



In situ investigations of structure-activity relationships of a Cu/ZrO₂ catalyst for the steam reforming of methanol

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Abstract

Structure-activity relationships of a nanostructured Cu/ZrO₂ catalyst for the steam reforming of methanol (MSR) were investigated under reaction conditions by in situ X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) combined with on-line mass spectrometry (MS). Temperature programmed activation by reduction in hydrogen or by reduction in a mixture of methanol and water (feed) was studied by time-resolved Cu K edge XANES and TG/DSC/MS measurements. Small and disordered CuO particles were identified as the main copper phase present in the precursors. After extended time on stream and treatment at 673 K in hydrogen, no significant sintering of the copper particles or deactivation of the reduced Cu/ZrO₂ catalysts was detected indicating a superior stability of the material. The initially low steam reforming activity of the Cu/ZrO₂ catalyst after reduction in hydrogen could be significantly increased by a temporary addition of oxygen to the feed. This increased activity after oxidative treatment is correlated to an increasing amount of oxygen in the copper particles. ⁶³Cu NMR studies detected only a minor degree of microstrain in the active copper phase of the Cu/ZrO₂ catalyst. The decreased reducibility of CuO/ZrO₂, the low degree of microstrain, and the correlation between the amount of oxygen remaining in the copper particles and the catalytic activity indicate a different metal support interaction compared to Cu/ZnO catalysts.

Keywords: methanol steam reforming, copper, zirconia, XAS, XRD, TG/DSC, structure-activity correlations, in situ

Introduction

Hydrogen fuel cells are promising candidates to generate electrical power for mobile applications. Instead of handling H₂ under high-pressure or cryogenic conditions, steam reforming of methanol (MSR) can be employed to produce hydrogen on board.^[1,2] Improving the long-term stability, the hydrogen production rate, and the selectivity of suitable MSR catalysts are subjects of current research in heterogeneous catalysis. Recently, we presented a binary Cu/ZrO₂ catalyst which is more active compared to a commercial Cu/ZnO/Al₂O₃ catalyst, more stable during time on stream, and produces less CO.^[3] However, detailed struc-

ture-activity relationships of the Cu/ZrO₂ material are still lacking and shall be the subject of this work.

Copper based materials have been extensively studied under MSR and methanol synthesis reaction conditions. However, the structure of the active phase in the catalysts and corresponding structure activity relationships are still under debate. For Cu/ZnO based catalysts it has been suggested that the activity is influenced by the morphology and the structural disorder of the copper particles, or by incorporation of copper in ZnO.^[4-7] We have previously reported, that the activity of Cu/ZnO catalysts for the methanol synthesis reaction and the methanol steam reforming correlates to the microstrain in the copper phase.^[8,9] The strain in the copper nanoparticles originates at the Cu-ZnO interface and emphasizes the role of ZnO to influence the microstructure

of the active copper phase in addition to prevent sintering. For the MSR reaction we could also show that the increase in activity after a temporary addition of oxygen to methanol and water is correlated with an increase of the disorder in the copper particles.^[10] structure activity relationships, the stability of copper catalysts and the production of carbon monoxide are important issues with respect to using methanol as a source for hydrogen for fuel cell applications. Cu/ZnO/Al₂O₃ catalysts have been shown to deactivate considerably during extended time on stream and treatment at elevated temperatures, which may be not acceptable for the application in mobile fuel cell applications.^[11]

In addition to conventional Cu/ZnO based catalysts, Lindström et al.^[2] compared copper-based catalysts (where oxides of Cu, Zn, Cr, and Zr were impregnated on alumina pellets) in the MSR reaction and found, that a Cu/ZrO₂ catalyst exhibited the highest selectivity towards CO₂. Breen and Ross^[12] reported on co-precipitated Cu/ZrO₂ catalysts showing high turnover frequencies, comparable to those of Cu/ZnO catalysts at 498 K. They found that the copper surface area and, hence, the dispersion and the activity were lower compared to Cu/ZnO catalysts. Cu/ZrO₂ catalysts (with ~2 % Cu) were also reported to produce more methanol from a CO/H₂ mixture per copper surface area than a Cu/ZnO/Al₂O₃ catalyst (> 10 % Cu).^[13] Nitta et al.^[14] found that Cu/ZrO₂ is more active in methanol synthesis than Cu/ZnO at higher temperatures (> 473 K) and that ZrO₂ results in an increased methanol selectivity and diminishes the production of CO.

Here, we report studies on a nanostructured Cu/ZrO₂ catalyst for methanol steam reforming prepared by simultaneous precipitation of zirconium dioxide and copper oxide. The complementary bulk techniques in situ X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) were employed to elucidate correlations between activity, stability, and structural changes of the Cu/ZrO₂ catalyst under MSR reaction conditions.

Experimental

Preparation of the Cu/ZrO₂ catalyst

The Cu/ZrO₂ nanopowder was synthesized via a precipitation method.^[15] 11.15 mmol zirconium propylate (Aldrich, 5 ml, 70 wt.% in 1-propanol) were added to an aqueous solution of tetramethylammonium hydroxide (2.5 mmol, TMAOH) prepared by mixing 1.05 ml TMAOH (25% in methanol) with 43 ml distilled water. After stirring for 1h, 2.2 ml of a 0.5 molar copper nitrate solution was added. The amount of Cu and Zr were adjusted to yield a catalyst with 10 mol-% Cu and 90 mol-% Zr. The resulting white suspension was stirred at room temperature for 1 h and finally heated at 353 K for 20 h. After centrifugation and washing, the sample was calcined at 773 K under air for 12 h (ramp 2 K/min). X-ray fluorescence analysis (Seiko SEA 2010) revealed a copper concentration of 8.9 mol-% in the calcined CuO/ZrO₂ catalyst precursor.

X-ray diffraction (XRD)

Ex situ X-ray diffraction measurements were performed on a STOE theta/theta diffractometer (Cu K α radiation, secondary monochromator, scintillation counter) in reflection geometry. In situ XRD measurements were conducted on a STOE Bragg-Brentano diffractometer (secondary Si monochromator, scintillation counter) equipped with a Bühler HDK S1 high temperature chamber.^[16] For the in situ experiments 30 mg of catalyst were dispersed onto a steel ribbon. The gases (He, O₂, H₂), and MeOH and H₂O were introduced into the chamber as described in more detail in Ref. [10]. The composition of the gas phase was monitored with a quadrupole mass spectrometer (QMS 200, Pfeiffer).

The Cu/ZrO₂ catalyst was reduced in 2 vol-% H₂ in He with a total flow of 100 ml/min (heating rate of 6 K/min). At 523 K the sample was held for about 2 h. During this time XRD patterns were recorded in a 2 θ range from 25 to 65°, a counting rate of 3 sec/step, and a step width of 0.04° 2 θ . For studies under MSR reaction conditions helium was used as a carrier gas and saturated with methanol or water at 293 K and atmospheric pressure (volume ratio of methanol : water 2 : 1 (3 vol-% : 1.5 vol-%) (methanol (p_{MeOH} = 12496.1 Pa, 1,13 ml/min) and water (p_{H₂O} = 2337.8 Pa, 0,57 ml/min)) 8 ml/min He flow for MeOH and 24 ml/min He flow for H₂O). After the reduction in hydrogen and cooling down to room temperature the gases were changed to MSR conditions and the sample was again heated to 523 K at a rate of 6 K/min. Crystallite size calculations were based on the Scherrer equation.^[17] The K α ₂ contribution was removed from the pattern with the help of the software package STOE WinXPOW 1.06. Subsequently, the full width at half-maximum (FWHM) was determined by fitting a pseudo-Voigt profile function to the Cu 111 and the ZrO₂ 111 peak.

X-ray absorption spectroscopy (XAS)

XAS investigations at the Cu K edge (E = 8.979 keV) were performed at the beamlines X1 and E4 at HASYLAB at DESY (Hamburg, Germany). 68 mg of the calcined CuO/ZrO₂ precursor were mixed with 200 mg polyethylene and pressed at a force of 1 ton into a pellet of 13 mm in diameter. A copper reference foil was used for energy calibration. The energy range was limited to 8900-9500 eV because of the Hf L₃ edge at 9561 eV (Hf is a natural impurity in zirconium compounds). In situ XAS investigations of the catalyst under reaction conditions were also performed at the Cu K edge in the transmission mode. 10 mg of the catalyst (~200 μ m grain size) together with 30 mg boron nitride (BN) were pressed at a force of 1 ton (i.e. 500 MPa) into a pellet of 5 mm in diameter. The total flow through the in situ cell^[18] was set to 40 ml/min at a cell volume of 4 ml resulting in a methanol conversion of about 6.9 %. Two different activation procedures were applied. In the first procedure the

catalyst was heated with 6 K/min to 523 K in 2 vol-% H₂/He until no further changes in the XANES spectra could be observed. The in situ cell was rapidly cooled down to room temperature and an EXAFS spectrum was measured for detailed structural analysis. Subsequently, the feed of water and methanol for the steam reforming reaction (methanol : water, 2:1, see above for detailed concentrations) was introduced into the reactor and the catalyst was heated to 523 K at 6 K/min. In order to reveal the effect of a temporary oxidative treatment,^[5,3] after 5 h time on stream 10 vol-% O₂ were added to the feed for about 30 min.

In the second procedure the catalyst was reduced in a mixture of methanol and water (ratio 2:1, see above) at 523 K at a heating rate of 6 K/min. Because the catalyst was already active after this treatment, 10 vol-% O₂ were temporarily added to the feed after 1 h. Subsequently, the catalyst was treated at 673 K in 2 vol-% H₂/He for 30 min in order to test the stability of the material at elevated temperatures. After cooling down to 523 K the gas atmosphere was changed back to MSR conditions, followed by an addition of oxygen, and continuing methanol steam reforming.

Analysis of the XAFS spectra was performed with the software WinXAS 3.1.^[19] The spectra were energy calibrated with respect to the Cu K edge position of a copper reference foil. After background correction, normalization, and transformation into the k-space, an atomic background $\mu_0(k)$ was determined, using a cubic spline function. The radial distribution function $FT(\chi(k)*k^3)$ was obtained by Fourier transforming the k^3 - weighted experimental $\chi(k)$ function ($k = 2.3 - 10 \text{ \AA}^{-1}$), multiplied by a Bessel window, into the R space. Theoretical backscattering phases and amplitudes were calculated using FEFF 7.^[20] Refinements using the standard EXAFS equation were carried out in R space using the Cu-Cu coordination shells for copper metal and, when necessary, the first Cu-O shell of Cu₂O. One E₀ shift and one 3rd cumulant for all scattering paths, the Debye-Waller factors (DWF) for the single scattering paths, and the single shell distances were determined by a least-squares fit to the experimental data. Coordination numbers and S_0^2 (0.9) were kept invariant.

For the quantification of the contribution of Cu-O scatterers to the EXAFS $FT(\chi(k)*k^3)$ a refinement of the experimental spectra was performed as described above taking copper metal (first Cu-Cu shell at $R = 2.56 \text{ \AA}$) and the first Cu-O shell of Cu₂O ($R = 1.84 \text{ \AA}$) into account and varying the ratio of the two phases. The DWF of the Cu-O distance was set to 0.0037 \AA^2 and kept invariant. This value was determined by a refinement to an experimental spectrum of bulk Cu₂O and, therefore, is based on the static and dynamic disorder of bulk Cu₂O.

A principal component analysis (PCA) of the experimental XANES spectra recorded during the reduction of the catalyst was performed to obtain the number and type of chemical phases present.^[21] For the nanostructured catalyst studied here, XAFS spectra of common references like Cu foil or CuO were not able to sufficiently describe the experimental spectra (e.g. small and disordered copper phases). However, to describe the evolution of the phase

composition during reduction, the “abstract concentrations” resulting from the PC analysis are compared. The evolution of the “abstract concentrations” corresponds to the evolution of the primary components in the material during reduction. Their absolute values, however, do not represent the real concentration of these components.

N₂O decomposition

N₂O decomposition was used to determine the copper surface area after activation in methanol and water and after temporary oxygen addition at 523 K. N₂O decomposition (Reactive Frontal Chromatography, RFC) was first introduced by Chinchén et al.^[22] and can be readily applied to copper catalysts in situ after various treatment steps in a conventional quartz reactor. In the work reported here, the following procedure was employed. After activation in the feed (second procedure in the XAS section) the sample was purged for 1 h in He at 523 K with a flow of 50 ml/min to diminish the amount of adsorbed molecules. Afterwards, the sample was cooled down to 313 K. N₂O decomposition was performed at 313 K with a mixture of 0.5 vol-% N₂O/He at a flow of 15 ml/min with the sample placed on a quartz frit in a quartz tube reactor. The sample was diluted with boron nitride to provide a bed height of about 15 mm with a thermocouple positioned in the powder bed.

In contrast to the original RFC method described by Chinchén et al. we chose to monitor the amount of $m/e = 44$ (representing N₂O) consumed during the “reactive frontal chromatography”. For a blank measurement, the reactor was filled with an appropriate amount of boron nitride. N₂O/He was passed through the sample bed and the evolution of the MS ion currents of N₂O ($m/e = 44$), N₂ ($m/e = 28$), and He ($m/e = 4$) was monitored. For measurements of the catalyst, detection of the $m/e = 44$ current (N₂O) occurs later compared to the boron nitride blank experiment, because N₂O reacts with the surface of the copper particles to yield nitrogen. For calculating the Cu surface area, the inflection points of the N₂O ion current traces ($m/e = 44$) from the N₂O decomposition measurements were determined as the endpoint of the titration. Subsequently, the areas under the N₂O ion current traces of the catalyst (A) and the blank measurement (B) were calculated and the difference between the areas A and B was used to calculate the corresponding volume of N₂ produced by the decomposition of N₂O. The copper surface area was calculated assuming $1.47 \cdot 10^{19}$ copper atoms per m².^[22] In addition to measuring Cu/ZrO₂ samples, N₂O decomposition on Cu/ZnO samples was performed, where the copper surface areas have been previously presented.^[4] Comparable results were obtained by the procedure employed here. From repeated measurements of the material under the same reaction conditions the experimental error was estimated to be about 15 %.

TG-DSC/MS

The TG-DSC measurements were performed on a Netzsch STA 449C. The evolution of the gas phase composition was monitored with an Omnistar mass spectrometer (Pfeiffer). About 26 mg of the catalyst material were put into an Al₂O₃ crucible and positioned onto the TG/DSC sample holder. An empty Al₂O₃ crucible was used for the reference.

Nuclear magnetic resonance (NMR) spectroscopy

For NMR investigations, various samples were collected from a fixed bed reactor after various reaction steps and transferred into NMR tubes in a glove box without exposure to air. Cu NMR spectra of the Cu/ZrO₂ catalysts were measured with a Bruker MSL 300 spectrometer at 79.618 MHz for ⁶³Cu and 85.288 MHz for ⁶⁵Cu at 4.2 K in an Oxford cryostat. Spin-echo experiments (90°-tau-180°) were performed with a 90° pulse of 5.5 μs, a "recycling delay" of 2 s, and a tau value of 25 μs. The ⁶³Cu-NMR spectra shown are calibrated against CuBr₂ at -381 ppm.

Results

XRD investigation of the precursor and the reduced Cu/ZrO₂ catalyst

The XRD pattern of the calcined CuO/ZrO₂ shows tetragonal ZrO₂ as the major crystalline phase (Figure 1a) with a minor contribution of monoclinic ZrO₂ (5 - 8 %). The pattern exhibits no peaks corresponding to a copper oxide

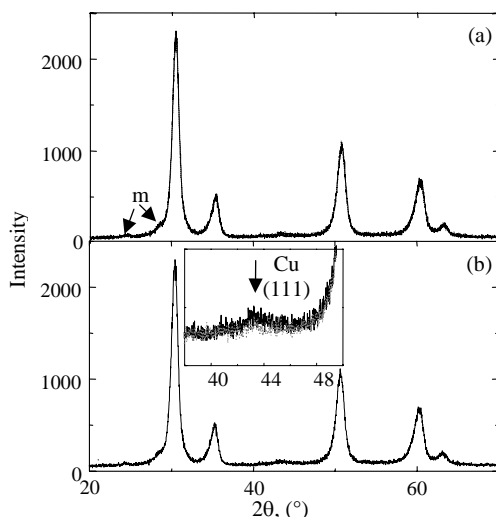


Figure 1: XRD patterns of (a) CuO/ZrO₂ precursor and (b) after reduction in 2 vol-% H₂/He. Arrows indicate small peaks of monoclinic zirconia (m) and copper metal.

phase. Measurements with Al₂O₃ as an internal standard yielded a good crystallinity of the sample (> 95 %). The crystallite size of the tetragonal ZrO₂ is about 70 Å as calculated on the basis of the FWHM of the ZrO₂ 111 peak. After the reduction of the precursor material (inset in Figure 1b) in 2 vol-% H₂/He a small Cu 111 peak is observed (copper crystallite size ~ 20 Å). Exposure to the steam reforming feed or oxygen addition cycles have no significant influence on the diffraction patterns of Cu or CuO, and the zirconia phases.

Local structure of the CuO/ZrO₂ precursor

Figure 2a shows the Cu K-edge XANES spectra of the CuO/ZrO₂ precursor material and the CuO reference (obtained by calcination of malachite) measured at room temperature. Compared to the spectrum of CuO, the characteristic pre-edge at 8984 eV and the peaks after the absorption edge are less pronounced in the spectrum of the CuO/ZrO₂ precursor. The differences in the FT($\chi(k) \cdot k^3$) of the catalyst precursor and the CuO reference are clearly visible in Figure 3. Instead of one peak representing the

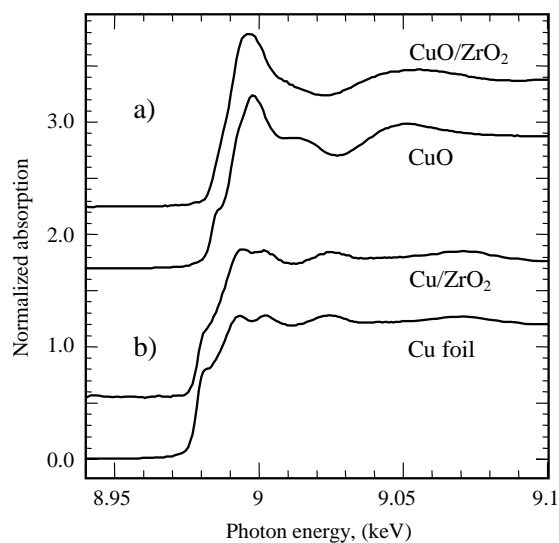


Figure 2: Cu K edge XANES spectra of (a) CuO/ZrO₂ precursor together with CuO, (b) Cu/ZrO₂ after reduction in 2 vol-% H₂/He at 523 K together with Cu metal.

second nearest oxygen and copper neighbors in CuO (at distances of 2.8 and 2.9 Å), the FT($\chi(k) \cdot k^3$) of the CuO/ZrO₂ precursor exhibits two strongly reduced peaks at ~ 3.0 Å. Nevertheless, a theoretical XAFS function of a CuO model structure could be successfully refined to the experimental spectrum of the CuO/ZrO₂ precursor resulting in a good agreement between theory and experiment in the range from 1.0 to 4.0 Å in the FT($\chi(k) \cdot k^3$) (Figure 3). This indicates that disordered CuO is the main copper phase present in the CuO/ZrO₂ precursors.

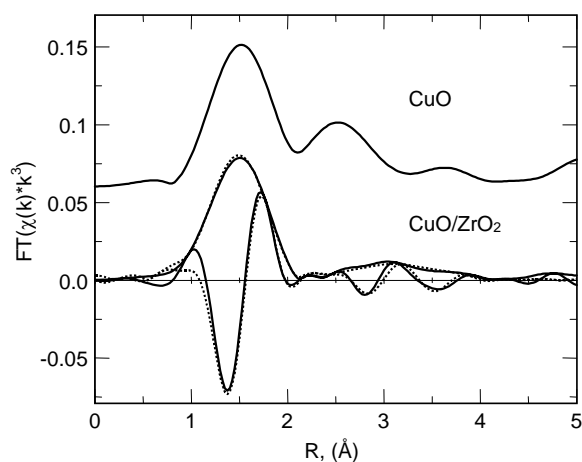


Figure 3: Refinement of a theoretical Cu K edge $FT(\chi(k)*k^3)$ (dotted line) of CuO to the experimental $FT(\chi(k)*k^3)$ of the CuO/ZrO₂ precursor (solid line) together with the experimental $FT(\chi(k)*k^3)$ of a CuO reference.

N₂O decomposition

The specific copper surface area was determined by N₂O decomposition (A) after reduction of the CuO/ZrO₂ material in a quartz glass tube reactor in methanol and water, (B) after temporary addition of oxygen to the feed, (C) after treatment at 673 K in hydrogen, and (D) after a second addition of oxygen to the feed. Although the first oxygen addition yielded a slight decrease in Cu surface area of the Cu/ZrO₂ catalyst, the resulting Cu surface exhibited a higher activity in the steam reforming of methanol. The corresponding turnover frequencies (TOF) were calculated on the basis of the specific copper surface area S_{Cu} (m²/g_{Cu}) and the corresponding hydrogen production rate (μmol/sec*g_{Cu}) (Table 1). The hydrogen production rate and the specific copper surface area were determined after ~ 30 min time on stream when the activity of the Cu/ZrO₂ catalyst had reached

a constant level. While the MSR activity exhibited a constant increase after the first addition of oxygen, a spiked increase followed by deactivation was observed after the high temperature treatment and the second addition of oxygen. Based on the crystallite size (XRD) and assuming spherical particles, the volume ($\rho_{Cu} = 8.92 \text{ g/cm}^3$) of all copper particles and the corresponding surface area was also determined. Except for the copper surface area after treatment at 673 K and oxygen addition to the feed, the surface areas based on the XRD crystallite size compare well to those obtained by N₂O decomposition (Table 1). For comparison, the catalytic performance and the copper surface area of an industrial Cu/Al₂O₃/ZnO catalyst with about 50 weight-% copper were determined under identical conditions. Although this catalyst possesses a higher surface area (32.4 m²/g_{Cu}) than the Cu/ZrO₂ catalyst (13.2 m²/g_{Cu}) it exhibits an inferior turnover frequency (Table 1).

Reduction of CuO/ZrO₂ in 2 % H₂/He

The normalized XANES spectrum of the catalyst at 523 K after reduction in hydrogen is plotted in Figure 2b together with that of a reduced copper reference at 523 K (commercial CuO, Merck). The reduced Cu/ZrO₂ catalyst shows edge features similar to that of Cu metal obtained from the reduction of CuO. The characteristic doublet in the post-edge region (8.99 – 9.0 keV) is also well resolved. The $FT(\chi(k)*k^3)$ of the Cu/ZrO₂ catalyst (Figure 4b) strongly resembles that of the copper reference (Figure 4a). Only slight differences can be seen in the shape of the peaks and in the small shoulder visible left of the first Cu-Cu shell in the $FT(\chi(k)*k^3)$ of the Cu/ZrO₂ catalyst. Figure 5 shows the result of a XAFS refinement of a copper model structure with an additional Cu-O distance ($R = 1.84 \text{ Å}$, ~ 21 %) to the experimental $FT(\chi(k)*k^3)$ of the Cu/ZrO₂ catalyst after reduction in 2 % H₂ at 523 K. With the addition an oxygen

Table 1: Specific copper surface areas calculated on basis of N₂O decomposition measurements or crystallite sizes from in situ XRD investigation and hydrogen production rates (industrial Cu/ZnO/Al₂O₃ catalyst, $S_{Cu} = 32.4 \text{ m}^2/\text{g}_{Cu}$, $R_{H_2} = 33.2 \text{ μmol}/\text{g}_{Cu} \cdot \text{s}$, $\text{TOF} = 4.8 \text{ min}^{-1}$).

Treatment	S_{Cu} (m ² /g _{Cu})	H ₂ production rate	TOF (min ⁻¹)	S_{Cu} (m ² /g _{Cu})
	[N ₂ O]	(μmol/g _{Cu} * s)		[XRD]
After reduction in feed at 523 K	13.2	44.0	82	9.2
After first addition of O ₂ after reduction in feed	10.4	48.0	113	11.5
After high temperature treatment	15.7	42.3	67	6.7
in hydrogen				
After second addition of O ₂ after high temperature treatment in hydrogen	30.7	47.0	41	10.6

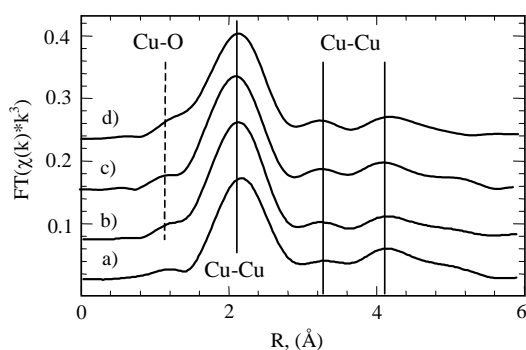


Figure 4: FT($\chi(k)*k^3$) of (a) copper metal, (b) Cu/ZrO₂ after reduction in 2 vol-% H₂/He at 523 K, (c) Cu/ZrO₂ after reduction in 2 vol-% H₂ followed by MSR, and (d) Cu/ZrO₂ after reduction in methanol and water (feed).

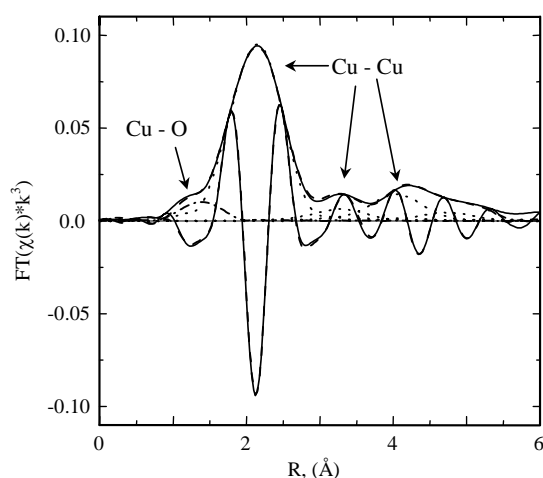


Figure 5: Refinement of a theoretical Cu K edge FT($\chi(k)*k^3$) (dotted line) of copper metal and one additional Cu-O distance to the experimental FT($\chi(k)*k^3$) of the Cu/ZrO₂ catalyst after reduction in 2 vol-% H₂ at 523 K (solid line).

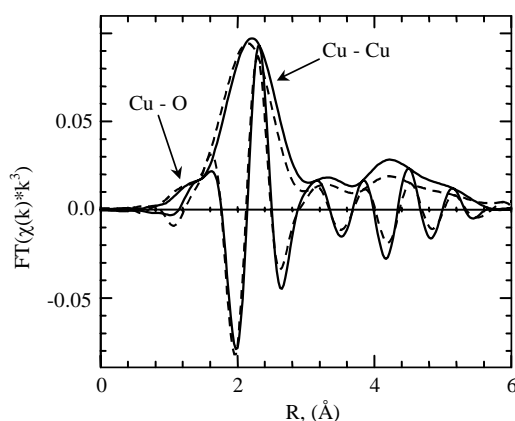


Figure 6: Simulated FT($\chi(k)*k^3$) (solid) for a mixture of 20 % Cu₂O and 80 % Cu in comparison with the experimental FT($\chi(k)*k^3$) (dashed) of the Cu/ZrO₂ catalyst after reduction in methanol and water at 523 K.

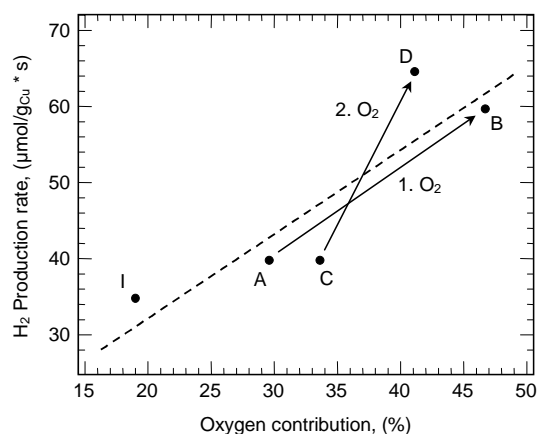


Figure 7: Oxygen contribution to the Cu K edge FT($\chi(k)*k^3$) of the Cu/ZrO₂ catalyst (I) after reduction in 2 vol-% H₂/He at 523 K followed by switching to feed (methanol and water), (A) after reduction in feed, (B) after first addition of oxygen to the feed, (C) after heating to 673 K in 2 vol-% H₂/He and switching to feed, and (D) after second addition of oxygen to the feed together with the corresponding H₂ production rates (not normalized to the specific copper surface area) measured in the XAS in situ cell (Figure 10). The arrows indicate the increase in oxygen contribution and production rate after first (1. O₂) and second (2. O₂) addition of oxygen.

nearest neighbor it was possible to simulate the first peak in the FT($\chi(k)*k^3$), while contribution from higher shells of copper oxide phases were not detectable in the remaining spectrum. In order to corroborate the validity of our approach to analyze the experimental Cu K edge XAFS data of the Cu/ZrO₂ catalyst under reaction conditions, Figure 6 shows a simulated FT($\chi(k)*k^3$) for a mixture of 20 % Cu-O in Cu₂O and 80 % Cu metal at 523 K together with an experimental FT($\chi(k)*k^3$) of the catalyst after reduction in 2 vol-% H₂/He. The amplitude of the oxygen shoulder and the imaginary part are well reproduced by the simulation.

Reduction kinetics

A PC analysis of time-resolved XANES spectra of CuO/ZrO₂ measured during reduction in 2 vol-% H₂ yielded three primary components sufficient to reconstruct the experimental data. The evolution of the abstract concentrations during the reduction in 2 vol-% H₂/He indicates a third component as an intermediate phase (Figure 8b), probably corresponding to Cu₂O. Figure 8a shows that the reduction in hydrogen started at a lower temperature compared to the reduction in methanol and water. Peak reduction temperatures (corresponding to the maximum reduction rate, i.e. the inflection point of the sigmoidal trace) were determined to be 461 K and 496 K, respectively.

Prior to TG-DSC measurements, the CuO/ZrO₂ sample was heated twice to 523 K in He and held at that temperature for 1 h to remove adsorbed water and CO₂.

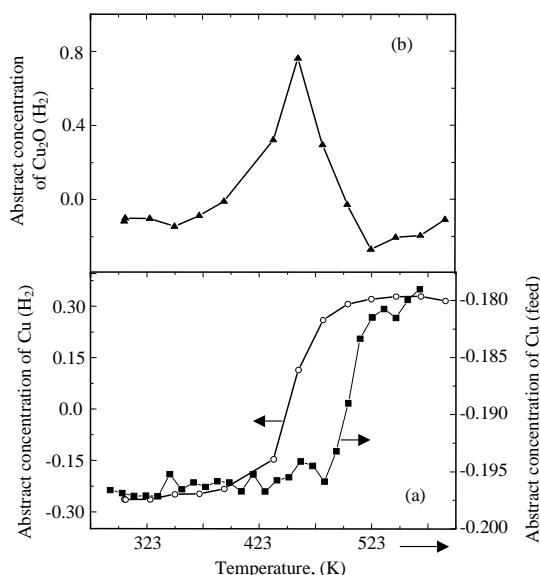


Figure 8: Evolution of (a) the abstract concentrations (PCA) of Cu during reduction in 2 vol-% H₂ and during reduction in methanol and water (feed) and (b) of the abstract concentration of the intermediate Cu₂O phase during reduction in 2 vol-% H₂.

Subsequently, the catalyst was heated in 2 vol-% H₂/He from 300 K to 523 K at a heating rate of 6 K/min. Two exothermic DSC signals between 423 and 440 K (Figure 9a) correlate with two peaks in the MS water signal (Figure 9b). During reduction the sample exhibits a weight loss of ~0.9 %. This is less than calculated for a complete reduction of CuO/ZrO₂ to Cu/ZrO₂ (1.2 %) and corroborates the incomplete reduction detected by in situ XAS.

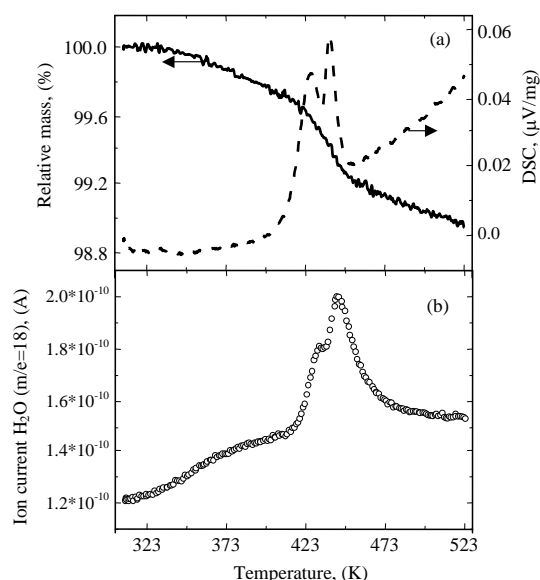


Figure 9: (a) Evolution of mass loss (solid) and DSC signal (dashed) during reduction of the CuO/ZrO₂ precursor in 2 vol-% H₂/He from 300 K to 523 K at 6 K/min and (b) evolution of the corresponding MS signal of water ($m/e = 18$).

Steam reforming of methanol

Figure 4d depicts the FT($\chi(k)*k^3$) of the Cu/ZrO₂ catalyst reduced in methanol and water. The position and shape of the first peak (i.e. first Cu-Cu shell) are very similar to the peak of the sample reduced in hydrogen (Figure 4b). The main difference can be seen in the reduced amplitude of the Cu-Cu peak in the FT($\chi(k)*k^3$) and the increased height of the Cu-O shoulder. After reduction in 2 vol-% H₂ the Cu/ZrO₂ catalyst exhibits a low initial activity in the steam reforming of methanol (Figure 7). After reduction in the feed, however, the Cu/ZrO₂ catalyst possesses a significantly increased activity in the MSR. The FT($\chi(k)*k^3$) of the catalyst reduced in the feed exhibits a Cu-O peak with a higher amplitude (~ 30 %) (Figure 4c, d) compared to that of the catalyst reduced in hydrogen (~ 20 %) (Figure 7).

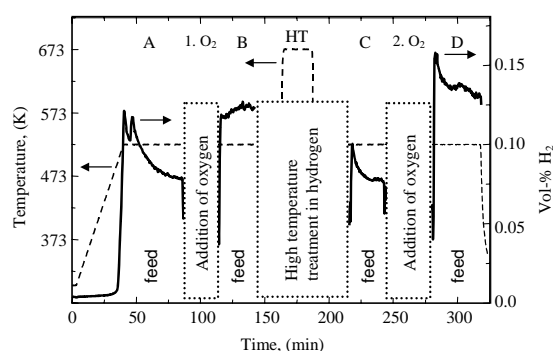


Figure 10: Evolution of H₂ production rate during methanol steam reforming on a Cu/ZrO₂ catalyst measured in the in situ XAS cell during and after various treatments: (A) reduction in methanol and water at 523 K (feed), (1. O₂) first temporary addition of oxygen (10 vol-% O₂) to the feed, (B) feed after first addition of oxygen, (HT) treatment in 2 vol-% H₂ at 673 K, (C) feed after treatment at 673 K, (2. O₂) second addition of oxygen to the feed, (D) feed after second addition of oxygen.

After reduction of the Cu/ZrO₂ catalyst in the feed at 523 K the temperature was kept constant until no further changes were observed in the XAFS spectra. Temporary addition of oxygen and partial re-reduction in the feed resulted in a considerably increased activity of the Cu/ZrO₂ catalyst (Figure 10). The Cu K edge FT($\chi(k)*k^3$) measured after various reaction steps are depicted in Figure 11. Significant differences are observable in the amplitude of Cu-O shoulder and the first Cu-Cu peak. The corresponding oxygen contribution to the FT($\chi(k)*k^3$) are depicted in Figure 7 and indicate that an increasing amount of oxygen remains in the copper particles after oxidation and re-reduction. Figure 7 shows that after the first and second addition of oxygen the increase in hydrogen production rate of the Cu/ZrO₂ catalyst (Figure 10) correlates with an increasing amount of oxygen.

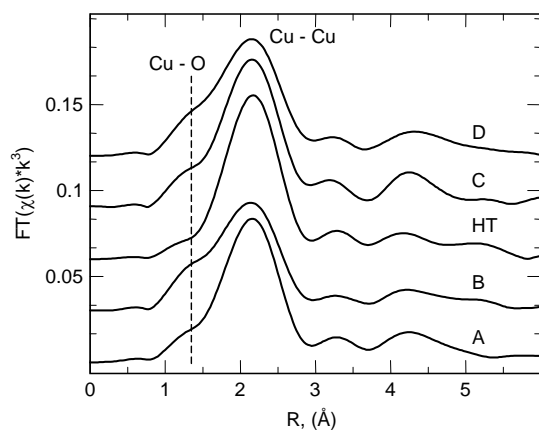


Figure 11: Cu K edge $FT(\chi(k) \cdot k^3)$ of the Cu/ZrO₂ catalyst measured in situ after various treatments (Figure 10): (A) reduction in methanol and water at 523 K (feed), (B) feed after first temporary addition of oxygen (10 vol-% O₂), (HT) treatment in 2 vol-% H₂ at 673 K, (C) feed after treatment at 673 K, (D) feed after second addition of oxygen.

High temperature treatment of Cu/ZrO₂ in H₂

After MSR and addition of oxygen, the Cu/ZrO₂ catalyst was heated in 2 vol-% H₂/He to 673 K. After cooling down to 523 K in hydrogen, a XAFS analysis of the experimental Cu K edge $FT(\chi(k) \cdot k^3)$ revealed complete reduction of the copper phase to copper metal clusters on ZrO₂. The only slightly increased amplitude of the first Cu-Cu peak in the $FT(\chi(k) \cdot k^3)$ excludes major sintering of the Cu particles during the high temperature treatment in hydrogen. Subsequent steam reforming of methanol resulted in similar activities as after initial reduction of the catalyst in the feed (Figure 10). The XAFS $FT(\chi(k) \cdot k^3)$ measured under MSR reaction conditions after hydrogen treatment exhibits again a pronounced contribution of an oxygen nearest neighbor. Moreover, adding oxygen to the feed (Figure 10) resulted in a strong increase in activity and an increase of the amount of oxygen in the copper particles (Figure 7, Figure 11). The corresponding turnover frequencies (based on the specific copper surface area per gram copper) of the various reaction steps as determined in a quartz reactor are given in Table 1. It can also be seen from Table 1 that the copper surface area as determined by N₂O decomposition increased considerably after hydrogen treatment at 673 K and addition of oxygen to the feed.

A copper crystallite size of ~ 20 Å was determined from the Cu 111 XRD line exhibiting only small changes after the various reaction steps. Changes in the copper crystallite size should also be detectable in the Debye-Waller factors of the first Cu-Cu shell.^[23] However, for the nanostructured Cu/ZrO₂ catalysts described here the additional Cu-O shell and the limited data range render a reliable determination of crystallite size effects from an EXAFS analysis difficult.

Nuclear magnetic resonance (NMR) spectroscopy

Similar to X-ray diffraction line broadening, a symmetric and narrow ⁶³Cu NMR line profile indicates large and ordered crystallites. Hence, a decrease in the copper crystallite size results in a symmetric NMR line broadening, while an increase in strain or disorder causes an asymmetric NMR line profile.^[9,24] Figure 12 shows the ⁶³Cu NMR spectra of the Cu/ZrO₂ catalyst after various reaction steps. Besides differences in the amplitude it can be seen, that the width of the NMR lines varies only slightly as a function of the treatment conditions.

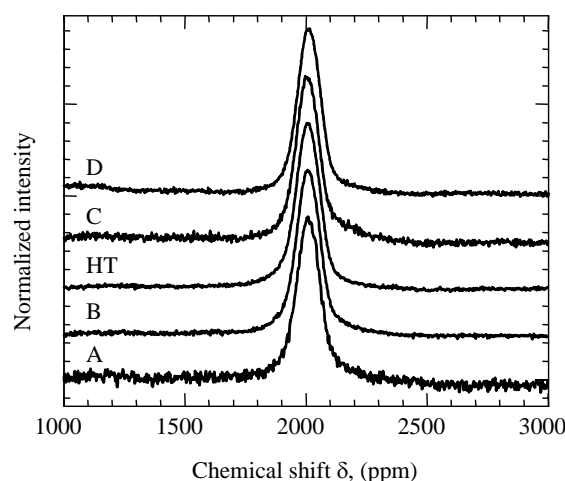


Figure 12: ⁶³Cu NMR spectra of the Cu/ZrO₂ catalyst measured ex situ after various treatments: (A) reduction in methanol and water at 523 K (feed), (B) feed after first temporary addition of oxygen (10 vol-% O₂), (HT) treatment in 2 vol-% H₂ at 673 K, (C) feed after treatment at 673 K, (D) feed after second addition of oxygen.

Discussion

Structure of the CuO/ZrO₂ precursor

Small CuO particles and low concentration of Cu in the material (8 %) accounts for the fact that no copper oxide phases are detected in the XRD pattern of the CuO/ZrO₂ precursor (Figure 1). XAFS measurements of the precursor material identified CuO as the main copper phase (Figure 2, Figure 3). The deviations between the $FT(\chi(k) \cdot k^3)$ of the reference CuO and the CuO/ZrO₂ precursor in the amplitude of the higher shells (Figure 3) are caused by a strongly disordered structure and/or small crystallite sizes of the nanostructured CuO/ZrO₂ precursor.^[3] Okamoto et al. proposed highly dispersed Cu²⁺ in CuO/ZrO₂ to account for the deviations from ideal CuO in the $FT(\chi(k))$.^[25] However, a calcination temperature of 973 K used by these authors may have resulted in a considerable incorporation of Cu in ZrO₂ which renders a comparison with the Cu/ZrO₂ material prepared here difficult.

Zhou et al. have reported on Cu/ZrO₂ catalysts, consisting mostly of tetragonal zirconia for copper concentration less than 10 wt-%.^[26] They suggested an interaction between copper oxide and the ZrO₂ support that prevents phase transformation to monoclinic ZrO₂ according to the oxygen vacancy model of Sanchez and Gazquez.^[27] Various metal centers in ZrO₂ (e.g. Y, Ce, Al, Cu) were reported to stabilize tetragonal zirconia.^[28-30] Because no incorporation of Cu into the ZrO₂ lattice was detectable by XRD or EXAFS (complete reduction of Cu at 673 K, detection limit ~ 1 %), a significant stabilizing effect of Cu centers in ZrO₂ can be excluded for the nanostructured Cu/ZrO₂ catalysts.^[3] Garvie et al.^[31,32] and Chraska et al.^[33] discussed the influence of the particle size on the stability of the tetragonal phase and found, that for small particles ($r_{\text{critical}} \approx 9 \text{ nm}$ to 30 nm) the stability of the tetragonal phase at room temperature can be explained by the lower surface energy of t-ZrO₂ compared to m-ZrO₂. This may explain the stabilization of the tetragonal ZrO₂ particles with a diameter of about 7 nm in addition to the influence of the copper phase and the particular preparation technique on the surface termination of the ZrO₂ particles.

Reduction of the CuO/ZrO₂ precursor

Two DSC signals at 423 K and 440 K measured during reduction of the CuO/ZrO₂ precursor correspond to the reduction of CuO to Cu₂O and Cu₂O to Cu metal, respectively, with Cu₂O as an intermediate of the reduction (Figure 9). The PC analysis of the in situ XAFS spectra also shows that the reduction in 2 vol-% H₂/He and methanol/water proceeds via an intermediate phase (Figure 8a). Hence, a bimodal particle sizes distribution like that suggested for Cu on Y-doped ZrO₂^[34] with small CuO clusters and bulk CuO that reduce at ~ 423 K and ~ 448 K, respectively, should not be the main source for the DSC/MS signals measured. The formation of an intermediate Cu₂O phase during the reduction of CuO/ZrO₂ in both hydrogen and methanol/water (feed) is in agreement with our previous results on Cu/ZnO catalysts. The reduction temperatures determined by the PC analysis indicate that the reduction of CuO/ZrO₂ in the feed is shifted to higher temperatures probably because of the oxidizing influence of water and carbon dioxide^[10,35] (Figure 8). The increased reduction temperature, however, does not seem to result in significantly larger Cu particles. In contrast to the reduction of Cu/ZnO under similar conditions, the reduction of the CuO/ZrO₂ precursor in 2 vol-% H₂/He at 523 K did not result in pure copper metal clusters on ZrO₂ but in a partially oxidized copper phase (Figure 5, Figure 7).

Structure of the activated Cu/ZrO₂ catalyst

In contrast to Cu/ZnO catalysts that appear completely reduced at 523 K in 2 % H₂, the activated Cu/ZrO₂

catalyst exhibits a lower degree of reduction with a considerable amount of oxygen still detectable in the Cu K edge XAFS data (Figure 4, Figure 7). High temperature treatment of the Cu/ZrO₂ catalyst in hydrogen resulted in a complete reduction of the copper oxide phase to copper metal (Figure 11). Hence, the remaining amount of oxygen detectable after initial reduction in methanol and water or after re-reduction following the addition of oxygen to the feed cannot be ascribed to isolated copper centers in the ZrO₂ or copper oxide particles inaccessible to the gas phase. From the XAFS data of the Cu/ZrO₂ catalyst shown here it is difficult to distinguish between oxygen in the copper particles, a mixture of separated Cu clusters and very small Cu oxide particles, or a copper oxide interface between the Cu clusters and the ZrO₂ support. Because the experimental FT($\chi(k)$)*k³ of activated Cu/ZrO₂ catalysts can be well described beyond the first shell by Cu metal alone (Figure 5), a considerable amount of large or well-crystalline Cu₂O particles can be excluded. Additionally, no isolated copper oxide particles were detected in TEM measurements on a Cu/ZrO₂ sample prepared and activated similarly to the one described here. This seems to corroborate the presence of either oxygen in the copper particles or a copper oxide interface layer.

High temperature treatment of Cu/ZrO₂ in H₂

During reduction in H₂ at 673 K, the Cu/ZrO₂ catalyst exhibited only minor sintering of the Cu particles (Table 1, Figure 11, Figure 12). Conversely, Cu/ZnO catalysts treated at 673 K in hydrogen exhibit strong sintering accompanied by loss of copper surface area and catalytic activity. This process appears to be irreversible for Cu/ZnO materials, whereas the fully reduced Cu/ZrO₂ catalyst can be re-activated by an oxidation/re-reduction treatment. Hence, the Cu/ZrO₂ catalyst described here possesses a considerable stability towards temporarily increasing temperatures which may make it more suitable for use in mobile applications under changing reaction conditions.

Methanol steam reforming on a Cu/ZrO₂ catalyst

A linear correlation between the specific copper surface area and methanol synthesis activity has already been proposed by Chinchén et al.^[4] However, additional factors influence the activity of copper catalysts and deviations in the microstructure of the catalysts may result in differently active copper surfaces. Similar to our results on Cu/ZnO catalysts,^[8-10] the MSR activity of the Cu/ZrO₂ catalyst described here (Table 1) exhibits no simple linear correlation with the specific Cu surface area. A sufficient copper surface area is a prerequisite for an active methanol catalyst, however, it cannot account for the differences observed after the various oxidation/reduction treatments (Table 1). While after the first addition of oxygen to the

MSR feed the detectable Cu surface area decreased, the corresponding H₂ production rate increased indicating a more active specific copper surface (i.e. higher TOF). Conversely, after high temperature reduction and addition of oxygen to the feed the Cu surface area increased considerably accompanied by a constant H₂ production rate. This corresponds to a less active specific Cu surface (i.e. a lower TOF) after the second addition of oxygen possibly because of a deteriorated interaction between the Cu metal and ZrO₂ support. It seems that also in the Cu/ZrO₂ systems additional microstructural parameters need to be considered to account for differently active specific Cu surfaces observed.

In contrast to our previous reports on the correlation of microstrain and activity of Cu/ZnO catalysts,^[8,9] ⁶³Cu NMR spectroscopy studies on differently treated Cu/ZrO₂ catalysts yielded nearly symmetric NMR lines (Figure 12) independent on the treatment conditions. This is indicative of only minor amounts of microstrain in the copper phase in the Cu/ZrO₂ materials. Moreover, it seems that the varying amount of oxygen in the copper phase dependent on the treatment conditions has very little effect on the degree of strain detectable in the copper particles. The characteristic epitaxial relationship between Cu and ZnO in the conventional Cu/ZnO catalysts is the most likely origin of the microstrain in the copper phase of these materials. Apparently, Cu on ZrO₂ exhibits a different metal support interaction, which does not result in detectable strain in the copper particles.

After reduction in hydrogen, the Cu/ZrO₂ catalyst exhibited little initial catalytic activity. However, under methanol steam reforming conditions, temporarily adding oxygen to the feed before or after the high temperature reduction resulted in an increased catalytic activity (Figure 7, Figure 10) accompanied by an increased amount of oxygen in the copper particles (Figure 4, Figure 7). Similarly, addition of oxygen results in an increase in copper crystallite size of Cu/ZnO catalysts and, thus, a decrease in specific copper surface area.^[10] After addition of oxygen, the Cu/ZnO catalysts re-reduced completely in the feed and an increased catalytic activity was obtained correlating with an increased degree of microstrain in the copper particles. In contrast to Cu/ZnO, the increased amount of oxygen remaining in the copper particles of Cu/ZrO₂ after oxygen addition to the feed is indicative of an incomplete re-reduction. A comparable correlation between activity and oxidation of copper has been reported for Cu/Al₂O₃ and Cu/ZnO catalysts suggesting a partial re-oxidation of copper metal to Cu₂O after a certain activation time in the MSR feed.^[37,36] Cheng et al.^[28] correlated the MSR activity of copper on an oxygen ion conducting yttria-ceria-alumina support with the availability of oxygen adsorption sites and, hence, enhanced oxidation of Cu to Cu⁺. For the catalyst investigated here such an interaction is not evident, nevertheless it is possible that oxygen stored at the surface of the ZrO₂ support stabilizes partially oxidized copper clusters or a copper oxide interface layer.

The lower reducibility of Cu/ZrO₂ and the small degree of microstrain in the copper particles strongly suggest a different metal support interaction between Cu and ZrO₂ compared to Cu and ZnO. Apparently, the defective microstructure of the Cu/ZrO₂ catalyst under reaction conditions considerably influences the catalytic activity and results in differently active specific copper surfaces depending on the treatment conditions. For the nanostructured Cu/ZrO₂ catalyst studied here it is proposed, that the incomplete re-reduction after temporary addition of oxygen to the feed, increases the effect of the oxidized copper bulk structure on the electronic structure of copper sites at the surface. Hence, the increase in reactivity observed after the addition of oxygen may be correlated to a change in the filling of the copper d-band and, thus, changes in adsorption or dissociation energies. A comparable influence on the electronic Cu surface structure is ascribed to the microstrain in Cu/ZnO catalysts indicating that both effects may be complementary in modifying the catalytic activity of copper in methanol chemistry.

Summary

In situ bulk structural investigations of a nanostructured Cu/ZrO₂ catalyst under methanol steam reforming conditions were performed to reveal structure-activity relationships. Small and disordered CuO particles were identified as the main copper phase present in the precursors. The initial low steam reforming activity of the Cu/ZrO₂ catalyst after reduction in hydrogen could be significantly increased by a short addition of oxygen to the feed. Reduction of the Cu/ZrO₂ catalyst in the feed or re-reduction after oxidation resulted in supported nanoparticles with an increased amount of oxygen in the copper particles which correlates to the increased activity of the Cu/ZrO₂ catalyst. In contrast to conventional Cu/ZnO catalysts, only a minor degree of microstrain is detected in the active copper phase of Cu/ZrO₂ catalysts. The decreased reducibility of CuO/ZrO₂, the low degree of microstrain, and the correlation between the amount of oxygen remaining in the copper particles and catalytic activity indicate a different metal support interaction compared to Cu/ZnO catalysts. Similar to Cu/ZnO catalysts, however, the interaction between Cu and ZrO₂ stabilizes an active copper microstructure that strongly deviates from bulk copper metal.

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References

- [1] B. Lindström, L.J. Pettersson, *Int. J. Hydrogen Energy* 26 (2001) 923.
- [2] P.J. de Wild, M.J.F.M. Verhaak, *Catal. Today* 60 (2000) 3.
- [3] H. Purnama, F. Girgsdies, T. Ressler, J.-H. Schattka, R.A. Caruso, R. Schomäcker, R. Schlögl, *Catal. Lett.* 94 (2004) 61.
- [4] G.C. Chinchin, K.C. Waugh, D.A. Whan, *Appl. Catal.* 25 (1986) 101.
- [5] P.L. Hansen, J.B. Wagner, S. Helveg, J.R. Rostrup-Nielsen, B.S. Clausen, H. Topsøe, *Science* 295 (2002) 2053.
- [6] J.B. Bulko, R.G. Herman, K. Klier, G.W. Simmons, *J. Phys. Chem.* 83 (1979) 3118.
- [7] B.S. Clausen, J. Schiøtz, L. Gråbæk, C.V. Ovesen, K.W. Jacobsen, J. K. Nørskov, H. Topsøe, *Top. Catal.* 1 (1994) 367.
- [8] M.M. Günter, T. Ressler, B. Bems, C. Buscher, T. Genger, O. Hinrichsen, M. Muhler, R. Schlögl, *Catal. Lett.* 71 (2001) 37.
- [9] B.L. Kniep, T. Ressler, A. Rabis, F. Girgsdies, M. Baenitz, F. Steglich, R. Schlögl, *Angew. Chem.* 116 (2004) 114.
- [10] M.M. Günter, T. Ressler, R.E. Jentoft, B. Bems, *J. Catal.* 203 (2001) 133.
- [11] M. Kurtz, H. Wilmer, T. Genger, O. Hinrichsen, M. Muhler, *Catal. Lett.* 86 (2003) 77.
- [12] J.P. Breen, J.R.H. Ross, *Catal. Today* 51 (1999) 521.
- [13] B. Denise, R.P.A. Sneeeden, *Appl. Catal.* 30 (1987) 353.
- [14] Y. Nitta, O. Suwata, Y. Ikeda, Y. Okamoto, T. Imanaka, *Catal. Lett.* 26, (1994) 345.
- [15] Y. Wang, R.A. Caruso, *J. Mater. Chem.* 12 (2002) 1442.
- [16] T. Ressler, R.E. Jentoft, J. Wienold, M.M. Günter, O. Timpe, *J. Phys. Chem. B* 104 (2000) 6360.
- [17] H.P. Klug, L.E. Alexander, *X-ray diffraction procedures*, John Wiley and Sons, New York (1945) 491 pp.
- [18] Designed by M. Hagelstein, T. Neisius, et al., ESRF, France in a collaborative effort with the Fritz-Haber-Institute, Berlin, Germany (see also Ref. 17).
- [19] T. Ressler, *J. Synch. Radiat.* 5 (1998) 118.
- [20] S.I. Zabinsky, J.J. Rehr, A. Ankudinov, R.C. Albers, M.J. Eller, *Phys. Rev. B: Condens. Matter* 52 (1995) 2995.
- [21] T. Ressler, J. Wong, J. Roos, I.L. Smith, *Environ. Sci. Technol.* 34 (2000) 950.
- [22] G.C. Chinchin, C.M. Hay, H.D. Vandervell, K.C. Waugh, *J. Catal.* 103 (1987) 79.
- [23] B.S. Clausen, L. Grabek, H. Topsoe, L.B. Hansen, P. Stoltze, J.K. Nørskov, O.H. Nielsen, *J. Catal.* 141 (1993) 368.
- [24] A.V. Chadwick, I.J.F. Poplett, D.T.S. Maitland, M.E. Smith, *Chem. Mater.* 10 (1998) 864.
- [25] Y. Okamoto, H. Gotoh, H. Aritani, T. Tanaka, S. Yoshida, *J. Chem. Soc., Faraday Trans.* 93 (1997) 3879.
- [26] R-x. Zhou, T-m. Yu, X-y. Jiang, F. Chen, X-m. Zheng, *Appl. Surf. Sci.* 148 (1999) 263.
- [27] M.G. Sanchez, J.L. Gazquez, *J. Catal.* 104 (1987) 120.
- [28] W-H. Cheng, I. Chen, J-s. Liou, S.-S. Lin, *Top. Catal.* 22 (2003) 225.
- [29] M.K. Dongare, V. Ramaswamy, C.S. Gopinath, A.V. Ramasamy, S. Scheurell, M. Brueckner, E. Kemnitz, *J. Catal.* 199 (2001) 209.
- [30] M.M. Cervera, M. Escobar, M.C. Caracche, P.C. Rivas, A.M. Rodriguez, *Hyperfine Interact.* 120/121 (1999) 469.
- [31] R.C. Garvie, *J. Phys. Chem.* 82 (1978) 218.
- [32] R.C. Garvie, *J. Phys. Chem.* 69 (1965) 1238.
- [33] T. Chraska, A.H. King, C.C. Berndt, *Mater. Sci. Eng. A* 286 (2000) 169.
- [34] L. Kundakovic, M. Flytzani-Stephanopoulos, *Appl. Catal.* 171 (1998) 13.
- [35] R.O. Iden, N.N. Bakhshi, *Indian J. Eng. Chem. Res.* 33 (1994) 2065.
- [36] K. Klier, V. Chatikavani