

XAS Studies on the structure of copper oxide / zinc oxide catalyst: oxidic and reduced state

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Cu/ZnO supported on alumina is a well-known catalyst for the hydrogenation of CO and CO₂ and are utilized extensively in the process of methanol synthesis and for the water gas shift reaction [1]. The individual components exhibit only little activity, maximum activity is observed with an intermediate Cu/ZnO composition [2]. The objective of the work presented here is a combination of inorganic synthesis and physical-chemical characterization to assess the influence of preparation parameters (coprecipitation followed by calcination and activation) on the resulting active copper phase. A wet chemical coprecipitation method was used to prepare binary metal hydroxycarbonate precursors of a systematic series of samples with varying Cu/Zn ratios. Calcination of the precursors at ~ 300 °C afforded a defect rich mixed CuO/ZnO material. Crystallite size determination from X-ray diffraction line profile analysis showed that the obtained domain size is a function of the Cu/Zn ratio [3]. In order to corroborate the XRD results we have performed ex situ XAFS studies on calcined and reduced CuO/ZnO samples.

XAFS measurements of the oxidized precursors have been carried out at the Cu K edge ($E = 8.979$ keV) and the Zn K edge ($E = 9.659$ keV) in transmission mode at beamline E4. Analysis of the Fourier transformed (FT) spectra showed that both copper oxide and zinc oxide exhibit considerable deviations from a linear dependence of structure on composition. In agreement with XRD measurements those deviations coincide with the formation of different hydroxycarbonate precursors with different Cu/Zn ratios.

In addition, selected samples have been investigated in situ during temperature programmed reduction (TPR) experiments at beamline X1. Reduction was performed in 8 vol.% H₂ in He at a heating rate of 5 K/min in the range 175 °C – 250 °C. Gas phase composition was continuously monitored using on-line mass spectrometry. It can be seen from Figure 1 that the onset of reduction coincides with the evolution of H₂O and the uptake of H₂. Hence, compared to in situ XRD results [3] where the detection of copper metal requires a certain particle size and therefore appears to be shifted with respect to the evolution of water, XAS can afford complementary information on the early stage of reduction.

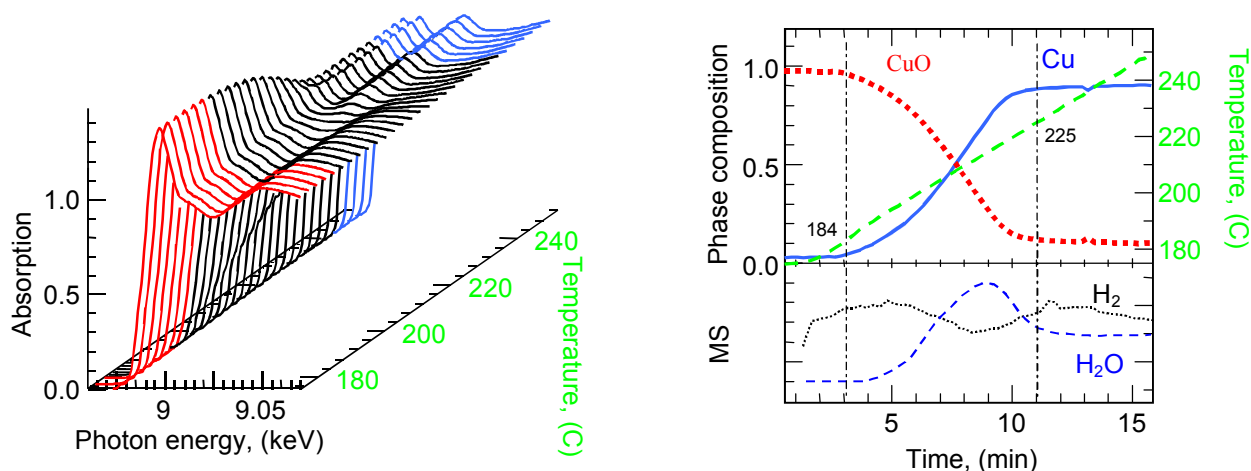


Figure 1. Evolution of time-resolved XANES spectra of the Cu K edge of a CuO/ZnO sample during TPR in 8 % H₂. Reaction of Cu oxide to metallic copper (left) can be seen. The corresponding change in phase composition during the reaction together with the MS signal of H₂O and H₂ is shown on the right.

From time-resolved experiments measuring the Cu K edge (15 s/frame) the degree of reduction can be monitored using a combination of principal component analysis (PCA) and least-squares XANES fitting with suitable reference spectra (e.g. Cu metal and CuO XANES spectra). The intermediate presence of Cu(I) species could not be confirmed which indicates that for more dilute binary Cu/ZnO the reduction may proceed directly to pure copper [4, 5]. In addition, the available time-resolution in the QEXAFS mode enabled us to follow the very rapid reoxidation of the reduced copper clusters at 250 °C (18 vol.% O₂ in He, 8 s/spectrum). It can be seen from Figure 2 that smaller copper crystallites exhibit a faster reaction rate during reoxidation.

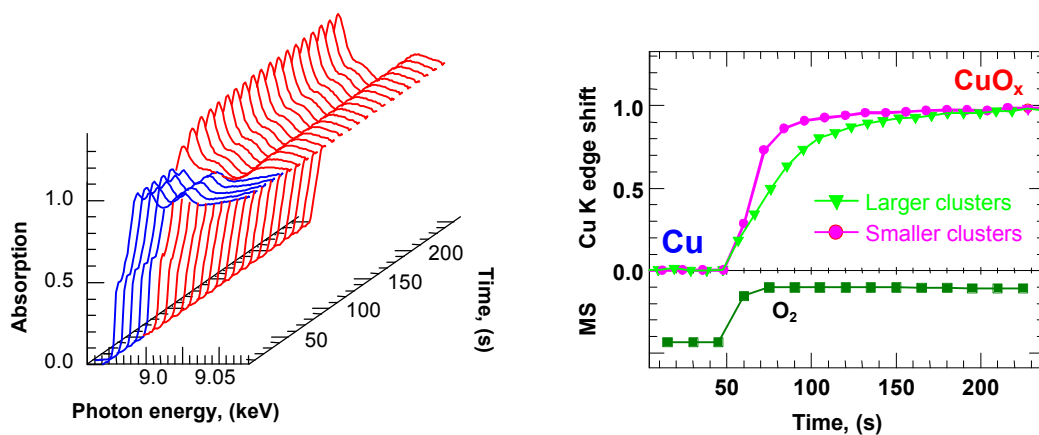


Figure 2. Time-resolved XANES spectra of the Cu K edge of a Cu/ZnO sample during isothermal oxidation at 250 °C in 18% O₂. Rapid reaction from Cu to copper oxide (left) can be seen. Normalized Cu K edge shift data are shown for two Cu/ZnO systems possessing different particle sizes (right). Different reoxidation rates can be observed.

Repeated cycles of reduction and reoxidation at 250 °C were investigated with in situ XAFS. A reversible change between copper oxide and reduced copper clusters is evident from the Fourier transformed Cu K edge EXAFS of reoxidized and re-reduced Cu/ZnO samples (Figure 3). Moreover, the increased magnitude of the Cu-Cu shell (2.4 Å) together with the appearance of higher shells in the re-reduced state indicates an increased crystallinity and/or particle size. The Zn FT($\chi(k)$) also reveals

an increased intensity of higher Zn-O shells after reduction, while ZnO remains unreduced under the conditions employed.

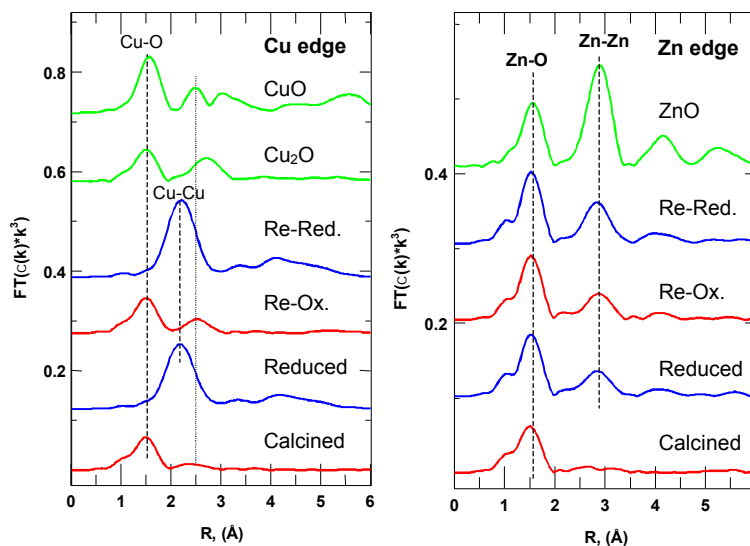


Figure 3. Cu and Zn K edge FT[$\chi(k)$] after repeated reduction and oxidation cycles. Sample composition: 60 at. % Cu and 40 at. % ZnO

References

- [1] K. Klier, *Adv. Catal.* 31, 243 (1982); J.C.J. Bart and R.P. Sneed, *Catal. Today* 2, 1 (1987)
- [2] T. Fujitani, and J. Nakamura, *Cat. Lett.* 56, 119 (1998)
- [3] M.M. Günter, T. Ressler, B. Bems, and R. Schlögl, in preparation
- [4] B.S. Clausen, *Catal. Today* 39, 293 (1998)
- [5] G. Fierro, M. LoJacono, M. Inversi, P. Porta, F. Cioci, and R. Lavecchia, *Appl. Cat. A* 137, 327 (1996)