

## Microstructural Characteristics of Cu/ZnO Catalysts for Methanol Steam Reforming as a Function of Precipitate Ageing

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### Introduction

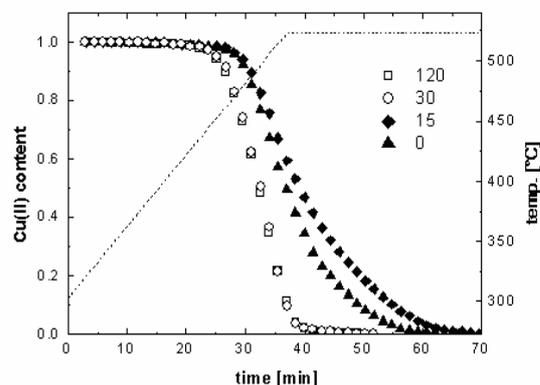
Copper zinc oxide catalysts are of important industrial relevance for the methanol synthesis, water gas shift reaction, and are also known to be active for the methanol steam reforming reaction ( $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3 \text{H}_2$ ). Recently, we were able to show that the catalytic activity of binary Cu/ZnO catalysts correlates with the microstrain in copper particles [1]. In order to tailor microstructural characteristics such as structural disorder, impurities, microstrain, and particle size and thus open up pathways to a rational catalyst design, we investigated the effect of precipitate ageing on structure activity relationship. Therefore, Cu-Zn hydroxycarbonate precursors (ratio Cu/Zn = 70/30 mol%) were co-precipitated at constant pH (pH = 7). The precipitates were aged for 0, 15, 30 and 120 min in the mother liquor, followed by drying, washing, and calcination in air for 3h. Reduction kinetics and phase transitions of the CuO/ZnO catalysts were investigated by detailed Cu K-edge XANES analysis in comparison with thermogravimetric experiment. Microstructural properties of the freshly reduced and activated catalyst were elucidated by using the two complementary methods in situ X-ray diffraction and in-situ X-ray adsorption spectroscopy (XAS) combined with mass spectrometry.

### Experimental

In situ XAS experiments were performed in transmission geometry on the Cu K-edge ( $E=8.979 \text{ eV}$ ) at beamline E4 and X1. The measurements carried out in a flow reactor containing a pellet with a mixture of Cu/ZnO catalysts diluted in boron nitride (ratio Cu/ZnO : BN = 1:10) pressed for 1 min at 1,5 t. Reduction of the catalysts takes place in 2%  $\text{H}_2$  in He (1 bar, total flow 40 ml/min) in a temperature range of 303K – 523K with a heating ramp of 6K/min. The XANES spectra monitored during temperature programmed reduction (TPR) were measured with a time resolution of 100 sec/spectrum in an energy range of 8.9 to 9.1 keV. The number of phases needed to simulate a set of experimental XANES spectra was identified by principal component analysis (PCA). Phase transitions and kinetics during reduction were determined by refining a linear combination of appropriate reference spectra to the experimental XANES spectrum. After reduction, copper EXAFS was monitored in methanol steam reforming gas mixture (ratio  $\text{CH}_3\text{OH}:\text{H}_2\text{O} = 1:1$ ) at 523 K. Simulation of the experimental EXFAS was carried out in R space with a theoretical Cu EXAFS calculated by FEFF 8 [2]. For the data analysis the software package WINXAS v2.3 [3] was used.

### Results

Three reference compounds ( $\text{CuO}$ ,  $\text{Cu}_2\text{O}$ ,  $\text{Cu}$ ) were identified by PCA of the experimental XANES spectra measured during TPR. A sequential reduction pathway from  $\text{CuO}$  to the intermediate and metastable phase  $\text{Cu}_2\text{O}$ , and finally  $\text{Cu}$  metal was found, which is in good agreement with previous investigations [4]. The  $\text{CuO}$  content of the four differently aged CuO/ZnO catalysts during TPR is depicted in Figure 1. With increasing precipitate ageing time the onset of reduction is shifted from 462K (0 min and 15 min) to 444K (30 min and 120 min), accompanied by a decrease in particle size from 110Å (0 min) to 70Å (120 min). Thermogravimetric experiments under the same reduction conditions reveal identical shifts in onset temperature of reduction.



**Fig. 1:** Cu(II) content during TPR in 2%  $\text{H}_2$  from 50°C to 250°C of four Cu/ZnO catalysts aged for 0, 15, 30 and 120 min.

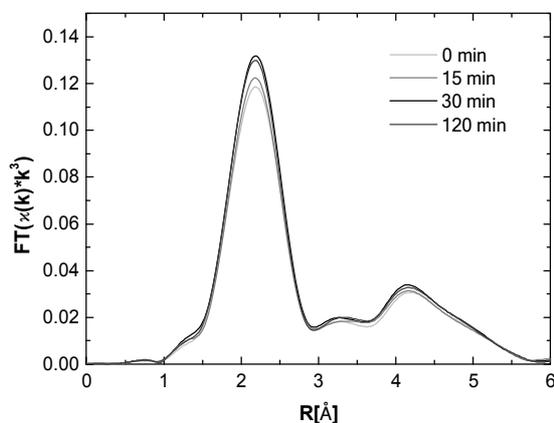


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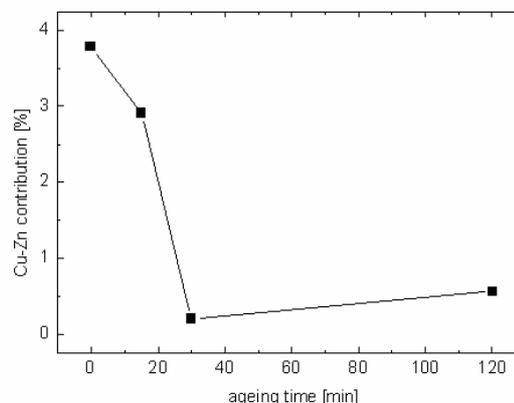


The Cu/ZnO catalysts prepared from precursors aged for longer times (30 and 120 min) exhibit a much-increased H<sub>2</sub> production rate. The decreasing Cu particle size (110 Å = 0 min ageing to 70 Å = 120 min ageing) obtained from a detailed XRD line profile analysis and the resulting higher surface area alone cannot explain the increase in activity. However, a positive correlation between microstrain in copper particles and catalytic activity was found [5]. Cu<sup>63</sup> NMR investigations confirm with the XRD results concerning the positive correlation between microstrain in copper nanoparticles and catalytic activity.

In addition to the in situ XRD experiments, the EXAFS of the catalysts was measured at the Cu K-edge in methanol steam reforming gas mixture at 523K. A comparison of the resulting radial distribution functions (RDF) for the four differently aged copper/zincoxide catalysts is given in Figure 2. Qualitatively, the experimental measured RDF can be described by theoretical calculated copper metal EXAFS. However, a strong increase in the amplitude of the first Cu-Cu shell ( $R_{\text{Cu-Cu}}=2.55\text{Å}$ ) with increasing ageing time is clearly visible, which is in contrast to the expected decrease in amplitude caused by an increase in Debye-Waller factors due to more strained copper particles. Moreover, the decrease in amplitude of the first Cu-Cu shell caused by changes in coordination number (CN) due to morphologic changes in copper particles can be excluded because of the relatively large particle size from 110Å to 70Å. EXFAS refinements assuming pure copper metal reveal significant deviations in the distances of the first Cu-Cu shell. These results can be traced back to the occupation of Zn on copper lattice sites. In order to determine the amount of Cu-Zn alloy (resp. the solid solution of Cu-Zn) an additional Cu-Zn alloy shell with a distance of  $R_{\text{Cu-Zn}}=2.66\text{Å}$  was assumed for theoretical EXAFS simulation. The Cu-Zn contribution necessary to simulate the first shell of the experimental spectra is shown in Figure 3. The results clearly demonstrate that the amount of Zn occupying Cu lattice sites decreases as function of ageing time.



**Fig. 2:** Cu EXAFS at 250°C in steam reforming gas mixture of for Cu/ZnO catalysts aged for 0, 15, 30 and 120 min



**Fig. 3:** Cu-Zn contribution to the first Cu-Cu shell obtained by EXAFS refinement as function of ageing time

In summary, ageing of Cu-Zn hydroxycarbonate precursors followed by calcinations and reduction leads to smaller copper nanoparticles. In addition to the resulting higher copper surface area, microstrain in copper particles increases with increasing ageing time. Both particle size and microstrain are necessary in order to explain the increase in methanol steam reforming activity as a function of ageing. It is assumed that the microstrain is induced by an epitactical orientation of copper on zincoxide. Precipitate ageing leads to a decreasing amount of Zn occupying Cu lattice sites in the active Cu/ZnO catalyst, which enables the extension of microstrain to the surface, and result in a modified electronic structure.

## References

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