



Structure–activity relationships of ternary Cu/ZrO₂/CeO₂ catalysts for methanol steam reforming

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Reduction of the emissions originating from mobile sources such as internal combustion engines has attracted much attention recently [1]. The combustion of hydrogen in a fuel cell is regarded as a clean process, providing energy and releasing only water as exhaust [1]. Methanol can be employed as a storage and transport medium for hydrogen. Its advantages are a high H/C ratio of 4/1 and the absence of C-C bonds. The production of H₂ from CH₃OH can be performed by steam reforming of methanol:



which affords a substantial H₂ yield, and high CO₂ selectivity (~96%) with Cu based catalysts [1]. Unfortunately, CO is formed as a byproduct of this reaction. In order to eliminate the need for gas purification, more highly selective catalysts need to be developed. Here structure–activity relationships for ternary Cu/ZrO₂/CeO₂ (CZC) catalysts were investigated under methanol steam reforming conditions.

Experimental

The catalysts were prepared by coprecipitation followed by a templating technique [2]. Materials with different Cu content were obtained (5%, 15%, 25%, and 35%), with a molar ratio of ZrO₂/CeO₂ of 1. First, the metal sol was prepared by mixing of (NH₄)₂Ce(NO₃)₆, ZrO(NO₃)₂·H₂O, and Cu(NO₃)₂·2.5H₂O. The sol obtained by the precipitation treatment was used for templating on polystyrene beads. A strong interaction between the beads and the metal compounds was established by the

subsequent heating, drying, and washing procedures. The CZC catalysts were obtained by calcination in nitrogen and air at 773K.

The samples were characterized with X-ray fluorescence analysis (XRF), N₂ adsorption-desorption, N₂O decomposition, X-ray diffraction (XRD), and X-ray absorption spectroscopy (XAS). Catalytic investigations were performed in a fixed bed reactor at atmospheric pressure, by applying a mixture of methanol and water (1:1) at various temperatures.

Results

A decreasing BET surface area was determined for samples with increasing Cu content. Comparison between the long-term activity of the CZC catalysts is plotted in Fig.1. No linear correlation exists between the catalytic activity and the Cu surface area. The CO partial pressures determined during the catalytic measurements show higher values for the sample with the lowest Cu content.

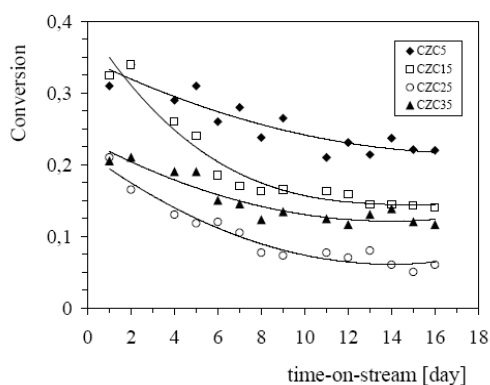


Fig. 1: Methanol conversions during SRM as function of time-on-stream ($m_{\text{CuO}} = 0.0225 \text{ g}$, $T = 523 \text{ K}$, $p = 10^5 \text{ Pa}$, $w = 0.07 \text{ cm}^3 \text{ min}^{-1}$, $\text{CH}_3\text{OH}/\text{H}_2\text{O} = 1/1$)

Characteristic CuO peaks in the XRD patterns could be distinguished only for the samples with the highest Cu contents. The in situ XRD experiments of the sample CZC35 clearly showed the formation of Cu₂O and Cu after reduction either in H₂ or in a mixture of H₂O and CH₃OH. Simultaneously, the gas phase composition was monitored with a mass spectrometer. The data showed an increased production of H₂ after an O₂ pulse for the 2 samples with the lowest Cu content, and a decreased production of H₂ for the other 2 samples.

The reduction in H₂ was also measured with XAS at the Cu K edge. Already the unreduced samples showed a different surrounding for the Cu atom. The XANES investigations during the heating ramp from 25°C to 250°C revealed for the samples with more than 5% Cu a higher reduction temperature with increasing Cu content. Apparently, the variation in the Cu concentration altered the microstructure of the Cu particles and, thus, the active Cu surface, which considerably affected the catalytic behavior of these catalysts.

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