

Bulk structural in situ catalysis on Cu/ZrO₂ catalysts for the steam reforming of methanol

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1.1. Introduction

Conventional Cu/ZnO catalysts that can be used to produce hydrogen for fuel cell applications exhibit an unsatisfactory long-term stability and selectivity to CO under changing reaction conditions. Based on our knowledge about Cu/ZnO^{1,2,3,4} systems the objective of this work was to prepare and characterize an improved catalyst for the steam reforming of methanol (rational catalyst design). Using various starting materials and templates, nanostructured, mesoporous and macroporous Cu/ZrO₂ catalysts were prepared and subsequently investigated under methanol steam reforming (MSR) conditions. XAS (X-ray absorption spectroscopy) combined with mass spectrometry were used to monitor structural changes, stability, and catalytic activity under reaction conditions.

1.2. Experimental

The Cu/ZrO₂ nanopowders were synthesized by precipitation of Cu(NO₃)₂⁵. Mesoporous CuO/ZrO₂ structures were obtained using copper acetate and a block copolymer as a templating agent. The macroporous CuO/ZrO₂ was prepared using a polymer gel templating technique and copper acetylacetonate. Zirconium propylate was employed as zirconia precursor in all syntheses. Subsequently the materials were calcined at temperatures between 450 and 500°C

In situ X-ray absorption experiments were performed at beamline E4 at atmospheric pressure and temperatures up to 400°C under MSR conditions (total flow of maximum 36 ml/min). The spectra were recorded in the transmission mode at the Cu K- edge. The evolution of the gas phase was monitored with a *Pfeiffer QMS 200* mass spectrometer. Due to the design of our reactor the powder catalysts are used as pellets (5 mm in diameter). Therefore the powder is mixed with boron nitride (mass ratio catalyst: BN=1:3) and pressed with 1t. Ex situ measurements were performed at the beamline X1 and these data were used to characterise the precursor states of the catalysts. The XAS data were analysed with the software package WinXAS⁵ v2.1.

Results

Ex situ XAS measurements identified very small and/or highly disordered CuO particles as the main copper phase present in the precursors.

No significant changes in the long-range or short-range order structure of Cu and ZrO₂ during extended methanol steam reforming conditions were detected.

The initial low MSR activity of the Cu/ZrO₂ after reduction in 2 vol-% H₂ or feed could be significantly improved by a short addition of oxygen to the feed. We could also show that



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after extended times in the MSR feed and elevated temperatures (673 K, 2 vol-% H₂/He), the catalysts were still active or could be activated (via O₂ addition) again (figure 2). This indicates a superior stability of the material, which is an important improvement compared to the conventional Cu/ZnO catalyst.

For most of the samples the reduction in 2 vol-% H₂/He or the activation in the MSR feed at 523 K resulted in copper clusters (observed with XAS) that cannot be described by pure copper metal alone. However, the experimental EXAFS spectra could be very well simulated with the addition of a Cu-O shell to those of copper metal (figure 3). Determining the corresponding amount of oxygen in the copper metal clusters revealed that the improvement of the initial low activity for MSR after the short addition of oxygen to the feed can be correlated to an increase of the oxygen content in the copper catalysts.

In situ TPR experiments were performed at the Cu K edge in 2 vol-% H₂/He at a heating rate of 6 K/min. To describe the evolution of the phases involved we decided to compare the abstract concentration (due to the lack of appropriate) resulting from PC analysis. Figure 1a shows the formation of copper metal during reduction in hydrogen and methanol/water. Probably due to the oxidising influence of water or the reaction product CO₂ the reduction in the feed is retarded. During the reduction in hydrogen an intermediate component could be observed and the appearance correlates well with the evolution of water (fig 1b).

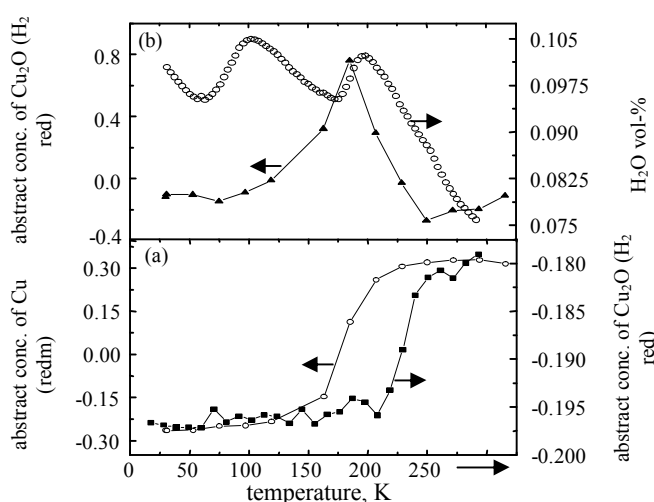


Figure 1. Evolution of the abstract concentrations of Cu during red. in 2 vol-% H₂/He and activation in the feed (a) and the corresponding evolution of water and intermediate phase during reduction in 2 vol-% H₂/He (b)

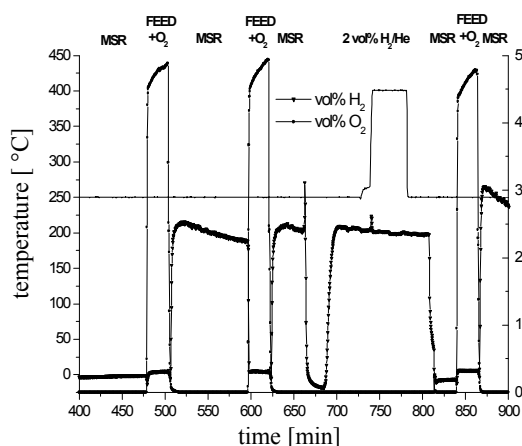


Figure 1. Evolution of the H₂ production over Cu/ZrO₂ during methanol steam reforming (MSR), oxygen pulses and heating to 400°C in 2 vol-% H₂/He

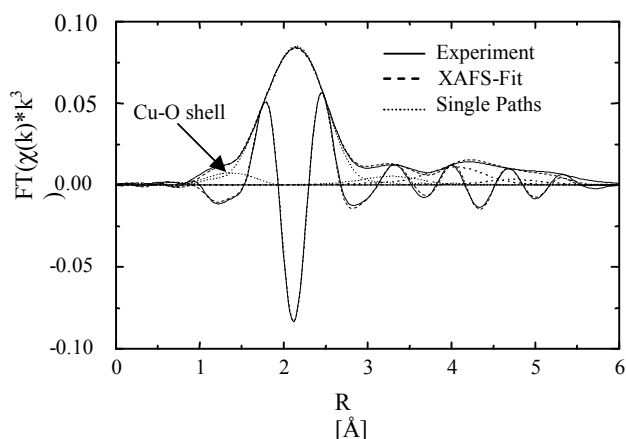


Figure 1. Refinement of a theoretical EXAFS function (dotted line) of one Cu-O distance from Cu₂O in addition to Cu to an experimental FT(chi(k)) for a nanostructured sample after reduction in 2 vol-% H₂ at 523 K



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References:

- 1) M.M. Günter et al., *Journal of Catalysis* **203**(1) (2001), 133-149
- 2) M.M. Günter et al., *Catal. Lett.* **71**(1-2) (2001), 37-44
- 3) B. Kniep et al., *Angew. Chemie*, accepted
- 4) H. Purnama et al., *Applied Catalysis*, accepted
- 5) Y. Wang et al., *Jour. Mater. Chem.* **12** (2002), 1442-1445