

In situ studies on the structure of copper oxide/zinc oxide catalysts

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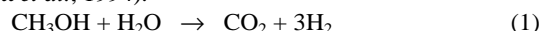
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Cu/ZnO supported on alumina is a well-known catalyst for steam reforming of methanol. In this work it is attempted to assess the influence of elemental composition on the resulting active copper phase. XAFS measurements of calcined precursors were carried out at the Cu K edge and the Zn K edge. Corresponding RDF show that both copper oxide and zinc oxide exhibit considerable deviations from a linear dependence of their structure on the composition coinciding with changes in phase composition of hydroxycarbonate precursor. From time-resolved in situ experiments at the Cu K edge the degree of reduction can be monitored using a combination of factor analysis (PCA) and least-squares XANES fitting with suitable reference spectra (e.g. Cu metal, Cu₂O, and CuO). It is shown that Cu₂O forms prior to Cu. The extent of reduction to Cu exhibited a typical nucleation growth behavior with an enhanced reaction rate for more diluted samples. Adding oxygen to the feed gas leads to the formation of mixed Cu²⁺ and Cu⁺ phases accompanied by a complete loss of activity in methanol steam reforming. After switching back to steam reforming conditions the activity is regained.

Keywords: Cu/ZnO catalyst, XANES, in situ, temperature programmed reduction, structure and selectivity/activity correlation

1. Introduction

The Cu/ZnO catalyst can be used to produce hydrogen by steam reforming of methanol with high selectivity and activity (Kobayashi *et al.*, 1981). Therefore methanol is considered as an alternative “automotive” fuel and could serve as a potential hydrogen source for fuel cell applications (Peters *et al.*, 2000). However, current effort is dedicated to the minimization of CO concentration which acts as a poison in fuel cell application (Amphlett *et al.*, 1994).



The steam reforming reaction (eq. 1) can be regarded as the reversed methanol synthesis reaction. However, it is assumed that the concept of micro-reversibility can not be applied to make predictions about the mechanism and kinetics of methanol steam reforming (Pepply *et al.*, 1999). Whereas the Cu/ZnO system has been studied in great depth after reduction and under working conditions for the methanol synthesis (Clausen *et al.*, 1991, 1998) the active Cu phase for methanol reforming is not fully elucidated yet. It is expected that the copper bulk structure, and hence the chemical state shows a different structural response to the reactant gas mixture as compared to methanol synthesis conditions. In this study we used X-ray absorption spectroscopy to elucidate bulk structural changes of Cu in Cu/ZnO systems during activation and under methanol steam reforming conditions. First, the evolution of bulk phases during activation of the catalyst with hydrogen was investigated. Second, correlations

between the bulk structure of Cu on ZnO and activity or selectivity in the steam reforming of methanol are presented.

2. Experimental

2.1 CuO/ZnO preparation and characterization

The precursors were prepared according to the coprecipitation method both at a constant pH (7.0). Binary hydroxycarbonate precursors of a systematic series with varying Cu/Zn (ranging from 0/100 to 100/0) ratio were obtained and are denoted in the following according to their nominal ratio. Calcination of the hydroxycarbonate precursor at 600 K for 3 h in a muffle furnace in static air afforded mixed CuO/ZnO.

2.2 Ex situ X-ray Absorption spectroscopy

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) at room temperature in transmission mode at beam line E4 (Hamburger Synchrotron Radiation Laboratory, HASYLAB).

2.3 In situ X-ray Absorption spectroscopy

The in situ XAS experiments were performed at beam line X1.1 at the Hamburger Synchrotron Radiation Laboratory, HASYLAB, using a Si(111) double crystal monochromator for ΔE 8959–9100 eV. The storage ring operated at 3.6 GeV with injection currents of 150 mA.

The in situ XAS experiments were carried out in the transmission mode in a flow-reactor at atmospheric pressures (Ressler *et al.*, 2000). Reactant gas flow was controlled with Bronkhorst mass flow controllers. 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 absorption jump at the Cu K edge was ~ 1.5 . XANES spectra were measured in the Quick-EXAFS mode with a time resolution of 15 s/spectra

A calibrated mass spectrometer (QMS200 Pfeiffer) operated in a multiple ion detection mode permitted a quantitative analysis of the gas phase during the experiments. In situ EXAFS spectra was measured after oxidation and re-reduction to reveal structural changes of the Cu and Zn phases present.

2.4 XANES and EXAFS Data Analysis

The software package WinXAS v2.0 (Ressler, 1998) 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 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 (Ressler *et al.*, 2000).

2.5 Activation and Catalysis

Temperature programmed reduction (TPR) runs were performed with 2 vol-% H₂ from 448 – 523 K with 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. 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.

3. Results

3.1 Ex situ analysis of the CuO/ZnO precursor

In Fig. 1 the Fourier transformed (FT) Cu K and Zn K edge spectra for the whole series of CuO/ZnO is displayed. Considerable deviations from a linear dependence of structural features on composition can be seen. In agreement with previous findings (Bems *et al.*) those deviations coincide with changes in the phase composition of hydroxycarbonate precursor.

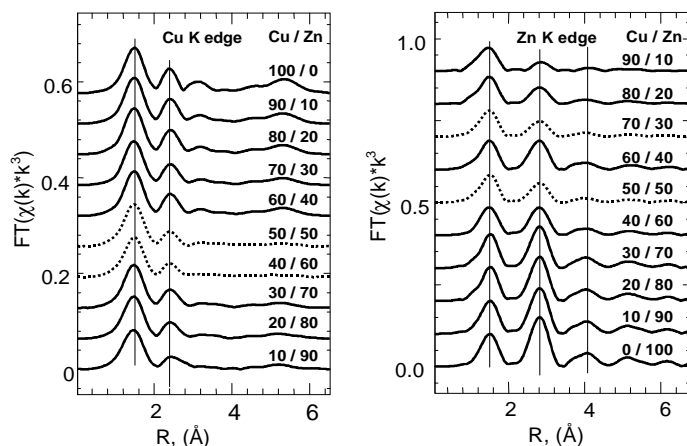


Figure 1 Non-continuous change in EXAFS of systematic series of calcined samples at the Cu K and Zn K edge. Dashed lines represent spectra that deviate from a linear trend in structure with composition.

3.2 Temperature programmed Reduction

A principal component analysis of the Cu K edge XANES spectra revealed that three primary components were necessary to reconstruct the experimental XANES spectra. Using target transformation copper, CuO and Cu₂O were found to be suitable reference compounds. The evolution of the phase composition during TPR of a 70/30 sample under reduction conditions (2 vol-% H₂ in 25 ml/min He, heating ramp 5 K/min, temperature ramp 448 K to 523 K) is depicted in Fig. 2. It can be seen that the onset of reduction coincides with the evolution of H₂O and the uptake of H₂. Hence, complementary information on the early stage of reduction is gained that can be used for further investigation on the reduction kinetics.

3.3 Oxidation and Re-reduction

Repeated cycles of reduction and re-oxidation at 523 K investigated by *in situ* EXAFS are presented in Fig. 3. A reversible change between copper oxide and reduced copper clusters is evident from the Fourier transformed Cu K edge EXAFS of re-oxidised and re-reduced Cu/ZnO sample with 60 mol-% Cu (see Fig. 3). Moreover, the increased magnitude of the Cu-Cu nearest neighbour shells (2.4 Å) in the re-reduced state indicates an increased crystallinity and/or crystallite size.

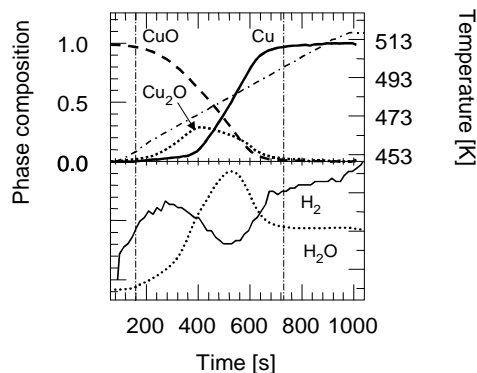


Figure 2 Change in phase composition together with the MS signal of H₂O (dotted) and H₂ (solid) during the TPR experiment in 2 vol-% H₂ with 5 s/spectrum and applying a heating ramp of 5 K/min in the *in situ* XAS cell. The intermediary presence of Cu₂O which is formed prior to metallic Cu can be seen.

The ZnO FT(χ(k)) also reveals an increased intensity of higher Zn-O shells after reduction, which coincides with the increased crystallinity or particle size of the Cu phase.

3.4 Catalysis in methanol steam reforming

The gas phase composition and changes in activity and selectivity measured during steady state methanol steam reforming conditions and the oxygen pulse experiment is shown in Fig. 4. It can be seen that after each oxygen pulse and subsequent reduction cycle the copper phase obtained exhibited an increased activity and selectivity compared to the initial values obtained after the first reduction.

4. Discussion

Time-resolved XANES experiments at the Cu K edge indicate that Cu₂O is an intermediate of the reduction of the CuO/ZnO systems studied. In addition these experiments afforded the evolution of the three phases CuO, Cu and Cu₂O during temperature-programmed reduction of CuO/ZnO.

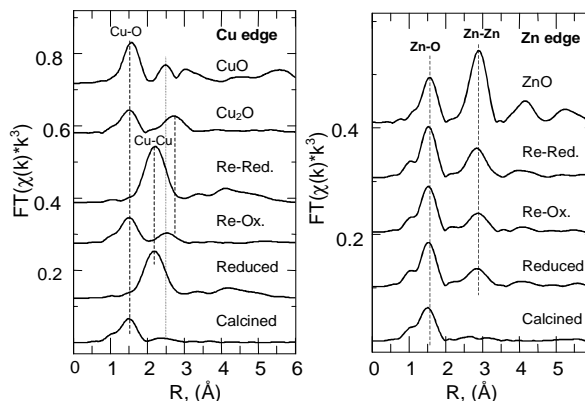


Figure 3 Fourier transformed $\chi(k)$ of the oxidized (calcined and re-oxidized (Re-Ox.)) and reduced state (Reduced, Re-Red.) at Cu K and Zn K edge at 523 K together with XAFS $\chi(k)$ of pure phase CuO, Cu₂O; ZnO (both at room temperature). Reduction (2 vol.% H₂) and oxidation (15 vol.% O₂) cycles were performed on a sample with 60 mol-% Cu.

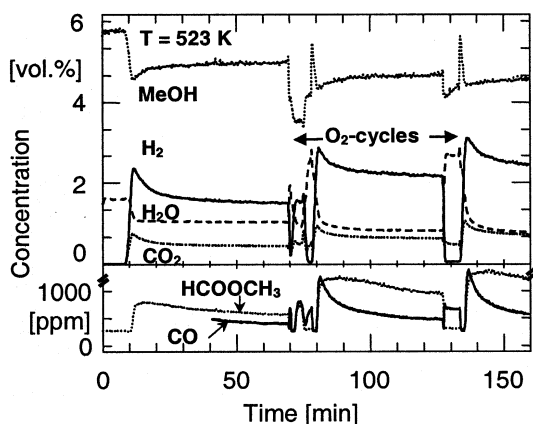


Figure 4

Reversible change in gas phase concentration of H_2 , MeOH, CO_2 , and H_2O during steam reforming conditions upon two oxygen pulses. The concentration for CO and HCOOCH_3 is shown in the bottom part in the graph.

The sigmoidal shape of the reduction curves (formation of Cu, see Fig. 2) can be described by the 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.

The copper bulk phases (*i. e.* oxidation and re-reduction) and the corresponding gas phase composition during one oxygen treatment are shown in Fig. 5. Apparently, reversible changes of the oxidation state of copper can be observed during oxygen pulses due to oxidation and subsequent *re*-reduction process in the feed. After the O_2 has been switched off the CO and H_2O concentration decrease, whereas the H_2 and CO_2 concentration increase (see Fig. 4). This could imply that the water gas shift reaction is favored in this regime of Cu oxidation states, whereas methanol steam reforming proceeds only as a minor parallel reaction. In this regime right after the oxygen pulse (III in Fig. 5) Cu^+ - and Cu^{2+} oxide constitute the major copper bulk phases. The formation of CO and methyl formate is observed after the concentration of metallic copper in the bulk phase exceeds 90 w%. The maximum concentration of CO and methyl formate (1000 ppm) coincides with the complete reduction of the copper phases to Cu metal. In this regime (I in Fig. 5) methanol steam reforming appears to be the predominant reaction. The existence of copper suboxides during the methanol steam reforming conditions can be excluded within the detection limits of XAFS (~ 1 w%).

5. Conclusion

The evolution of bulk phases of Cu/ZnO catalysts under reduction conditions was monitored using in situ XAFS. It could be shown under the temperature programmed reduction conditions employed that the CuO constituent of the mixed oxide CuO/ZnO is completely reduced to Cu on ZnO (lower detection limit $\sim 1\%$). From time-resolved in situ XAFS experiments at the Cu K edge the evolution of the copper phases during TPR was determined using a combination of factor analysis (PCA) and least-squares XANES fitting with suitable reference spectra (*e. g.* Cu metal, Cu_2O , CuO). Cu_2O was found to be an intermediate of the reduction of CuO/ZnO according to a two step reduction process ($\text{CuO} \rightarrow \text{Cu}_2\text{O} \rightarrow \text{Cu}$).

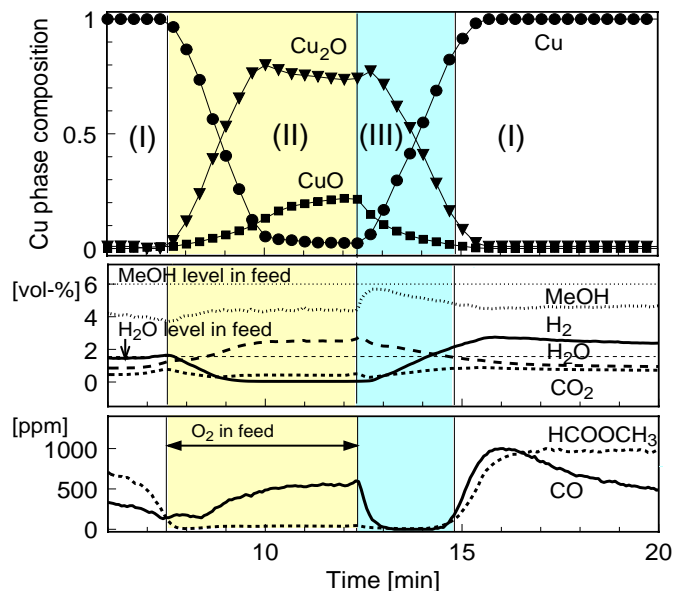


Figure 5

Changes in Cu phase composition during oxygen addition to the feed under steam reforming reaction conditions at 523 K. In the two lower sections of the graph the changes in gas phase composition in percent and ppm-range is given. Three regions of transitions in bulk and gas phase composition are marked in shaded area: I.) metallic copper and steam reforming products, II.) oxidation to CuO_{1-x} and products of methanol partial oxidation, III.) re-reduction of CuO_{1-x} phases to metallic Cu and water-gas shift production.

The reduction proceeds via a nucleation-grain growth kinetic. Completely reduced Cu clusters on ZnO constitute the active bulk phase for methanol steam reforming with no further oxidized Cu species detectable. Upon repeated oxidation and re-reduction cycles minor structural changes are found to increase the catalyst 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.

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