

The influence of the preparation on the catalytic performance of Cu/ZrO₂ for the steam reforming of methanol

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1.1. Introduction

Improved supported copper catalysts for the steam reforming of methanol (SRM) have been successfully prepared from various copper and zirconium dioxide precursor materials. Cu/ZrO₂ proved to be very stable under changing reaction condition over a long time on stream. Furthermore, Cu/ZrO₂ catalysts are more selective and produce less CO than conventional Cu/ZnO catalysts. Our investigations of Cu/ZnO^{1,2,3,4} revealed, that a large Cu surface area and a modified Cu microstructure are important prerequisites for an active SRM catalyst. Therefore, various inorganic starting materials and organic templates were used to prepare nanostructured, mesoporous, and macroporous Cu/ZrO₂ catalysts. X-ray absorption spectroscopy (XAS) combined with mass spectrometry was applied to monitor structural changes, stability, and catalytic activity under methanol steam reforming conditions.

1.2. Experimental

The Cu/ZrO₂ nanopowders were synthesized by precipitation of Cu(NO₃)₂.⁵ 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 XAS experiments were performed at beamline E4 at atmospheric pressure and temperatures up to 673 K under MSR conditions in a flow-through catalysis cell (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. The powder Cu/ZrO₂ catalysts were mixed with boron nitride (mass ratio catalyst: BN=1:3) and pressed with a force of 1 t into pellets of 5 mm in diameter. The XAS data were analysed with the software package WinXAS v3.1.⁶

Results

XAS measurements identified very small and highly disordered CuO particles as the main copper phase present in the CuO/ZrO₂ precursors. The initial low SRM activity of some of the Cu/ZrO₂ catalysts could be improved by a temporary addition of oxygen to the feed (Figure 3b). We could show that 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. This indicates a superior stability of the material, which is an important improvement compared to the conventional Cu/ZnO catalyst. For the CuO/ZrO₂ materials studied the activation in the SRM feed at 523 K resulted in copper clusters (observed with XAS) that contained a significant amount of oxygen (Cu-O shell in Figure 1). It was shown that the

improvement of the initially low MSR activity after the short addition of oxygen to the feed, can be correlated to an increase of the oxygen content in the nanostructured and the macroporous copper catalysts (Figure 3a). Conversely, the mesoporous catalyst, which exhibits the highest activity (Figure 2), showed a slight decrease in the initially high oxygen content. This may be attributed to a decreasing amount of organic template material in the catalysts after the oxidation and re-reduction cycle.

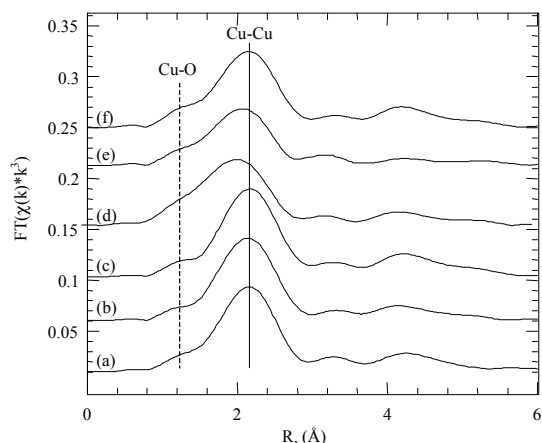


Figure 1. $FT(\chi(k) \cdot k^3)$ of the Cu/ZrO_2 catalysts directly reduced in $\text{MeOH/H}_2\text{O}$; (a) Nano-INS, (b) Nano-SBS-1, (c) Nano-SBS-2, (d) Meso-pre, (e) Meso-post, (f) Macro

The influence of the copper content on the catalytic behaviour was investigated in detail for a series of nanostructured catalysts obtained by a “co-precipitation” route.

The normalized Cu K edge spectra of three catalysts after the activation in methanol and water are presented in Figure 3. The edge features of Nano-INS with ~ 9 atom-% copper strongly resemble those of copper metal. However, significant deviations can be observed with decreasing copper concentration. The analysis of the Cu K edge XAFS $FT(\chi(k) \cdot k^3)$ revealed an increasing amount of oxygen in the copper clusters with a decreasing copper concentration, that correlates with a significant improvement of the activity in methanol steam reforming.

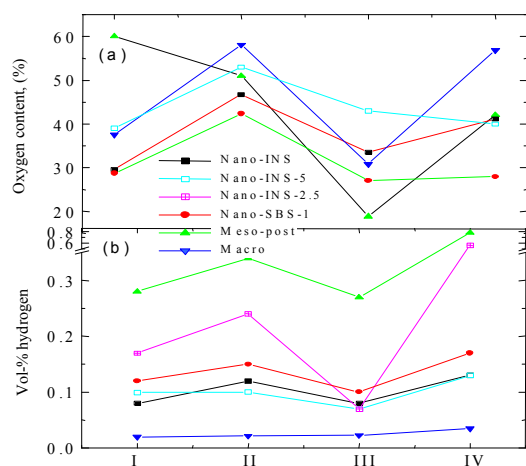


Figure 2. Evolution of the oxygen contribution (a) and hydrogen activity (b) during reaction, (I) after reduction in feed, (II) after 1. O_2 addition, (III) after heating to 673 K in 2 vol-% H_2/He , measured in feed, (IV) after 2. O_2 addition

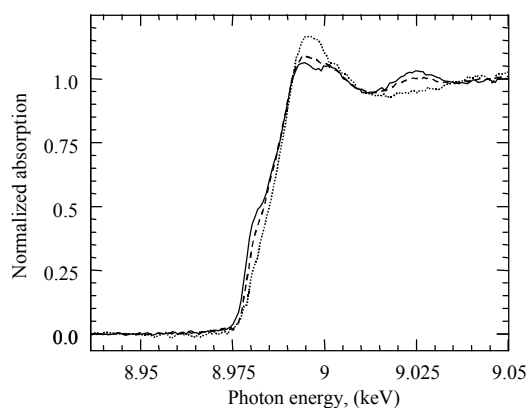


Figure 3. Normalized Cu K edge spectra of nanostructured Cu/ZrO_2 catalysts with different copper concentrations; solid: Nano-INS (8.9 atom-%), dashed: Nano-INS-5 (6.2 atom-%), dotted: Nano-INS-2.5 (2.2 atom-%)

References:



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