

## **Cu/ZrO<sub>2</sub> catalysts for methanol steam reforming: structure activity correlations**

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### **Motivation**

Conventional Cu/ZnO<sup>1,2,3,4</sup> 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. Using various starting materials and templates nanostructured<sup>5</sup>, mesoporous and macroporous Cu/ZrO<sub>2</sub> catalysts were prepared and subsequently investigated under methanol steam reforming 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, whereas a three channel plug flow reactor was used to perform detailed catalytic characterizations.

### **1.1. Preparation**

The Cu/ZrO<sub>2</sub> nanopowders were synthesized by precipitation of Cu(NO<sub>3</sub>)<sub>2</sub><sup>5</sup>. Mesoporous CuO/ZrO<sub>2</sub> structures were obtained using copper acetate and a block copolymer as a templating agent. The macroporous CuO/ZrO<sub>2</sub> was prepared using a polymer gel templating technique<sup>6,7</sup> 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

### **Structural Characterization**

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/ZrO<sub>2</sub> after reduction in 2 vol-% H<sub>2</sub> 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-% H<sub>2</sub>/He), the catalysts were still active or could be activated (via O<sub>2</sub> 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-% H<sub>2</sub>/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.

### *Catalytic study*

The study of the catalytic properties of the novel CuO/ZrO<sub>2</sub> catalysts by means of the fixed bed reactor reveals that the activity of the CuO/ZrO<sub>2</sub> catalysts can be improved by introducing oxygen (50 ml/min) for a short time (5 min) into the feed at reaction condition. The enhanced

activity of the catalysts after the treatment correlates well with the increase of the specific copper surface area of the used catalysts compared to the fresh catalysts. However, the opposite result concerning the change of the specific copper surface area of the commercial  $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$  was observed. This result indicates that the  $\text{CuO}/\text{ZrO}_2$  catalysts provide higher stability with respect to inhibition of the sintering of the metal particles than the  $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$  catalyst. The measurement of methanol conversion as a function of contact time shows clearly that the macroporous  $\text{CuO}/\text{ZrO}_2$  catalyst is more active than the commercial  $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$  catalyst (figure 3). Moreover, the CO concentration plotted as a function of methanol conversion measured (figure 4) over  $\text{CuO}/\text{ZrO}_2$  catalysts and  $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$  catalyst show that less CO was formed over the  $\text{CuO}/\text{ZrO}_2$  catalysts, especially significant at higher methanol conversion.

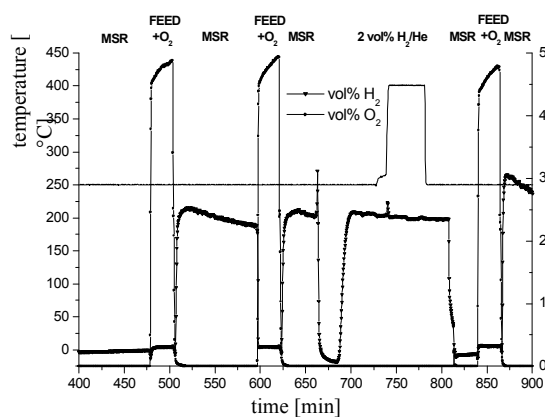


Figure 1. Evolution of the  $\text{H}_2$  production over  $\text{Cu}/\text{ZrO}_2$  during methanol steam reforming (MSR), oxygen pulses and heating to 400°C in 2 vol-%  $\text{H}_2/\text{He}$

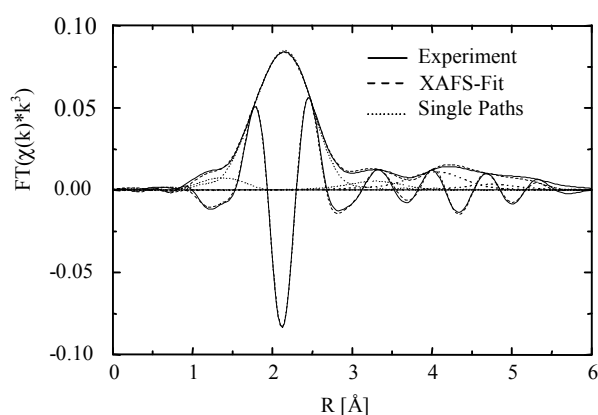


Figure 2. Refinement of a theoretical EXAFS function (dotted line) of one Cu-O distance from  $\text{Cu}_2\text{O}$  in addition to Cu to an experimental  $\text{FT}(\chi(k))$  for a nanostructured sample after reduction in 2 vol-%  $\text{H}_2$  at 523 K

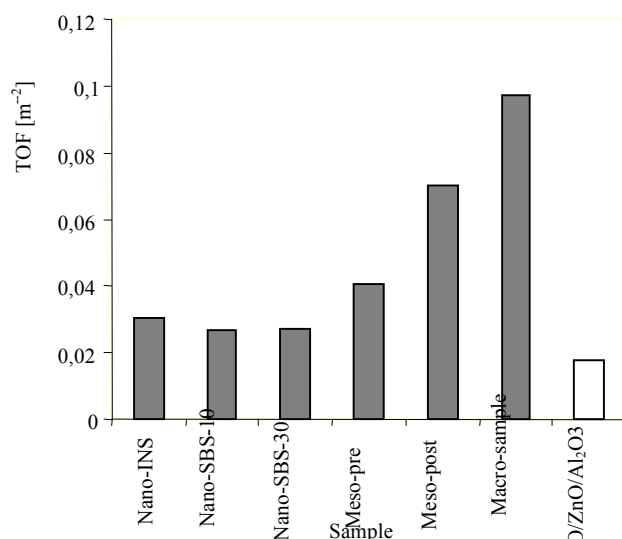


Figure 3 Methanol conversion per copper surface area for the  $\text{Cu}/\text{ZrO}_2$  in comparison with commercial  $\text{Cu}/\text{ZnO}$  catalyst

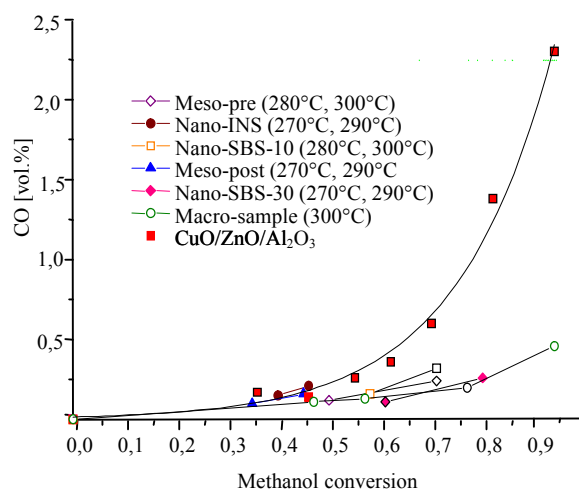


Figure 4 Methanol conversion versus CO production for the  $\text{Cu}/\text{ZrO}_2$  in comparison with commercial  $\text{Cu}/\text{ZnO}$  catalyst



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### 13. International Congress on Catalysis Paris 2004



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