Structure-Activity Correlations for Cu/ZrO_2 catalysts in the Methanol Steam Reforming

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Conventional Cu/ZnO 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 under methanol steam reforming (MSR) 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. In situ X-ray diffraction and X-ray absorption spectroscopy in combination with mass spectrometry were used to monitor structural changes and catalytic activity under reaction conditions.

The various catalysts show a different reduction (2% H_2/He at 523K) behaviour with increasing reaction temperature. Using Principle Component Analysis, the amount of Cu and CuO in the sample was determined during reduction. The reduction results mostly in Cu. The initial low activity for MSR ($MeOH:H_2O = 2:1$) could be significantly improved by a short addition of oxygen to the feed. This activation procedure results in characteristic mixtures of Cu and CuO phases. During extended times in MSR feed and at elevated temperatures (400°C, 2%H_2/He) only minor changes in the long- or short-range order structure of Cu and ZrO_2 are detected indicating a superior stability of the material.