

In situ XAS studies on Cu/ZnO catalysts in methanol steam reforming

M.M. Günter, R.E. Jentoft, B. Bems, and T. Ressler

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Abteilung Anorganische Chemie,
Faradayweg 4-6, 14195 Berlin, Germany

Abstract

Cu/ZnO catalysts can be used to produce hydrogen by steam reforming of methanol with high selectivity and activity [1,2]. Therefore methanol is considered as an alternative “automotive” fuel and could serve as a hydrogen source for fuel cell applications. The steam reforming reaction can be regarded as the reversed methanol synthesis reaction ($\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2$). Whereas the Cu/ZnO system has been studied in great depth after reduction and under working conditions for the methanol synthesis [3 and references therein] the active Cu phase for methanol reforming is not fully elucidated yet. In this study we used time resolved X-ray absorption spectroscopy to elucidate bulk structural changes of Cu in Cu/ZnO systems during activation and under methanol steam reforming conditions while the gas phase is analyzed on-line with a calibrated mass spectrometer [4].

The precursors were prepared according to the coprecipitation method at a constant pH (7.0). Binary hydroxycarbonate precursors with varying Cu/Zn ratios were obtained. Calcination of the hydroxycarbonate precursor at 600 K for 3 h in a muffle furnace afforded mixed CuO/ZnO. The in situ XAS experiments were carried out in the transmission mode in a flow-reactor at atmospheric pressures. Selected CuO/ZnO-samples (70/30, 60/40, 40/60, 30/70, 10/90) were investigated. The samples were mixed with boron nitride (ratio CuO/ZnO: BN = 1:6) and 45 mg of the mixture was pressed into a 5 mm in diameter self supporting pellet. The in situ XAS experiments at the Cu K edge ($E = 8.979 \text{ keV}$) were performed at beam line X1. XANES spectra were measured in the Quick-EXAFS mode with a time resolution of 15 s/spectra. A calibrated mass spectrometer (QMS200 Pfeiffer) permitted a quantitative analysis of the gas phase during the experiments. The software package WinXAS v2.0 [5] was used for a statistical analysis of time resolved Cu K edge XANES data to reveal qualitative and quantitative information on copper bulk phases under temperature programmed reduction (TPR) and steam reforming conditions. The identification of the number and type of phases was achieved by principal component analysis (PCA) of the experimental XANES spectra. Reference spectra of these phases were then used in a least-square fitting procedure of the time-resolved spectra to determine the fraction of each phase present [6].

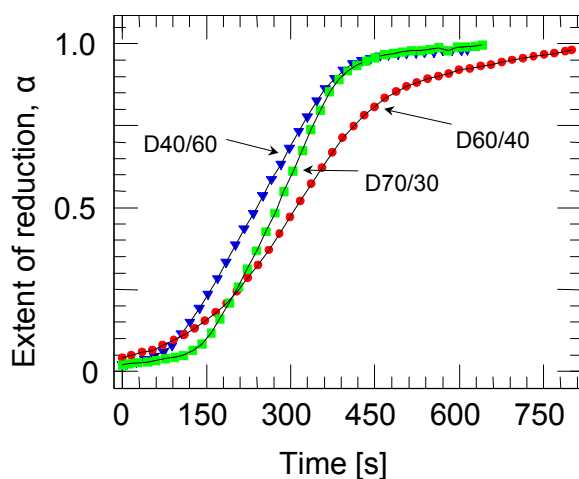


Figure 1: Extent of reduction α (formation of Cu) during TPR of three CuO/ZnO samples with different copper concentration (atomic ratio of Cu and Zn indicated) in 8 vol-% H_2 at 5 K/min between 433 K and 523 K.

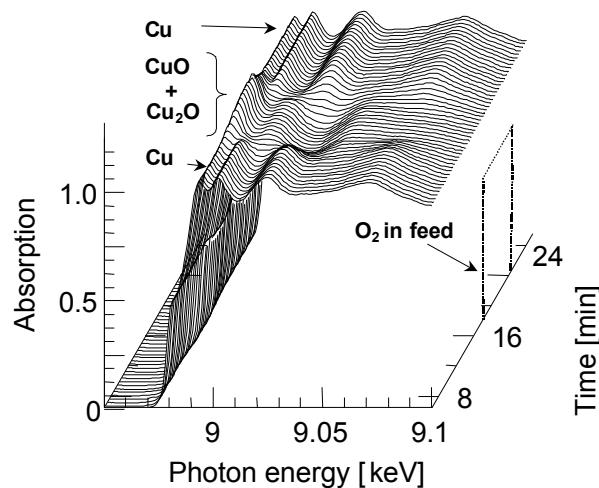


Figure 2: Evolution of Cu K edge XANES of CuO/ZnO (60:40) at 523 K during oxygen addition (15 vol-%) to a methanol steam reforming feed (MeOH ~ 6 vol-%, H_2O ~ 1.5 vol-% in 25ml/min).

Temperature programmed reduction (TPR) was performed with 8 vol-% H_2 from 433 – 523 K at a temperature ramp of 5 K/min. The catalytic activity of the Cu/ZnO samples for steam reforming of methanol was determined at atmospheric pressure at 523 K using saturators for methanol and water at room temperature.

For the TPR experiments PCA of the Cu K edge XANES spectra revealed that three primary components were necessary to reconstruct the experimental spectra (CuO, Cu_2O , and Cu). In that way the evolution of the copper phases during TPR is determined and reduction curves (extent of reduction to metallic copper, α) can be obtained (Figure 1). The sigmoidal shape of the reduction curves can be described by an Avrami-Erofeev kinetic behaviour indicating a solid state process whose rate is determined by the formation of product nuclei. For the catalyst studied the reducibility of the CuO/ZnO systems (Cu nuclei formation during reduction) does not depend linearly on the Cu content in the catalyst as different reduction rates are observed.

After temperature programmed reduction and cooling the sample to 298 K, the binary Cu/ZnO samples were exposed to a He-flow saturated with MeOH/H₂O in a ratio of 4/1 (total flow 25 ml/min). Reactants and products (MeOH, H₂O, H₂, CO₂, CO) occurring during the reaction were quantitatively monitored with a mass spectrometer.

In Figure 2 the Cu K edge XANES spectra measured over a period of 20 min during oxygen addition to the feed at 523 K is presented. It can be seen that adding O₂ (15 vol-%) to the feed results in an increase of the Cu K pre-edge feature. Apparently, reversible changes of the oxidation state of copper can be observed during oxygen cycles due to oxidation and subsequent re-reduction in the feed (Figure 3). Furthermore, different reaction products are detected upon changes in copper bulk phase composition (Cu oxidation state). It can be concluded that the changes of bulk phases and product composition during the oxygen cycles permit to distinguish between different active copper states.

Hence, completely reduced Cu clusters on ZnO constitute the active bulk phase for methanol steamreforming with no further oxidized Cu species detectable. Further experiments showed that upon repeated oxidation and re-reduction cycles minor structural changes are found to increase selectivity. This indicates that the Cu surface is a necessary prerequisite for the catalytic activity but cannot uniquely account for the observed changes in activity and selectivity.

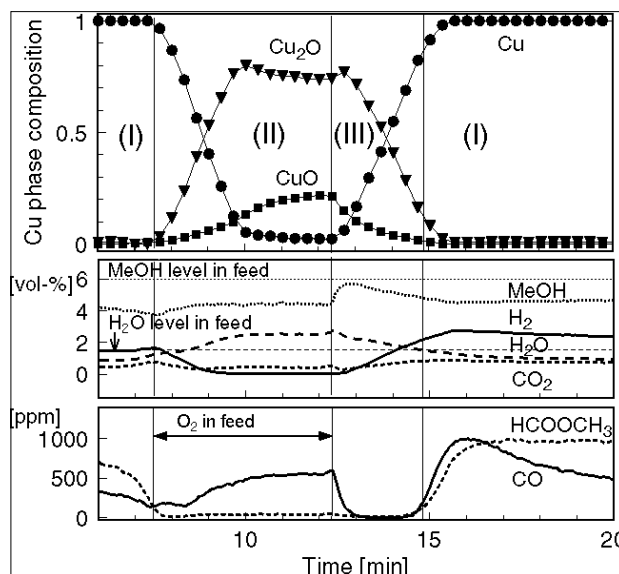


Figure 3: Changes in Cu phase composition during same period. Phase analysis was obtained from least-squares fit of reference spectra to the corresponding spectra. Two lower sections of the graph depict the evolution of the gas phase in percent and ppm, respectively.

References

- [1] K. Takahashi, N. Takezawa, H. Kobayashi, Appl. Cat. 2, 363 (1982)
- [2] J.C. Amphlett, M.J. Evans, R.F. Mann, and R.D. Weir, Can. J. Chem. Eng. 63, 605 (1985)
- [3] B.S. Clausen, H. Topsøe, and R. Frahm, Adv. Catal. 42, 315 (1998)
- [4] M.M. Günter, T. Ressler, R.E. Jentoft, and B. Bems, submitted to Journal of Catalysis
- [5] T. Ressler, J. Synch. Rad. 5, 118 (1998)
- [6] T. Ressler, J. Wong; J. Roos, and I.L. Smith, Environ. Science Tech. 34, 950 (2000)