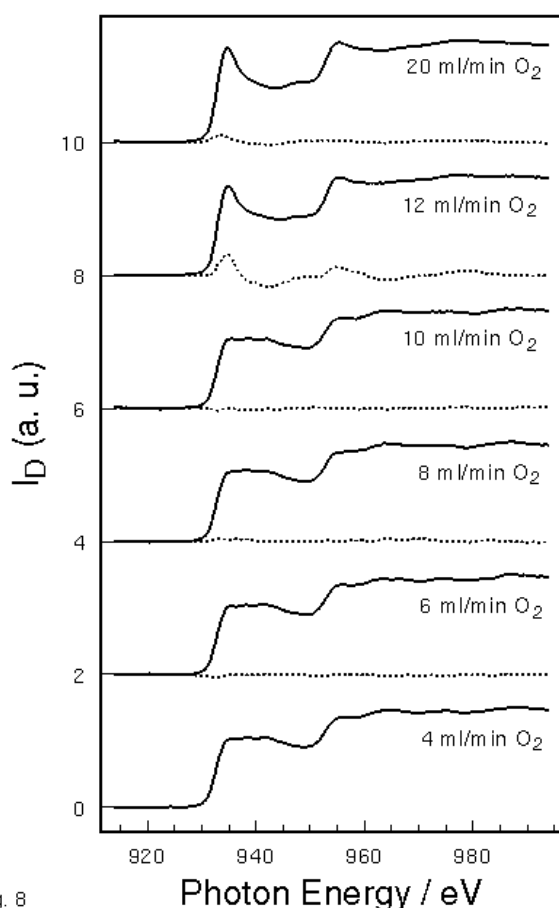

Fig. 8

Figure 8. X-ray absorption spectra at the copper L2,3 edge for an in situ reaction experiment with copper foil. The total pressure is 0.4 mbar and the temperature is set to 670 K. The methanol gas feed was fixed to 20 ml/min. The oxygen feed was varied from net oxidising to net reducing as indicated in the Figure. The difference spectra indicate the respective change from top to bottom between successive spectra.

Carbon species

No carbon species are present on the reacting surface in amounts detectable by the XAS technique. As no carbon is present in the bulk, all signal which is not accounted for by the gas phase species would come from the adsorbates giving the method here a much higher sensitivity than in the case of the copper spectra. The gained sensitivity is lost, however, by the intrinsically lower signal which is obtained

at the carbon K edge due to the presence of carbon in the window and on the optical elements of the light source. The detection limit in high pressure mode is estimated to be 0.1 monolayers for methoxy species. Significantly more than this coverage was detected in ex situ studies at Cu (111) [13] allowing to conclude that this stable adsorbate is a spectator species.

The conversion of methanol was found to be about 1×10^{15} molecules/cm^2 catalyst. Would the whole surface be active then a turnover frequency of about 1s^{-1} would result. This is in contradiction to the fast reaction kinetics deduced from the high conversion despite the unfavourable reactor geometry and to the absence of site blocking by either oxygen (no oxide) or by stable methoxy (no carbon signal). It has thus to be concluded that only a small fraction of the total surface atoms is actually involved in the catalytic action.

In situ O K edge spectra

The oxygen K edge absorption spectra from the experiment discussed with Figure 7 are shown in Figure 9. At 540 K the surface is still covered with Cu_2O. The shape and position of the white line as well as the position of the σ^* resonance at
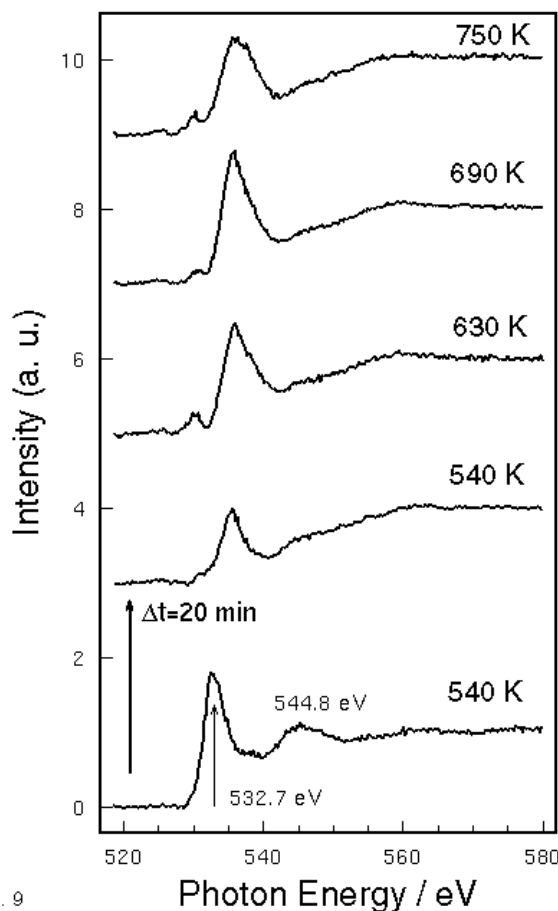

Fig. 9

Figure 9. X-ray absorption spectra at the oxygen K edge. The data were obtained in the experiment described in Figure 7. The maximum of the main new feature is situated at 535.2 eV.

High-Pressure Low-Energy XAS: A New Tool for Probing Reacting Surfaces of Heterogeneous Catalysts, A. Knop-Gericke et al., Topics in Catalysis, 2000

8

higher energy agree well with earlier studies and are identical to the data from ex situ XAS experiments [3,4,5,16,18]. At higher temperatures where the copper L edge spectra indicate the metallic character of the surface there remain oxygen species. The bonding characteristics change, however markedly with the reduction of the oxide. XPS data were insensitive to the spectral change at 540 K as under non-reaction conditions only copper Cu_2O could be detected. The broad feature at 535.5 eV has not been observed in any copper oxide before. Its position and shape is incompatible with a white line feature. It is thus concluded that this species is an atomic oxygen which interacts only via the s-p bands with copper but which has no hybridisation with the copper d-band [5]. The very small feature at 630 K and higher is a small white line which is not associated with the main species but which arises from additional normal copper oxide as will be shown below. Its changed position relative to that of a thick layer of Cu_2O is ascribed to the intimate contact with metallic copper over which it forms a tin layer as seen in STM studies [14,19].

The drastic difference in the O K edge spectral properties between normal oxide and the weakly bonded species is illustrated in Figure 10. The absence of resolved high-energy
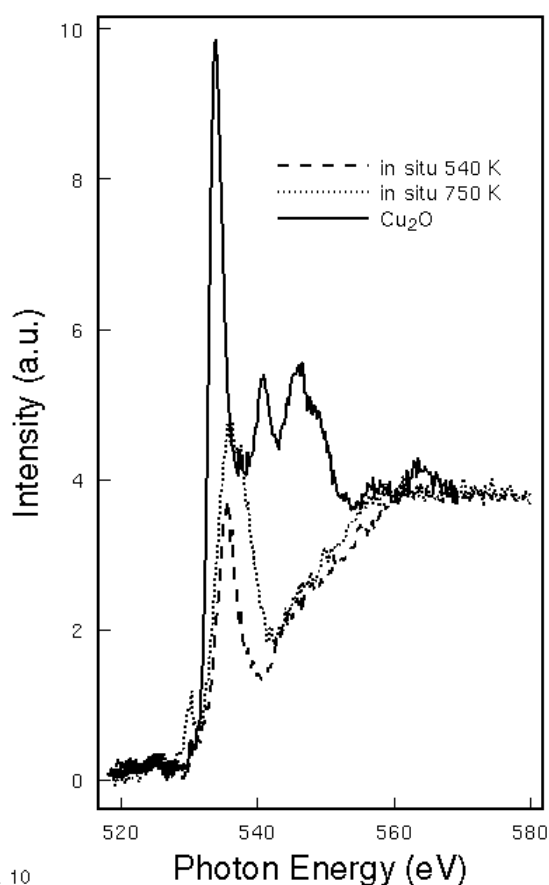

Figure 10. X-ray absorption spectra at the oxygen K edge of copper oxygen species. The in situ data were taken from Figure 9. The ex situ Cu_2O was obtained by reacting a Cu (111) crystal at 0,05 mbar with oxygen at 600 K. All spectra are normalised for a common edge jump at 580 eV. The energy scale was calibrated with the Cu L3 edge position. The onset of all spectra coincide and fit to the position of the XPS oxygen 1s photoemission spectra determined ex situ.

features in the in situ spectra is not due to the mode of observation as was shown with worse resolution in a reference experiment [3,5]. The new oxygen species is closely related to the catalytic conditions as it was not possible to keep the species in its state upon removing the atmosphere or cooling it down from reaction temperature. In such experiments the new species disappeared and Cu_2O remained on the surface. The data of Figure 10 further show that the shape of the only resonance of the in situ species changes with sample temperature. It was easily possible to fit two components with the same profile and width under the resonance lines. With increasing temperature the high energy component increases in abundance as can be seen by the broadening of the line. The assignment is done in analogy to the silver-oxygen system where atomic oxygen is known to exist in adsorbed and bulk dissolved states without forming an oxide [5,24]. In this picture the lower energy contribution describes weakly bonded oxygen atoms at the surface and the higher energy component arises from oxygen atoms dissolved in the bulk of copper without forming an oxide. The shift would indicate the electronic influence of the free electrons on the oxygen atom which is different at the surface and in the bulk of the metal substrate. The weak interaction between oxygen and copper is taken as sign of the mere atomic rather than anionic form of this metastable species.

The identification of oxygen species relies on the absence of carbon, as methoxy and possibly formate which could obscure the analysis [12]. In the literature the oxygen XAS signature of methoxy is well documented with positions of 534 and 539 eV (main peak) on Cu (100) [25]. At these positions no peaks are observed in the present study corroborating the absence of a detectable coverage of the active catalyst with carbon oxygenates. In a recent study of methoxy on Cu (111) a third peak at 531.5 eV was ascribed to methoxy [26]. This peak seems to be, however, well accounted for by an oxide species co-adsorbed with methoxy.

The X-ray absorption data at the oxygen K edge from the experiment described with Figure 8 are shown in Figure 11. The position of the sharp feature at 531.6 eV is shifted compared to that of Cu_2O (532.8 eV). Penetrating oxygen atoms create strain in the copper network. The strain results in a shift of the Cu 3d states [30]. The main peak in Figure 11 is with 536.4 eV also not identical to the position of the same feature in Figure 9 where it occurs at 535.5 eV. The strain terminates in defects at the copper surface. These defects might be different. The features around 536 eV in the oxygen K edge spectra shown in Figure 9 and Figure 11 represents the signal of oxygen atoms probing these distribution of defects.

The significant change in the character of the oxygen species seen at stoichiometric gas phase composition in the copper spectra is well reflected in the oxygen spectra. Under oxidising conditions the metastable weakly bound oxygen species co-exists with "normal" oxygen. The top two spectra of Figure 11 are superpositions of the spectral features shown in Figure 10. The other spectra in Figure 11 indicate

High-Pressure Low-Energy XAS: A New Tool for Probing Reacting Surfaces of Heterogeneous Catalysts, A. Knop-Gericke et al., Topics in Catalysis, 2000

9

the dominance of the weakly interacting species over an oxidic form which is, however, neither bulk Cu_2O nor the species seen in Figure 9. Electrochemical studies [27] revealed modified spectral parameters of mixed-valence sub-oxides occurring during oxidation of bulk copper in a surface-near region in contact with bulk metal. Such Cu_xO compounds are candidates for the species seen here with in situ XAS. The data in Figure 11 further show the change in the oxygen bonding by a modification in the high energy (EXAFS) part of the spectra. No attempts have been made, so far, to exploit this additional information.
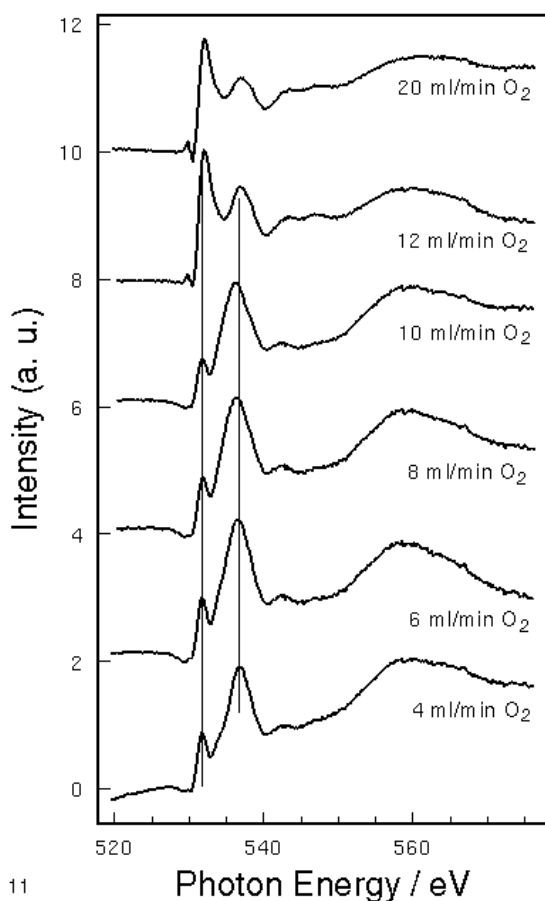

Figure 11. X-ray absorption spectra at the oxygen K edge of copper oxygen species. The data were obtained in the experiment described with Figure 8.

Correlations between catalytic activity and electronic surface-structure of the catalyst

The fact that under reaction conditions the weakly interacting species was identified at all ratios of methanol to oxygen should give rise to the occurrence of formaldehyde in the reaction gas mixture irrespective of the oxidised or reduced state of the copper surface. Exactly this is found in the conversion data of the experiment described with the spectra in Figures 8 and 11. Figure 12 summarises the analysis. In inset A the conversion is plotted against the oxygen flow. At all conditions a significant conversion is observed. As in the spectral responses there is a strong change in the conversion at the point of stoichiometry of the

methanol to oxygen gas mix. At overstoichiometric conditions the conversion is much lower than at understoichiometric conditions which is surprising in the light that oxygen is required for the oxidehydration and total
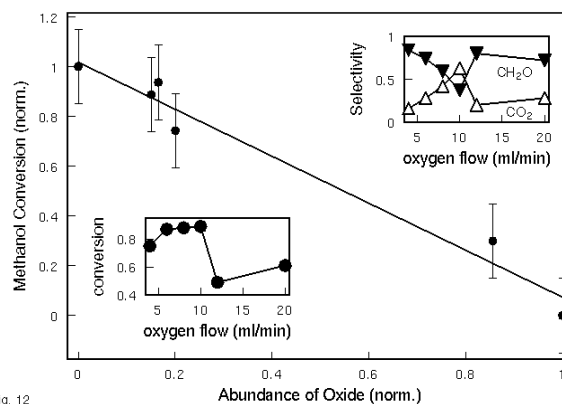

Figure 12. Correlation of the catalytic and spectroscopic parameters for the isothermal in situ experiment described with Figures 8 and 11. In the main plot the relative abundance of the copper oxide (feature at 531.5 eV) is correlated with the conversion of methanol. The maximum of conversion is normalised at 1 after subtraction of the conversion minimum. Inset A shows the evolution of the conversion of methanol with the amount of oxygen in the gas phase. Inset B shows the effect of this parameter change on the selectivity of total and partial oxidation respectively.

oxidation reactions. The data suggest that the oxidic species found in XAS is inhibiting the reaction. This was already concluded from the conversion vs. temperature curves seen in Figures 3 and 5. The main plot in Figure 12 relates the conversion of methanol with the abundance of the oxide species detected in Figure 11 (low energy feature). The correlation is good in view of the difficulties to accurately determine the abundance of the inhibiting oxide from one peak area lying in the onset of a spectrum of a different species. It occurs that the oxide is indeed inhibiting the methanol conversion. This is in line with the surface science experiments assuming that the data of the correlation indicate the fractional coverage with oxide.

The inset B in Figure 12 reports the selectivities to total and partial oxidation as function of the oxygen abundance in the reaction mix. As seen in the spectra of Figure 11 and in consequence of the correlation of the main part of Figure 12 the partial oxidation path is open under all conditions. The total oxidation selectivity is low at excess oxygen indicating very clearly the inhibiting character of an oxide layer easily detectable with the in situ XAS technique.

The in situ experiment with variable temperature and fixed stoichiometry was also analysed for its correlation between spectral features and yield data for total and partial oxidation pathways respectively. The result is reported in Figure 13. There is a negative correlation between abundance of the weak low-energy feature and the CO_2 yield indicating that the oxide is consumed with the total oxidation reaction. The

High-Pressure Low-Energy XAS: A New Tool for Probing Reacting Surfaces of Heterogeneous Catalysts, A. Knop-Gericke et al., Topics in Catalysis, 2000

10

change in slope occurring at high concentrations of oxide may be attributed to a change in the specific activity of the oxide at a temperature of 573 K. Intermediate copper oxides such as Cu_3O_2 have been reported [28] to exist in the Cu_2O/O system above 473 K. On the copper surface this temperature could be higher. Such intermediate oxides may well exhibit a higher oxidation potential than the thermodynamically stable Cu_2O which would be a product of total oxidation of methanol in a gas phase containing oxygen.
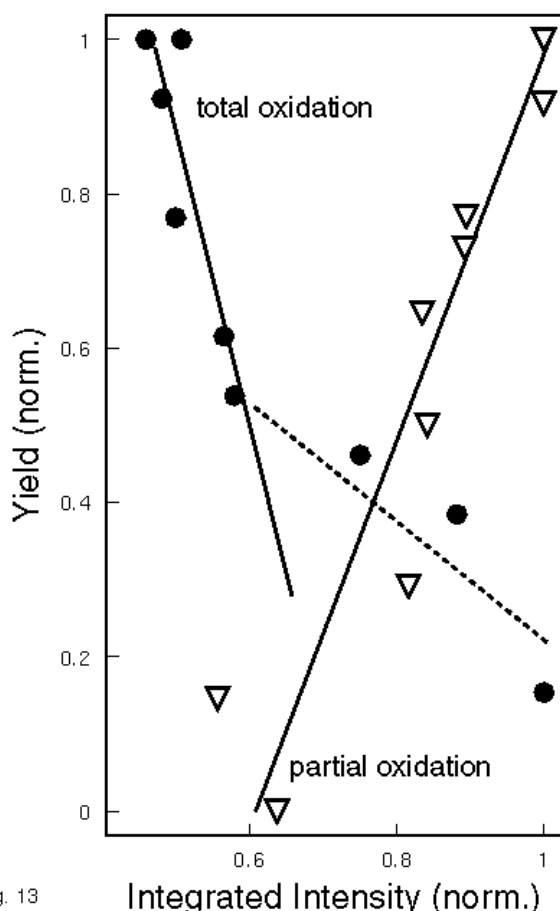

Fig. 13

Figure 13. Correlation of the normalised yields of total and partial oxidation routes with the normalised amounts of oxide (531 eV) and weakly bound oxygen species (535.5 eV) in the variable temperature experiment described with Figures 7 and 9. The changeover in slope in the total oxidation route occurs at 573 K. After subtraction of yield minima the yields were normalised at maxima. The same normalisation procedure was used for the integrated intensities.

The yield of partial oxidation scales positively with the abundance of the weakly bound species. The positive correlation implies that oxygen atoms decorate the active sites and count the increase in active sites with increasing temperature. The origin of this process is ascribed to the motion of copper atoms during the formation and destruction of copper oxides which occur at the oxide/gas phase interface. This motion creates massive stress/strain

fields as can be measured conveniently at macroscopic samples in metallurgy [29] and as has been concluded from the in situ Cu K edge EXAFS results [8]. Recent theoretical results strongly support the relevance of stress for surface chemical processes. It was predicted that adsorption energies can vary strongly with small changes in the lattice constant as resulting from local stress/strain [30].

The present study gave an indication of the atomistic nature of the "dual site" combination suggested in surface science [13] as the active species for partial oxidation. In these studies a combination of an atomic copper location with an activated "nucleophilic" oxygen was predicted to exist. The weakly bonded oxygen located at lattice defects of mobile copper metal is a good representation of such a site. The prediction of surface science that "fully oxidised" copper should be inactive for methanol oxidation was also confirmed. Intermediate situations with metastable oxides and incomplete coverage of a metallic surface were found to exist under practical reaction conditions. The linear correlation between oxide coverage and catalytic activity can be taken as indication that the perimeter model suggested in the literature [19] is the boundary case for a poorly mobile catalyst surface at low temperature and pressure. Under the reaction conditions applied here the copper mobility should be much higher and thus preclude the formation of oxide islands. Only very small nuclei would form before the surface is restructured. Such a situation would result in more isotropic distribution of active sites as expressed in the linear correlation.

Methodical conclusions

The results demonstrate that in situ X-ray absorption spectroscopy at low energy edges can be used to study the electronic structure of a reacting catalyst surface. Such information is very difficult to obtain by other means. The method is surface-sensitive enough that strong correlations can be obtained between spectral features and catalytic parameters which inherently reflect surface reactions. To obtain these correlations it is important that the gas phase information is available together with the spectral data from the solid surface.

The key feature in the present example was the detection of a new weakly bonded species of atomic oxygen which exists only under simultaneous presence of oxygen and methanol. This species is closely correlated to the partial oxidation activity of the system. Its bonding character would render it a good candidate for the nucleophilic oxygen species postulated in surface-science studies of the reaction. From the spectroscopy – activity correlation only a marker function for the number of active sites can be concluded. This would not exclude, however, that this species is also directly involved in the reaction provided that its recovery is much faster than the change in the number of active sites.

The notion that the shape of the conversion vs. temperature curve indicates an oxygen inhibition was clearly supported. Besides the oxide species inhibiting the reaction, there is also a different oxide which catalyses the total oxidation of methanol. The energy position of the white line reflects well

High-Pressure Low-Energy XAS: A New Tool for Probing Reacting Surfaces of Heterogeneous Catalysts, A. Knop-Gericke et al., Topics in Catalysis, 2000

11

these differences between overall oxidic species. No information is obtained from XAS, however, whether the differences in function of these oxides are due to their micromorphology or due to discrepancies in their chemical and electronic structure.

These conclusions indicate the type of information which can be gained from in situ XAS experiments. The application of the method is possible to a wide range or reactions and substrates. We have used besides copper catalysts of silver, platinum and various oxides including zeolites and molybdates. The study reactions should be fast and kinetically non-demanding in order not to create too large problems with the kinetic behaviour of the tank/flow reactor. Pressed wafers of catalyst powder at the end of a flow reactor tube can replace the planar model catalysts used now allowing to study in the future even more realistic systems. With planar substrates the polarisation of synchrotron radiation can be used to determine the orientation of adsorbates under reaction conditions provided they are preferentially oriented and form a sufficient surface abundance under reaction conditions [31]. A limit to surface sensitivity is placed at about 0.1 monolayer which can be lower in fortunate cases.

It is clear that the method has its limitations in deducing structural information. Attempts will be made in the future to exploit the EXAFS information of these data. The very limited energy range at which they can be acquired without interference from other soft-X-ray absorption features will allow only for limited structural analysis which is, however, very valuable as it is obtained under in situ conditions.

The pressure range can be extended with more intense light sources available at third generation synchrotrons. We expect an order of magnitude increase by moving the experiment from BESSY I to BESSY II. The present pressure range appears, however, not as severe limitation, as the pressure is above the critical limit below which no more reactions occur between reactants from the gas phase and the sub-surface regime of the catalyst.

In summary, a new method for studying the electronic structure of reacting surfaces in gas-solid interaction processes such as heterogeneous catalysis has been developed. The example presented gave new insight into a well-studied reaction, as a new surface species was discovered occurring uniquely under reaction conditions. Such information requires extensive studies by supporting experimental and theoretical efforts but can help to bridge the gaps between surface science and the understanding of heterogeneous catalysis.

References

1 J.M. Thomas, R. Lambert, Characterisation of Catalysts, (Wiley, New York, 1980)

2 D.J. Dwyer, F.M. Hoffmann, Surface Science of Catalysis (ACS Symposium Series, 482, ACS, Washington, 1992

3 A. Knop-Gericke, M. Hävecker, Th. Neisius, Th. Schedel-Niedrig, Nucl. Instr. Meth., A, 406, (1998), 311

4 M. Hävecker, A. Knop-Gericke, Th. Schedel-Niedrig, Appl. Surf. Sci., 142, (1999), 438

5 Th. Schedel-Niedrig, X. Bao, M. Muhler, R. Schlögl, Ber. Buns. Phys. Chem., 101 (1997), 994

6 H. Werner, D. Herein, G. Schulz, U. Wild, R. Schlögl, Catal. Lett., 49, (1997), 109

7 A. Amariglio, O. Benali, H. Amariglio, J. Catal. 118, (1989), 164

8 I. Böttger, O. Timpe, R. Gottschall, M. Hävecker, Th. Ressler, Th. Schedel-Niederig, R. Schlögl, PCCP, (1999), submitted

9 B.S. Clausen, H. Topsoe, Catal. Today, 9, (1991), 189

10 R. Schmid, Metall. Trans., 14, (1983), 473

11 I. Wachs, R.J. Madix, Surf. Sci., 84, (1979), 375

12 A.F. Carley, A.W. Owens, M.K. Rajumon, M.W. Roberts, S.D. Jackson, Catal. Lett., 37, (1996), 79

13 S,M, Francis, F.M. Leibsle, S. Haq, N. Xiang, M. Bowker, Surf. Sci., 315, (1994), 284

14 F. Besenbacher, I. Stensgaard, in "Chemical Physica of Solid Surfaces and Heterogeneous Catalysis", (D.A. King, D.P. Woodruff, eds), vol. 7, chapter 14, Elsevier, Amsterdam (1994)

15 G. Ertl, Surf, Sci., 6, (1967), 208

16 M. Grioni, J.F. van Acker, M.T. Czyzyk, J.C. Fuggle, Phys. Rev., B, 45, (1992), 3309

17 P. Marksteiner, P. Blaka, K. Schwarz, Z. Phys. B, 64, (1986), 119

18 F.M.F. de Groot, M. Grioni, J.C. Fuggle, J. Ghijsen, G.A. Sawatzky, H. Petersen, Phys. Rev., B, 40, (1989), 5715

19 F.M. Leibsle, S.M. Francis, R. Davis, N. Xiang, S. Haq, M. Bowker, Phys. Rev. Lett., 72, (1994), 2569

20 C. Barnes, P. Pudney, Q. Guo, M. Bowker, J. Chem. Soc., Faraday Trans., 86, (1990), 2639

21 P. Pudney, M. Bowker, Chem. Phys. Lett., 171, (1990), 373

22 Ullmann, Encyclopaedia of Industrial Chemistry, VCH, Weinheim, (1982), vol. 21, 311

23 D.Briggs, M.P. Seah, "Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy", Wiley, New York, (1993).

24 M. Hävecker, A. Knop-Gericke, Th. Schedel-Niedrig, R. Schlögl, Angew. Chem. Int. Ed., 37, (1998), 1939

25 D.A. Outka, R.J. Madix, J. Stöhr, Surf. Sci., 164, (1985) 235

26 K. Amemiya, Y. Kitaijma, Y. Yonamoto, S. Terada, H. Tsukabayashi, T. Yokoyama, T. Ohta, Phys. Rev. B., 59, (1999), 2307

27 M. Lenglet, K. Kartouni, D. Delahaye, J. Appl. Electrochem., 21, (1991), 697

28 M. Lenglet, K. Kartouni, J. Marcheferet, J.M. Claude, P. Steinmetz, E. Beauprez, J. Heinrich, N. Celati, Mater. Res. Bull., 30, (1995), 393

29 V.I. Kibets, A.P. Kulik, Powder Metal. and Metal Cer., 33, (1994), 236

30 M. Mavrikakis, B. Hammer, J.K. Norskov, Phys. Rev. Lett., 81 (198), 2819

High-Pressure Low-Energy XAS: A New Tool for Probing Reacting Surfaces of Heterogeneous Catalysts, A. Knop-Gericke et al., Topics in Catalysis, 2000

12

31 Th. Bürgi, F. Atamny, A. Knop-Gericke, M. Hävecker, Th. Schedel-Niedrig, R. Schlögl, A. Baiker, Catal. Lett., submitted 1999
32 W. H. Press, B. P. Flannery, S. A. Teukolsky, W. T. Vetterling Numerical Recipies in C (Cambridge University Press, 514)