Cu/ZrO_2 catalysts for methanol steam reforming

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Introduction

Conventional Cu/ZnO[1,2] catalysts that can be used to produce hydrogen for fuel cell applications exhibit an unsatisfactory long-term stability under changing reaction conditions. Therefore, in this work nanostructured Cu/ZrO_2 systems have been investigated to elucidate correlations between activity, stability, and structural changes in these materials under methanol steam reforming conditions. Three different groups of Cu/ZrO_2 catalysts were studied. First, CuO/ZrO_2 nanopowders synthesized by precipitation. Second, mesoporous CuO/ZrO_2 structures obtained using a block copolymer for the preparation. Third, macroporous CuO/ZrO_2 prepared using a polymer gel templating technique [4,5]. XRD (X-ray diffraction) and XAS (X-ray absorption spectroscopy) in combination with mass spectrometry were used to monitor structural changes and catalytic activity under reaction conditions.

Results

For most of the catalysts studied, reduction of the CuO/ZrO_2 material in 2 vol-% H_2/He at 523 K resulted in Cu/ZrO_2. The various catalysts show a different reduction behaviour with increasing reaction temperature which correlates with the cluster sizes (different preparation methods) and copper content of the corresponding Cu/ZrO_2 systems. The initial low activity for methanol steam reforming (MSR) (MeOH:H_2O = 2:1) could be significantly improved by a suitable activation procedure. This activation procedure resulted in characteristic mixtures of copper and copper oxide phases that exhibit a highly increased methanol steam reforming activity. During extended times in the methanol steam reforming feed and at elevated temperatures only minor changes in the long-range or short-range order structure of Cu and ZrO_2 were detected indicating a superior stability of the material.

References:

1) M.M. Günter, T. Ressler, et al. *Journal of Catalysis* **203** (1) (2001), 133-149.
2) M.M. Günter, T. Ressler, O. Hinrichsen, M. Muhler, R. Schlögl, *Catal. Lett.* **71** (1-2) (2001), 37-44
3) R.A. Caruso, M. Antonietti, M. Giersig, H.-P. Hentze, J. Jia, *Chem. Mater.* **13** (2001), 1114-1123
4) M. Antonietti, R.A. Caruso, C.G. Göltner, M.C. Weissenberger, *Macromolecules* **32** (1999), 1389