

Cu/ZrO₂ Catalysts for Methanol Steam Reforming: Structure - Activity

Correlations

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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. XRD (X-ray diffraction) and 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^{6,7} 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

Ex situ and in situ XRD measurements were conducted on Stoe STADIP diffractometers with Bragg–Brentano scattering geometry and a secondary monochromator. The in situ XRD

experiments were performed in a Bühler HDK cell with a total flow of 100 ml/min of 2 vol-% H₂/He or MeOH/H₂O (feed; 2:1). In situ XAS experiments were performed at the Cu K- edge (beamline E4, HASYLAB, Hamburg) at atmospheric pressure and temperatures up to 400°C under MSR conditions.

Results

Ex situ XAS measurements identified very small and/or highly disordered CuO particles as the main copper phase present in the precursors. XRD measurements showed that tetragonal zirconium dioxide is the major zirconia phase in the materials prepared.

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 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 1). 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 2). 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.

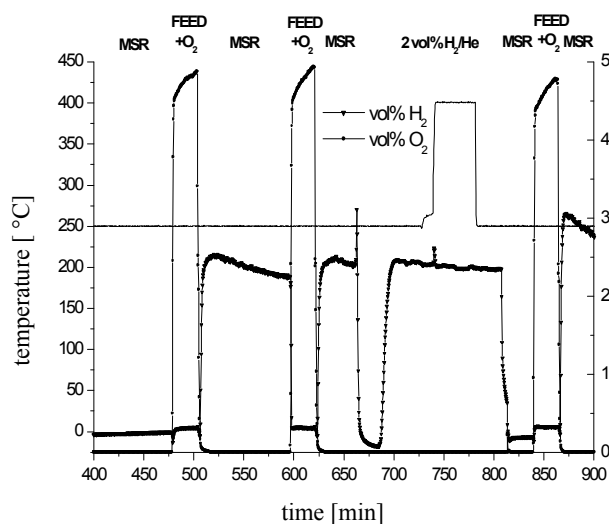


Figure 1. Evolution of the H₂ production over Cu/ZrO₂ during methanol steam reforming (MSR), oxygen pulses and heating to 400°C in 2 vol-% H₂/He.

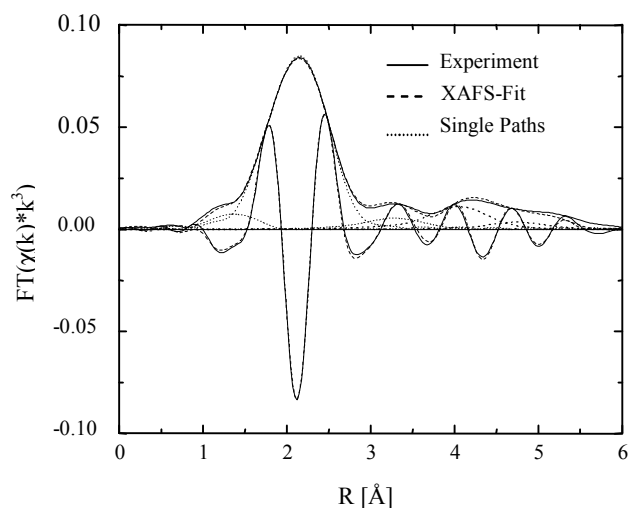


Figure 1. Refinement of a theoretical EXAFS function (dotted line) of one Cu-O distance from Cu₂O in addition to Cu to an experimental FT(chi(k)) for a nanostructured sample after reduction in 2 vol-% H₂ at 523 K



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