Activation of a Cu/ZnO catalyst for methanol synthesis

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Synopsis *In situ* resonant X-ray diffraction, *in situ* resonant small angle X-ray scattering and *in situ* electron energy loss spectroscopy have been applied to the study of nano-scale and crystalline structure during activation of a Cu/ZnO catalyst for methanol synthesis.

Abstract The structural changes during activation by temperature programmed reduction of a Cu/ZnO catalyst for methanol synthesis has been studied by several *in situ* techniques. The catalyst is prepared by co-precipitation and contains 4.76 wt. % Cu which forms a substitutional solid solution with ZnO as determined by resonant X-ray diffraction. *In situ* resonant X-ray diffraction reveals that the Cu atoms are extracted from the solid solution by the reduction procedure, forming metallic Cu crystallites. Cu is re-dispersed in bulk or surface Zn lattice sites upon oxidation by heating in air. The results are confirmed by *in situ* electron energy loss spectroscopy and *in situ* resonant small angle X-ray scattering. The average Cu particle size in the reduced catalyst as determined by the latter technique is ~27 Å. The observed structural behaviour may have important implications for catalyst design and operation. More than one type of Cu particles with different origin may be present in Cu/ZnO catalysts with Cu loadings higher than the solubility limit of Cu in ZnO: Particles formed by extraction of Cu from the (Zn,Cu)O solid solution and particles formed by reduction of CuO primary particles. The former type is highly dispersed and in intimate contact with the surface of the host ZnO particles. The possibility of re-forming the (Zn,Cu)O solid solution by oxidation may provide a means of redispersing Cu in a deactivated catalyst.

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1. Introduction

Methanol is a widely used chemical compound in large-scale chemistry. Catalytic reforming of methanol is an efficient and environmentally attractive way to produce hydrogen. This process is very well suited for small-scale applications and has a large potential in connection with the use of fuel cell technology in automobiles. Methanol is industrially manufactured from synthesis gas, which is a mixture of CO, CO₂ and H₂ produced typically by steam reforming of natural gas (Satterfield, 1980). The commercial catalysts for the methanol synthesis consist of Cu particles with ZnO and Al₂O₃ as chemical and structural promoters.

Numerous investigations have been performed on the Cu/ZnO system, but the nature of the active sites and the reaction mechanisms still generate substantial controversy. The central point of argument is whether catalysed methanol synthesis is a structure sensitive reaction or not, i.e. if activity is determined only by available Cu surface (Chinchen *et al.*, 1986; Rasmussen *et al.*, 1994; Yoshihara & Campbell, 1996; Spencer, 1998) or if the local structural environment of Cu also influences activity. Mehta *et al.* (1979) suggested that Cu⁺ in solid solution with ZnO is the active species for methanol synthesis, whereas Okamoto *et al.* (1983) concluded that Cu⁰-Cu⁺ species forming a two-dimensional epitaxial layer on ZnO are catalytically active for methanol synthesis. Several groups have advocated for adatoms or adspecies of Zn or ZnO on Cu with either Cu-Zn or Cu-O-Zn forming the active site (Topsøe & Topsøe, 1999; Fujitani & Nakamura, 2000; Greeley *et al.*, 2003). Choi *et al.* (2001) proposed that the Cu-Zn site is active for CO₂ hydrogenation and Cu-O-Zn is active for CO hydrogenation. Others claim that ZnO acts as a reservoir and site for H₂ dissociation, but does not otherwise influence metallic Cu as the site for CO₂ hydrogenation (Burch *et al.*, 1990). Günter *et al.* (2001b) found that the ZnO support induces a strain in Cu nano-particles, which is positively correlated with methanol synthesis turnover frequency. The observation of strain in Cu nano-particles has more recently been confirmed by an *in situ* EELS study (Wagner *et al.*, 2003). The dispute is still ongoing with more reports of structure sensitivity of methanol synthesis emerging from other *in situ* techniques. (1991), (1997) and Grunwaldt *et al.* (2000) demonstrated a correlation between catalyst activity, synthesis gas reduction potential, and apparent Cu coordination number as determined by *in situ* EXAFS. They interpreted the (reversible) change in coordination number as a shape change of the nano-metre sized Cu

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crystallites, exposing facets of different catalytic activity. Along the same lines, Hadden *et al.* (1997) suggested that the Cu surface is in a continuous state of restructuring during methanol synthesis from mixtures of CO/CO₂/H₂.

There appears to be wide agreement that the oxide catalyst formed by calcining co-precipitated (Cu,Zn)hydroxycarbonates contains ZnO with Cu in solid solution, and that Cu migrates to the ZnO surface during the reduction process, forming dispersed structures with particularly high catalytic activity (Ketchik *et al.*, 1982; Yurieva *et al.*, 1993; Stirling *et al.*, 1993; Yurieva *et al.*, 1995; Plyasova, 1996; Poels & Brands, 2000). Stirling *et al.* (1993) found that a maximum of about 1 mol % CuO can dissolve in ZnO, but they calcined the studied catalysts at very high temperatures, 780°C-900°C, whereas Ketchik *et al.* (1982) showed that ZnO in catalysts calcined at 350°C may contain up to 10 mol % CuO in solid solution. Klenov *et al.* (1998) and Yurieva *et al.* (2004) suggested by combination of HRTEM and XRD measurements and simulations that the Cu-doped ZnO contains a large number of defects along the (001) plane and that Cu atoms are primarily located close to these defects.

The present work focuses on the structure of the oxidic catalyst as prepared, structural changes during the process of catalyst activation by reduction of Cu oxide to metallic Cu and the effect of reoxidising the catalyst. The applied experimental techniques include *in situ* laboratory X-ray powder diffraction (XRD), *in situ* resonant X-ray powder diffraction (AXRD), *in situ* Electron Energy Loss Spectroscopy (EELS), and *in situ* resonant small angle X-ray scattering (ASAXS). The techniques that depend on resonant dispersion have historically been referred to as "anomalous", hence the "A's" in the acronyms (Hodeau *et al.*, 2001; Bazin *et al.*, 2002).

We have determined that Cu is present in solid solution with ZnO in the catalyst as prepared, substituting as Cu²⁺ for Zn²⁺. During the reduction process, Cu is reduced to the metallic state, migrating to the ZnO surface where it forms particles of a few nm in size. Re-oxidising the catalyst, one of two conformations has been observed: 1. A Cu₂O like film is formed on the ZnO surface. 2. The (Zn,Cu)O solid solution is re-formed. The structure formed, depends most likely on the oxygen partial pressure and thermal activation, and combinations of the two are possible. It is suggested that re-oxidation may provide a means of re-dispersing Cu in the catalyst, which could be useful for catalyst regeneration.

2. Experimental

2.1. Sample preparation

The analysed samples were taken from the same batch of sample material used by Clausen *et al.* (1994) and Grunwaldt *et al.* (2000) for *in situ* EXAFS studies of dynamic structural changes of metallic Cu particles as a function of synthesis gas reduction potential. It is a

Cu/ZnO model catalyst with 4.76 wt. % Cu prepared by co-precipitation from an aqueous solution of the Cu and Zn nitrates, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, to which an aqueous solution of Na_2CO_3 and NaOH is added. The precipitate is filtered and washed in hot distilled water to remove Na^+ ions. The filter cake is dried for 16 h at 100°C (Rasmussen *et al.*, 1987). At this stage the catalyst consists of hydrozincite, $(\text{Cu,Zn})_5(\text{CO}_3)_2(\text{OH})_6$ (determined by XRD), which is converted to $(\text{Zn,Cu})\text{O}$ by calcination for 1 h at 573 K .

2.2. Conventional X-ray powder diffraction

An XRD powder pattern of the calcined catalyst (as prepared) was recorded with $\text{Cu K}\alpha$ radiation on a Philips X'Pert diffractometer with automatic divergence slit, diffracted beam graphite monochromator and linear position sensitive detector.

In situ reduction-oxidation-reduction cycles of the catalyst sample were studied with the diffractometer described above, equipped with an Anton Paar XRK900 reaction cell for the Bragg-Brentano geometry. The 75–125 μm fraction was selected by sieving the sample. Reactant gases were supplied at 0.5 MPa, flowing through the sample. A sample of ZnO standard material, SRM 674a, was measured following the same reduction process. The certified lattice parameters were verified with an accuracy of $1 \cdot 10^{-4}$, and the thermal expansivity determined by Albertsson *et al.* (1989) was confirmed.

2.3. *In situ* resonant X-ray powder diffraction

The *in situ* resonant XRD experiments were carried out on the materials science beam line at the Swiss Light Source (SLS). The beam from the wiggler insertion device is collimated and filtered by a vertical mirror, and monochromatized by a double Si (111) monochromator, with the second monochromator crystal providing horizontal focusing. A second mirror provides focusing in the vertical plane. Minimum size of the focused beam is 0.5 mm x 0.5 mm (Patterson *et al.*, 2005).

The calcined sample was sieved and the 75–125 μm fraction was loaded in a micro reactor consisting of a $\sim 6\text{ cm}$ long quartz glass tube, 0.7 mm in diameter with .01 mm thick walls (Markröhrchen, Hilgenberg GmbH), mounted horizontally and fitted to a gas supply system with graphite ferrules. The entire *in situ* setup is described by Clausen *et al.* (1991). During operating conditions, a gas flow of 10 ml/min was passed through the sample under a maximum pressure of 400 kPa and the temperature was regulated in the interval 298–493 K by means of an N_2 heat blower.

The beam incident on the sample was defined horizontally to 1.4 mm and vertically to 0.8 mm by slits, illuminating the entire sample in the vertical direction. The diffractograms were recorded by a 5-fold scintillator detector bank with Si (111) analyser crystals in order to eliminate fluorescence when measuring at energies close to an absorption edge. Calibration of

the monochromator was done by measuring an absorption spectrum from a Cu metal foil. Calibration of angular offsets for the individual detector/analyser pairs was done by measuring NAC ($\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$). The diffractograms were corrected for the Lorentz factor and for absorption.

2.4. *In situ* electron energy loss spectroscopy

Specimens for EELS were prepared by dispersing calcined catalyst powder on either plasma cleaned stainless steel TEM grids or Cu grids with lacey carbon film. EELS measurements were performed on a Philips CM300 field emission gun (FEG) instrument, modified for *in situ* operation as described by Hansen *et al.* (2002) and Wagner *et al.* (2003). EEL spectra were acquired at the Cu $L_{2,3}$, Zn $L_{2,3}$ and O K-edges. For each edge, several EEL spectra were acquired on at least five different sample areas for each sample state. The spectra were recorded in the image mode, typically at 5900x magnification, with an objective aperture defining a collection semi-angle of 7.5 mrad using a Gatan Image Filter (GIF-2000) controlled by Gatan Digital Micrograph Software. The sample environment was varied with temperatures up to 493 K and gas pressures around 150-250 Pa. The resolution of the *in situ* EEL spectra, defined as the FWHM of the zero-loss peak, was better than 1.4 eV. The raw spectra were processed by background subtraction only (Egerton, 1996). The lacey C film was used as an internal reference for energy calibration of the Cu $L_{2,3}$, Zn $L_{2,3}$ and O K-edges.

2.5. Resonant small angle X-ray scattering

ASAXS measurements were carried out at the JUSIFA beamline in Hasylab, Germany (Haubold *et al.*, 1989). X-ray energies were selected with a fixed exit, double Si (311) crystal monochromator with an energy resolution of $\Delta E/E \leq 2 \cdot 10^{-4}$. The transmitted intensity of the direct beam was measured with a photo diode and the small angle scattering with a two-dimensional gas proportional detector. Scattering cross sections from scattering vector $q = 0.075 \text{ \AA}^{-1}$ to $q = 0.45 \text{ \AA}^{-1}$ ($q = 4\pi \sin\theta/\lambda$, where θ is half the scattering angle and λ is the X-ray wavelength) were covered by overlapping measurements in the shortest and longest sample-detector distance configurations at $q = 0.11 \text{ \AA}^{-1}$. Slit scattering, reference sample for absolute scaling, and samples were measured repeatedly at short intervals according to the procedure described by Polizzi *et al.* (2002). The energy scale was calibrated by measuring absorption spectra of Cu and Zn metal foils.

Samples were measured as prepared, in the form of pressed powder tablets and *in situ* in quartz glass tubes. Sample absorption limited the tube diameter to a maximum of 0.7 mm. The *in situ* measurements covered the catalyst reduction process, methanol synthesis conditions and oxidation as described in 3.2 and were carried out in a sample cell specifically

designed for *in situ* ASAXS at the JUSIFA beamline. A detailed description of the cell is found in Andreassen *et al.* (2003).

3. Results

3.1. Conventional XRD

The Cu K $\alpha_{1,2}$ X-ray diffractogram is shown in Figure 1 with a Le Bail fit (Le Bail *et al.*, 1988) including only the unit cell of ZnO. Weak peaks at $d^* = 0.28 \text{ \AA}^{-1}$ and $0.31 \text{ \AA}^{-1}$ almost hidden in the background, correspond to small remains of hydrozincite (<0.5%), the majority phase of the uncalcined catalyst. The ZnO reflections show significant anisotropic broadening with a complicated dependency on reflection indices.

Figure 1 Le Bail (Le Bail *et al.*, 1988) fit to Cu K α X-ray diffractogram of 5/95 CuO/ZnO catalyst, recorded in Bragg-Brentano geometry. Only the ZnO cell is used in the fit.

For the purpose of a qualitative analysis of the anisotropic broadening, integral breadths are determined by peak profile fitting, corrected for instrumental broadening by Fourier deconvolution (Stokes, 1948) (performed with the program Winfit (Krumm, 1994)), and represented in a Williamson-Hall plot (Williamson & Hall, 1953) (Figure 2). The instrumental broadening is characterized by profile fitting of the LaB₆ line profile standard, SRM 660a.

Figure 2 Williamson-Hall plot of reciprocal integral breadths for ZnO reflections, β_f^* , corrected for instrumental broadening, versus reciprocal lattice spacing, d^* . Reflections are marked according to the following grouping: Group I ($\circ$): $hk0$ and $h-k = 3n$ are theoretically unaffected by broadening caused by stacking faults on (001) planes, Group II ($\bullet$): $h-k = 3n \pm 1$, l odd are affected by stacking fault broadening, but less so than Group III ($\times$): $h-k = 3n \pm 1$, l even, with n any integer.

The strongest, best-resolved low-order reflections 100, 002 and 110, corresponding to the principal directions of the hexagonal unit cell, have similar integral breadths. This indicate equidimensional crystallites of an average volume weighted coherent dimension, $\varepsilon_\beta = \lambda/\beta \cos\theta = 96(3) \text{ \AA}$, where β is the integral breadth of a reflection (Wilson, 1962b). For spherical crystallites, this apparent size is related to the sphere diameter by $D = 4/3\varepsilon_\beta$, i.e. $D = 128 \text{ \AA}$ (Wilson, 1962b). Other reflections are considerably broader in comparison, notably the well-resolved 102 and 103 reflections. It has been shown theoretically (Wilson, 1962a) that stacking faults in hcp crystals give rise to anisotropic broadening affecting reflections corresponding to certain crystallographic directions. The broadening effect of stacking faults in hcp crystals is symmetric, and does not cause a shift in reflection positions (Warren, 1969). The reflections are affected differently, according to three groupings (Langford *et al.*, 1993):

Group I: $hk0$ and $h-k = 3n$

Group II: $h-k = 3n \pm 1$, l odd

Group III: $h-k = 3n \pm 1$, l even

where n is any integer. The reflections are marked in Figure 2 according to these groups. The contribution of stacking faults to reflection broadening is theoretically largest for group III whereas group I reflections are unaffected. This relation appears to hold for the investigated sample, at least for the low-angle reflections that are reasonably well resolved and intense

(Figure 1). At larger angles the separation according to groups is not so clear, presumably because of the difficulty in extracting reliable integral breadths for the severely overlapping high-angle peaks. It is in principle possible to separate the contributions to broadening from size, strain and stacking faults as was demonstrated for ex-oxalate ZnO by Langford *et al.* (1993), but in the present case the profile is broadened to an extent that render such a detailed analysis impossible. It is concluded however, that the diffraction pattern is significantly affected by stacking fault broadening, although quantification in terms of stacking fault frequency is not possible.

For the purpose of a precise lattice refinement and determination of minor diffracting phases, a full pattern refinement is performed by the Le Bail method (Le Bail *et al.*, 1988) with anisotropic broadening modelled by the phenomenological broadening model of Stephens (1999). The advantage of the Le Bail method with respect to profile fitting is that the structure factors of the reflections are allowed to vary freely, not constrained by the structural model. The fit is therefore not affected by sample texture or other systematic effects influencing reflection intensities, and the theoretically best fit for a given space group and peak profile function can be obtained. This provide for a sensitive test for the presence of minor diffracting phases and yields precise lattice parameters for the refined phases. A satisfactory fit of the data is obtained with the unit cell and space group of ZnO only and a pseudo-Voigt profile function. There is no evidence of other diffracting phases than ZnO with the wurtzite structure. Introduction of the anisotropic broadening model improves the weighted powder agreement factor, R_{wp} , from 4.0 % to 1.7 %. We do not attempt to reconcile the parameter values for the phenomenological broadening model with a model for stacking faults, as it is only introduced to allow the best possible profile fit in order to obtain reliable lattice parameters and to detect other diffracting phases. The fit was performed with the GSAS Rietveld software using the EXPGUI shell (Larson & Von Dreele, 2000; Toby, 2001). Lattice parameters refine to 3.2511(2) Å and 5.2082(4) Å for the a and c axis, respectively, which is somewhat larger than the values of 3.249921(52) Å and 5.206578(83) Å from the single crystal study of Albertsson *et al.* (1989).

The catalyst sample is reduced in a flow of 0.4% CO, 4% CO₂, 3% H₂ in N₂ at 0.5 MPa, heating from room temperature to 393 K at 2 K/min, holding 10 min at 393 K, followed by heating to 493 K at 0.5 K/min. The reduction process is followed with short X-ray diffraction scans (10 min) over the 2θ range 25°–75°. The patterns are fitted with the Le Bail method to determine lattice parameters as a function of time and temperature (Figure 3).

Figure 3 Evolution of the catalyst ZnO lattice parameters during reduction/oxidation cycles. Filled circles: a axis. Open circles: c axis. Broken line without markers: Reference ZnO a axis showing the effect of thermal expansion. Full line without markers: Reference ZnO c axis. Both determined by Albertsson *et al.* (1989) and confirmed in this study by *in situ* XRD of ZnO reference SRM 674a. " c/a " refers to the lattice parameter ratio.

Up to about 443 K, the unit cell size increases according to the effect of thermal expansion as determined by Albertsson *et al.* (1989). At 443 K the cell suddenly expands by 0.15 % along the a axis and 0.26 % along the c axis, over a temperature range of 25 K. The onset coincides with the onset of reduction as determined for the same catalyst from online analysis of H_2 and H_2O levels in the product stream (Grunwaldt *et al.*, 2000). The expansion is largest along the c axis, in terms of relative and absolute change, whereas the opposite is true for thermal expansion of pure ZnO, where the expansion is largest along the a axis. During the subsequent eight-hour period at constant temperature in reduction gas, a slight isotropic contraction proceeds. The relative decrease in lattice parameters during cooling at 1 K/min to room temperature in reduction gas follows the thermal contraction curves for pure ZnO. At room temperature, the ZnO lattice parameters for the reduced catalyst are 0.09% and 0.19% larger than reported values for ZnO a axis and c axis, respectively (Albertsson *et al.*, 1989), 0.03% and 0.13% larger than the initial lattice parameters of the catalyst sample, before reduction, at room temperature.

After the reduction program, the catalyst is oxidized in a flow of synthetic air (21% O_2 , 79% N_2) at 0.5 MPa by heating to 493 K at 1 K/min, holding for one hour, followed by cooling 2 K/min to room temperature. Thermal expansion is observed during heating in air, until reaching 443 K where the lattice parameters abruptly decrease. A slight expansion is

observed at 493 K, but the c axis decreases fast during the first part of cooling followed by a normal rate of thermal contraction to lattice parameter values almost coinciding with the values for the catalyst as prepared, at room temperature. After holding the catalyst in air at room temperature overnight, the second reduction process is initiated. Again, the lattice expands strongly, exceeding the effect of thermal expansion, most significantly along the c axis. The lattice is apparently stable at the elevated temperature and attains approximately the same values of lattice parameters after cooling to room temperature, as after the first reduction cycle, i.e. expanded by 0.07% and 0.16% relative to a and c reported by Albertsson *et al.* (1989). In Figure 3, the changes in lattice parameters are summarized in the c/a ratio, which changes from a room temperature average of 1.6023(2) in the catalyst as prepared/re-oxidized to 1.6035(1) in the reduced catalyst (1.6020(0)/1.6031(1) at 493 K). The observed changes are almost an order of magnitude larger than the estimated standard deviations. The interpretation of the results is addressed in the final discussion in connection with the accompanying experiments. The peak widths of the most well resolved stacking fault affected reflection, 102, and the unaffected 110 reflection, are constant within estimated standard deviations throughout the entire *in situ* experiment, indicating that the ZnO defect structure is stable during the reduction/oxidation cycles.

3.2. Resonant XRD

Diffraction patterns were acquired in a limited 2θ range of 19° – 48° corresponding to scattering vectors $q \sim 1.5$ – $3.7 \text{ \AA}^{-1}$ at X-ray energies 5 eV, 30 eV and 200 eV below the Cu K absorption edge for the catalyst (Figure 4).

Figure 4 Dispersion corrections to the atomic X-ray form factors for Cu and Zn, calculated by the Cromer-Liberman method (Cromer & Liberman, 1970; Sasaki, 1989). Energies used in resonant X-ray diffraction experiments are marked with circles.

The exact location of the edge is determined from an X-ray absorption scan as the inflection point of the absorption rise (Figure 5). In the calcined catalyst, Cu is clearly in the oxidized state, evident from the prominent white line, and the energy shift of +8 eV relative to metallic Cu. The X-ray photon energy for diffraction measurement is shifted according to the oxidation state of the sample to maintain the -5 eV displacement relative to the catalyst Cu absorption edge. The dispersion corrections have been derived from the experimental absorption measurements to estimate the effect of the local atomic environment, using the method previously reported by Templeton and Templeton (1988) and Samant *et al.* (1988). The real part of the dispersion correction, f' , is derived by the Kramers-Kronig transformation (Kronig & Kramers, 1928) from the imaginary part, f'' , directly related to the absorption cross section (Figure 5). The derivation was carried out using the software DIFFKK (Cross *et al.*, 1998; Newville & Cross, 1998). The experimental dispersion corrections deviate from the theoretical ones by less than 0.2 electrons below the absorption edge, at the energies used for diffraction measurements.

Figure 5 The X-ray dispersion corrections (shown as circle data points) as determined from experimental absorption measurements of the catalyst sample as prepared (a) and activated (b). The full lines correspond to the bare atom theoretical dispersion corrections.

The difference of corresponding diffraction patterns at X-ray energies 5 eV and 200 eV below the Cu K absorption edge give no indication of oxidic Cu present as either CuO ($q_{\text{CuO}} = 2.7 \text{ \AA}^{-1}$) or Cu₂O ($q_{\text{Cu}_2\text{O}} = 2.94 \text{ \AA}^{-1}$). There is however a significant dampening of ZnO reflection intensities at the energy just below the Cu K absorption edge, which indicates that resonating Cu atoms are contributing to the reflections (Figure 6). The intensities of ZnO reflections at an X-ray energy 30 eV below the Cu K edge, are intermediate between intensities at X-ray energies 200 eV and 5 eV below the edge. The same relations have been consistently reproduced on several samples in separate beamtimes.

Figure 6 X-ray diffraction at two energies, 200 eV and 5 eV below the Cu K edge. The difference curve shows the resonant dampening effect on Cu atoms contributing to the ZnO reflections. Minor peaks at $1.75 \text{ \AA}^{-1}$ and $1.95 \text{ \AA}^{-1}$ are from uncalcined hydrozincite.

A bulk kinematical simulation of ZnO crystallites with random substitution of 5% Cu for Zn yields a maximum effect of Cu resonance of -4.4% on the integrated intensity of the 101 reflection at a photon energy 5 eV below the Cu absorption edge with respect to the intensity at 300 eV below the edge. The maximum effect observed experimentally is -7% on the 101 reflection. Debye simulations indicate that this discrepancy could be caused by local distortions of the structure around the substituted positions, which causes a lowering of the overall scattered intensity from the ZnO lattice, enhancing the relative effect of Cu resonance. The catalyst is reduced by the same temperature programmed reduction procedure used in the conventional XRD *in situ* experiment, in a flow of 10 ml/min reduction gas (0.4% CO, 5% CO₂, 5% H₂ in Ar) at 0.5 MPa. The reduction process is followed with short X-ray diffraction scans (15 min) over the 2θ range 19° - 48° with X-ray energy at 8787.5 eV. The lattice parameters as determined from Le Bail fits show the same evolution with time and temperature as observed in the conventional XRD *in situ* experiment. The average coherent domain size along the $\langle 100 \rangle$, $\langle 002 \rangle$ and $\langle 110 \rangle$ directions is 106 Å with a relative standard deviation of 2%, corresponding to a sphere diameter of 141 Å, indicating a slight growth of the ZnO crystallites compared to the catalyst as prepared.

After reduction, an X-ray absorption scan confirms the reduced state of Cu in the catalyst (Figure 5). The effect of the temperature-programmed reduction is also evident from the resonant X-ray diffraction experiment, performed subsequently (Figure 7). The influence of

resonant dampening on wurtzite reflections is diminished by more than 95% and the concurrent appearance of a small hump at $q = 3.0 \text{ \AA}^{-1}$ indicates the formation of metallic Cu crystallites. The resonant dampening is also affecting this reflection, with the largest effect at the X-ray energy 5 eV below the Cu K-edge. Cooling the catalyst, and reheating in synthesis gas (5% CO, 5% CO₂ in H₂), the ZnO lattice parameters follow the thermal expansion curves determined by Albertsson *et al.* (1989), i.e. behaving as expected for pure ZnO.

Figure 7 *In situ* X-ray diffraction at two energies, 200 eV and 5 eV below the Cu K edge, with difference curve. The catalyst is held at 493 K in a flow of reduction gas. The effect of resonant dampening on ZnO reflections is clearly lessened and a small, broad feature is formed at $q = 3.0 \text{ \AA}^{-1}$ (inset with logarithmic scaling).

After holding the catalyst at 493 K in synthesis gas for a full day, the effect of resonant dampening on wurtzite reflections is almost eliminated whereas the intensity of the Cu 111 reflection is enhanced (Figure 8). The integral breadth of the Cu 111 reflection corresponds to a volume weighted average spherical crystallite size of 49(4) Å (Scherrer equation). This is a minimum estimate, assuming that the peak broadening is a size effect entirely. After cooling in synthesis gas, the sample is finally heated in air to re-oxidize the catalyst. The lattice expands less than the thermal expansion for pure ZnO during heating in air. The resonant X-ray diffraction experiment after this treatment again shows the resonant dampening effect on wurtzite reflections, the disappearance of the Cu 111 reflection, and no intensity attributable to either tenorite or cuprite (Figure 9).

Figure 8 *In situ* X-ray diffraction at two energies, 200 eV and 5 eV below the Cu K edge, with difference curve, after holding the catalyst at 493 K in a flow of methanol synthesis gas for 23 hours. The effect of resonant dampening on ZnO reflection is almost eliminated and the peak at $q = 3.0 \text{ \AA}^{-1}$ is larger and sharper (inset with logarithmic scaling).

Figure 9 *In situ* X-ray diffraction at two energies, 200 eV and 5 eV below the Cu K edge, with difference curve, after cooling in synthesis gas and reheating in air. The ZnO reflections are again affected by resonant dampening and there is no evidence of metallic Cu or Cu oxides.

3.3. Electron Energy Loss Spectroscopy

The catalyst was studied using an *in situ* transmission electron microscope. The specimen was exposed to 200 Pa hydrogen and heated to 493K in the *in situ* cell of the microscope. *In situ* high-resolution TEM images were acquired (Figure 10) and show that the ZnO particle size (10-20 nm) is in good agreement with the size determined by XRD. However, an unambiguous identification of Cu nano-particles is complicated by the low Cu loading and the fact that Cu and Zn have almost the same electron scattering power.

Figure 10 *In situ* TEM image of the catalyst in reduced state at 493 K, 200 Pa H₂.

In situ EELS was therefore pursued to probe the chemical state of the catalyst components at low magnifications (corresponding to the image field in Figure 10). EEL spectra were acquired at the O K-edge, the Cu L_{2,3}-edge and the Zn L_{2,3}-edge on the catalyst as prepared (i.e. calcined), and on CuO and ZnO reference samples (Figure 11). The effect of electron beam intensity was given special attention to avoid beam damage, e.g. unintentional reduction of oxide species, by acquiring spectra at several levels of beam intensity.

The significant white lines in the Cu L_{2,3} spectrum of the catalyst resemble the spectrum of the CuO reference, indicating that Cu is in the divalent state. Distinct features attributable to CuO, such as the prepeak at ~530 eV, are however not present in the catalyst spectrum at the O K-edge. It appears, from comparison with the O K-edge spectrum of the ZnO reference, that only ZnO is present in the catalyst. There are no significant differences between the catalyst and ZnO reference spectrum at the Zn L_{2,3}-edge. EEL spectra at the C K-edge were acquired from a sample dispersed on a plasma cleaned steel grid, to investigate for the presence of residual CO₃²⁻, reported by Ketchik *et al.* (1982). No carbon signal was observed in any part of the as-prepared catalyst.

Figure 11 EEL spectra of catalyst as prepared and reference samples. **a.** Cu L_{2,3} edge. Top: Catalyst. Bottom: CuO. **b.** O K edge. Top: Catalyst. Middle: ZnO. Bottom: CuO. **c.** Zn L_{2,3} edge. Top: Catalyst. Bottom: ZnO.

The catalyst is reduced *in situ* by heating to 553 K in 200 Pa H₂ at a rate of 60 K/min, holding it at 553 K for 20 min, followed by cooling to 493 K, the normal temperature for methanol synthesis. After reduction, the disappearance of the characteristic white lines, and the more edge like character of the features in the EEL spectra at the Cu L_{2,3}-edge (Figure 12), indicate the formation of metallic Cu (Wagner *et al* 2003). No changes relative to the as

Figure 12 *In situ* Cu L_{2,3} EEL spectrum of reduced catalyst at 493 K, 200 Pa H₂ with reference spectrum of metallic Cu (bottom), measured at 493 K in 250 Pa H₂.

The catalyst is oxidized by cooling to room temperature, replacing the inlet of H₂ with ~230 Pa O₂ and subsequent heating to 493 K at 60 K/min. The EEL spectra of the now re-oxidized catalyst at the Cu L_{2,3}-edge shows Cu in the divalent state whereas no change is observable at the Zn L_{2,3}-edge. At the O K-edge however, a completely new structure is evident (Figure 13), but only in spectra acquired with low electron beam intensity. A clear

identification of this structure is problematic, because the sample is sensitive to the beam intensity. The structure is only conserved in consecutive spectra, when measured at low electron flux. Corresponding spectra at the Cu L_{2,3}-edge, acquired with low electron flux does not allow evaluation of the Cu oxidation state because of the considerably smaller electron interaction cross section at the Cu L_{2,3}-edge. At a sufficiently high electron flux, the electron loss features at the Cu L_{2,3}-edge reveals that Cu is in the divalent state, but at this flux, the special features at the O K-edge disappears. This was repeatedly observed in several different sample areas. Once the structure was destroyed by increased beam intensity, it could not be recovered. The oxide is not reduced by the beam as evidenced by the divalent character of spectra acquired at the Cu L_{2,3}-edge at high electron flux.

Figure 13 O K-edge EEL spectra of re-oxidized catalyst, CuO and Cu₂O references (bottom) and ZnO reference (top). The four catalyst sample spectra are acquired on the same sample area with electron beam flux increasing from the spectrum marked "Low" to the spectrum marked "High". The energy scales of the spectra are calibrated as described in the experimental section.

Comparing the low-electron flux O K-edge spectrum of the re-oxidized catalyst with the reference spectra of CuO and Cu₂O, it is observed that there are similarities with both reference materials. The strong prepeak is characteristic of Cu₂O, but is shifted towards lower values of electron energy loss, almost coinciding with the smaller prepeak of CuO at 530.5

eV. No other features characteristic of the Cu oxides are recognisable in the catalyst spectra. The broad feature of ZnO at ~555 eV appears to be conserved in all the catalyst spectra, whereas the feature at ~540 eV, most prominent in the low flux spectrum, does not coincide with any features in the reference spectra. It is suggested that the prepeak observed at low electron flux is characteristic of a Cu oxide film on the ZnO surface and that the deviations from the bulk references is caused by either a size-effect of the film or by electronic interactions with the ZnO surface. Because the EEL spectra are acquired on very thin areas of the sample to minimize effects of multiple scattering, the spectra are disproportionately influenced by the particle surface layers, which may explain the pronounced effect of the oxide film on the spectra.

3.4. Resonant small angle scattering

Analogous to AXRD, the ASAXS technique exploits the X-ray photon energy dependent variation in scattering contrast determined by element-specific X-ray resonance near atomic absorption edges. For a mixture of k components, polydisperse in size, the small angle scattering cross-section modified by a structure factor, S_k , describing interparticle scattering interference (between particles of the same component) can be written as (Svergun *et al.*, 2000):

$$\frac{d\sigma}{d\Omega}(q, E)_{\text{TOTAL}} = \sum_{k=1}^K C_k S_k(q, R_k^{\text{hs}}, \eta_k) |\Delta\rho_k(E)|^2 \int_0^\infty \phi_k(R) V_k(R) P_k(q, R)^2 dR \quad (1)$$

with the scattering vector modulus q defined in §2.5. C_k are the volume fractions of the components, V is the particle volume and the volume distribution function $\phi(R) = V(R)N(R)$, where N is the particle number distribution as a function of a characteristic size parameter, R (radius in the case of spheres), P_k is the particle form factor (for spheres in this case). The structure factor, S_k , is described by a hard-sphere potential where R_{hs} is the hard-sphere interaction radius and η_k is the hard-sphere volume fraction.

The scattering contrast term $|\Delta\rho|^2$ depends on the scattering length density, $\rho = r_e v^{-1} \sum_i f_i$ where $r_e = 2.818$ fm is the Thomson electron scattering length, v is the scattering unit volume, and $f_i = f_i^0 + f_i' + if_i''$ is the atomic form factor of the i th atom in the scattering unit, including dispersion corrections. For crystalline materials, the number of atoms in the scattering unit volume is defined by the crystal structure. For the catalyst as prepared, we define the following scattering contrasts:

$$|\Delta\rho_{\text{CuO}}|^2 = \text{Re}(\rho_{\text{CuO}})^2 + \text{Im}(\rho_{\text{CuO}})^2 \quad (2)$$

$$|\Delta\rho_{\text{ZnO}}|^2 = \text{Re}(\rho_{\text{ZnO}})^2 + \text{Im}(\rho_{\text{ZnO}})^2 \quad (3)$$

assuming tenorite and zincite densities for CuO and ZnO, respectively, and atomic form factor dispersion corrections from Sasaki (1989). The use of theoretical dispersion corrections is justified by choosing energies sufficiently below (-7 eV to -300 eV) the absorption edges to avoid the effect of near-edge structure (Figure 5). The energy dependence of the scattering contrasts is shown in Figure 14.

Figure 14 Scattering contrasts for the catalyst as prepared, calculated by assuming tenorite and zincite densities for CuO and ZnO, respectively, and atomic form factor dispersion corrections from Sasaki (1989). Markers indicate the X-ray energies at which small angle scattering data were collected.

The scattering contributions are separated from the set of small angle scattering cross sections $\frac{d\Sigma}{d\Omega}(q, E_i)$, at X-ray photon energies E_i by means of singular value decomposition (Golub & Reinsch, 1970). The details of the application of this method will be published elsewhere. The solution from ASAXS measurements of the catalyst as prepared, reveals no significant contribution related to the CuO scattering contrast. The separation obtained is a negative, noisy pattern that largely follows the total scattering cross section amounting to about 1% of the total intensity. This indicates that Cu is dispersed and not occurring as a separate phase. Following the same temperature programmed reduction procedure as used in the AXRD experiments (section 3.2), the ASAXS measurements are repeated *in situ*, correcting the X-ray energies for the chemical shift of the Cu K edge, determined from an absorption spectrum that confirms the reduction of Cu to the metallic state, whereas ZnO is unaffected. The separated structure functions using the ZnO scattering contrast and the Cu scattering contrast for a Cu metallic phase are shown in Figure 15.

Figure 15 Separated scattering cross sections from *in situ* ASAXS measurements of the reduced catalyst with model fits. **a.** Scattering cross section related to the ZnO scattering contrast. The solid line corresponds to the model fit of two distributions of spherical particles with the dashed lines representing the contribution of each distribution, offset for clarity. **b.** Scattering cross section related to the Cu scattering contrast. The solid line corresponds to the model fit of two distributions of spherical particles with the dashed lines representing the contribution of each distribution, offset for clarity. The model for the distribution of smallest particles represented by the short dashed line includes a structure factor described by a hard sphere interaction potential.

The model fits shown in Figure 15 are calculated with the program MIXTURE (Svergun *et al.*, 2000; Konarev *et al.*, 2003; Konarev *et al.*, 2004) assuming polydisperse distributions of spherical particles described by Schulz size distributions, $\phi(R)$ (Schulz, 1939). For both separations i.e. that related to the ZnO scattering contrast and that related to Cu, a

combination of two distributions with very different mean radii is required for a satisfactory fit. For the Cu separation a structure factor due to particle interference is included for the distribution of smallest particles, described by a Percus-Yevick hard-sphere potential as derived by Robertus *et al.* (1989). The parameters obtained from model fits of the separated scattering contributions are reported in Table 1.

Table 1 Fit parameters of model fits to Cu and ZnO separations as illustrated in Figure 15.

ZnO separation	Volume fraction	Mean radius, R_{av} [Å]	Polydispersity, σ [Å]	Hard sphere radius [Å]	χ^2
$\phi_1(R)$	0.79	141.1	139.8	-	1.21
$\phi_2(R)$	0.21	61.0	11.8	-	
Cu separation	Volume fraction	Mean radius, R_{av} [Å]	Polydispersity, σ [Å]	Hard sphere radius [Å]	χ^2
$\phi_1(R)$	0.60	141.5	62.0	-	1.35
$\phi_2(R)$	0.40	13.4	6.4	32.2	

It is emphasized that the model parameters are highly correlated and it is therefore not trivial to ensure that the global minimum of the model fit is reached. An initial guess and boundary limits for each parameter is supplied to the fitting routine, depending on which different results are obtained, easily varying by 50%–100% with the magnitude of corresponding χ^2 values varying by only 5%–10%. The results reported above represent the solutions with the lowest value of χ^2 where all of the fitted parameters are unbound by the supplied boundary limits. The values obtained for the distributions of larger particles should be regarded with caution as the necessary information is at the limit of the experimental resolution.

The catalyst is re-oxidized by heating to 493 K at a rate of 5 K/min in an airflow of 10 Nml/min. The oxidation state is confirmed by X-ray absorption spectroscopy and ASAXS measurements are performed. As for the catalyst as prepared, the least squares solution does not yield a statistically significant contribution related to the CuO scattering contrast.

The lack of a scattering contribution from CuO in the catalyst as prepared, and re-oxidized, has been confirmed repeatedly, also from *ex situ* measurements (for the catalyst as prepared). Likewise, the separation of a Cu contribution in the reduced catalyst has been reproduced in separate experiments.

4. Discussion

Based on the results of complementary experiments as outlined above, we propose a model for the activation/re-oxidation of the Cu/ZnO catalyst as depicted in Figure 16.

Figure 16 Sketch of the proposed structural changes as a function of oxidation potential of the gaseous environment. **Bottom:** Catalyst as prepared. Cu is dissolved in ZnO, occupying Zn sites by substitution, possibly associated with ZnO planar defects, i.e. stacking faults. The "magnifying glass" shows the proposed local environment of an ABCBC stacking fault in ZnO in the (110) plane with the c axis vertical, with Cu atoms located in tetrahedral sites in the fault plane. **2nd from bottom:** Catalyst in the reduced state. Cu has formed nano-metre sized particles supported on the ZnO particles. The ZnO sites, occupied by Cu in the oxidized state, are either vacant or stabilized by protons. **2nd from top:** Catalyst in the oxidized state. The experimental results indicate a possible combination of Cu states: The initial state of the catalyst as prepared is at least partially recovered by reforming the (Zn,Cu)O solid solution and a Cu oxide thin-film is formed on the surface of the ZnO particles. The electronic structure as probed by EELS bears resemblance to both CuO and Cu₂O. **Top:** Catalyst after re-reduction. The nano-metre size Cu particles are re-formed on the surface of ZnO.

The results of XRD experiments lend support to a model of strong interaction between Cu and the ZnO support phase. *In situ* determinations of lattice parameters as a function of temperature and gas composition consistently show an abrupt expansion of the ZnO lattice during the reduction process, at the temperature corresponding to reduction of Cu²⁺ to metallic Cu. The lattice expansion is considerably larger than expected from the effect of thermal expansion (Albertsson *et al.*, 1989). This can be explained by segregation of Cu from a substitutional (Zn,Cu)O solid solution as suggested by Ketchik *et al.* (1982) (Figure 16, bottom). The model of a (Zn,Cu)O solid solution for the catalyst as prepared is corroborated

by the results of AXRD, which show that Cu contributes to the ZnO reflections, i.e. that Cu occupies the tetrahedral sites in the ZnO, wurtzite type structure. The results of EEL spectroscopy are in accordance with the model of a (Zn,Cu)O solid solution. The spectrum at the oxygen K-edge shows ZnO as the only oxide phase present. The spectrum collected at the Cu L_{2,3} edge shows that Cu is present in a divalent state. This is consistent with CuO being present in the wurtzite structure. Likewise, the results of ASAXS are in agreement with the model, as the lack of a Cu specific scattering contribution from the catalyst as prepared indicates that Cu is dispersed.

The lattice parameters of a (Zn,Cu)O solid solution would be expected to correlate with the Cu concentration because of the slightly smaller size of the Cu²⁺ ion, according to Vegard's law (Vegard, 1921). In the catalyst as prepared, the lattice parameters are close to the values determined for pure ZnO, or in fact a little larger. This could be an effect of the stacking faults along [001] evidenced by the XRD anisotropic line broadening. If Cu atoms are preferentially situated in the vicinity of these stacking faults as suggested by Klenov *et al.* (1998) and Yurieva *et al.* (2004), this may explain the anisotropic lattice expansion, strongest along the c-axis, when Cu segregates from the ZnO lattice during reduction.

The extraction of Cu from the ZnO lattice as indicated from the analysis of lattice parameters are strongly corroborated by the *in situ* AXRD, ASAXS and EELS experiments. It is consistently demonstrated by AXRD that the contribution of Cu to the intensity of ZnO reflections in the catalyst as prepared, disappears concomitantly with the appearance of the Cu 111 reflection during reduction, indicating the formation of metallic Cu nano-particles (Figure 16, 2nd from bottom). The oxidation state of Cu is confirmed by the EEL spectrum at the Cu L_{2,3}-edge, changing from Cu²⁺ in the catalyst as prepared, to Cu⁰ after reduction, whereas the O K-edge spectrum is unaffected. The *in situ* ASAXS experiments further corroborate the observations made by (A)XRD and EELS. The scattering contribution of Cu nano-particles that are formed during the reduction process can be separated with the *in situ* ASAXS technique and the model fits provide parameters of the catalyst particle size distributions, which are in good agreement with size estimates for ZnO from XRD line broadening. For the ZnO separation, (Figure 15a) it appears most likely that the contribution from the distribution of largest sizes originates from agglomeration of the primary ZnO particles. The mean average diameter, $2R_{av} = 122 \text{ \AA}$ of the primary particles is in good agreement with the ZnO crystallite sphere diameter of $141 \text{ \AA}$ as determined by X-ray diffraction. For the Cu separation (Figure 15b), the larger size distribution may be an effect of Cu particle agglomeration or an artifact of the ASAXS separation, i.e. incorrect separation from the ZnO scattering contribution. The size of the primary Cu particles ($2R_{av} = 27 \text{ \AA}$) is in reasonable agreement with the size estimate of $49 \text{ \AA}$ from AXRD, considering that XRD size estimates are biased by the larger particles of a size distribution (Langford, 1999). The

evidence for particle interference (structure factor) may indicate steric restrictions on the distribution of Cu particles, imposed by ZnO support particles.

Upon re-oxidation, the large change in lattice parameters induced by the reduction process is reversed, and the lattice parameters corresponding to the catalyst as prepared are recovered. This, together with the loss of a Cu specific scattering contribution in the *in situ* ASAXS experiments, indicates that Cu is dispersed and a (Zn,Cu)O solid solution is re-formed. The EELS experiments reveal a new structure in the O K-edge spectrum after *in situ* oxidation. It is suggested that it represents the electronic structure of a Cu oxide film interacting strongly with the ZnO surface (Figure 16, 2nd from top). The structure is not stable in the electron beam, and the oxidation state of Cu could therefore not be verified because the electron interaction cross section is much smaller at the Cu L_{2,3}-edge than at the O K-edge. The structure dissociates at the electron flux needed to acquire a Cu L_{2,3} spectrum. At high electron flux, the Cu L_{2,3} spectrum corresponds to Cu²⁺ and the O K-edge spectrum corresponds to that of pure ZnO, i.e. as in the catalyst as prepared.

It is possible that the Cu oxide film detected in the EELS experiments after oxidation is formed during oxidation in the XRD experiments but is too small in volume to be detected by X-ray diffraction. The very thin areas of sample used for EEL spectroscopy tend to bias the results by surface effects, whereas XRD probes the sample bulk. The EELS experiments, however, were carried out at an oxygen pressure of ~200 Pa, whereas the catalyst was exposed to an air pressure of ~0.5 MPa in the AXRD experiment. We can therefore not exclude the possibility that the Cu oxide film only forms at low oxygen pressure, and thus represents an intermediate state of the oxidation process. This has been observed in similar Cu/ZnO catalysts by X-ray absorption near edge spectroscopy (Günter *et al.*, 2001a) and by X-ray photoelectron spectroscopy (Okamoto *et al.*, 1983).

The results of *in situ* Cu K α XRD show that Cu is again extracted from the Cu/ZnO solid solution during re-reduction, leading to re-forming of metallic Cu particles as shown in Figure 16 (top). The abrupt increase in lattice parameters during the re-reduction process is not as pronounced as in the first reduction process. This could indicate that part of the Cu is distributed in lattice sites at the ZnO surfaces and not completely in bulk lattice sites after the first reduction-oxidation cycle.

All four *in situ* experiments indicate that the Cu particles disperse during re-oxidation and that a CuO–ZnO solid solution is re-formed. This suggests a high mobility of Cu atoms in response to changes in oxidation potential of the gaseous environment similar to what has been observed on larger Cu particles dispersed on an MgO substrate (Derouane *et al.*, 1984). Furthermore, a high rate of diffusion through ZnO is implied, which has also been observed in SiO₂ (Frederick & Ramanath, 2004), Si (Istratov *et al.*, 1998) and in V₂O₅ (Iraji-zad *et al.*,

2002). The latter study showed an increased Cu diffusion rate during annealing in 20% H₂ in N₂ compared to annealing in Ar, but did not explain this effect.

It remains to be explained how the ZnO structure is stabilized when Cu is removed from solid solution by the reduction process. In catalytic systems consisting of Cu/ZnO, CuCr₂O₄ and CuAl₂O₄ spinels, it has been suggested that the sites vacated by Cu are occupied by protons forming OH groups, stabilising the oxide structure (Yurieva *et al.*, 1995; Plyasova *et al.*, 2000a; Plyasova *et al.*, 2000b). None of the experimental techniques applied in this study can differentiate a vacant site in ZnO from a site occupied by a proton but we note that Plyasova *et al.* (2000b) confirmed by neutron diffraction such a mechanism of Cu vacated sites, stabilized by protons in reduced CuAl₂O₄, and in reduced CuCr₂O₄ spinels (Plyasova *et al.*, 1996). The presence of supposedly stabilising residual CO₃²⁻ in the catalyst as prepared reported by Ketchik *et al.* (1982), could not be verified, as no carbon signal was detected by EELS.

5. Conclusion

We have shown that advanced X-ray analysis techniques can be applied *in situ* to catalytic systems, providing structural information on the nanometre scale during realistic catalyst working conditions, sometimes referred to as measuring *in operando*. It is found that CuO forms a substitutional solid solution with ZnO when the catalyst is prepared by calcination of the co-precipitated precursor, as opposed to clusters of Cu ions in the ZnO structure proposed by Yurieva *et al.* (2004). Their suggestion, however, that Cu is preferentially situated near ZnO stacking faults, is supported by our observation of anisotropic expansion/contraction of the ZnO lattice in response to reduction/oxidation. During the reduction process, Cu atoms migrate to the ZnO surface forming finely dispersed nanometre sized metallic particles.

It has been suggested that such Cu particles in intimate contact with the ZnO surface (possibly epitaxial) have a substantially increased reactivity compared to isolated Cu particles. The present work does not address the issue of structure sensitivity of catalysed methanol synthesis, but the results may have several important implications for the understanding and design of Cu/ZnO based catalysts for methanol synthesis. It is necessary to determine to what degree the state of Cu as present in the calcined catalyst influences the activity of the reduced catalyst. If the active Cu metallic phase formed by reduction of a (Zn,Cu)O solid solution is substantially more reactive than Cu reduced from CuO particles, conclusions about structure sensitivity and correlations between Cu surface area and activity will be highly ambiguous when based on data from catalysts containing both types of Cu phases. This may explain the large diversity in reports on Cu surface-area/activity relationship, structural sensitivity of Cu/ZnO catalysed methanol synthesis, and optimal Cu/ZnO ratios for best performance.

The reduction of Cu from a (Zn,Cu)O solid solution is a reversible process by oxidation, which implies a means of catalyst regeneration by oxidation-reduction cycles.

Cu is in the divalent state in the calcined catalyst and is fully reduced to metallic Cu by the reduction procedure. The results of *in situ* X-ray experiments show that Cu is fully oxidized to the divalent state by heating in air, but in the *in situ* EELS experiments an intermediate/alternative state is detected that, although resembling a Cu oxide, cannot be identified unambiguously as either CuO or Cu₂O.

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