

Ternary Cu/ZrO₂/CeO₂ catalysts for methanol steam reforming

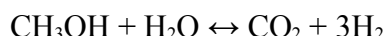
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Introduction

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 773 K.

Transmission X-ray absorption spectra of Cu K-edge, Zr K-edge and Ce L3-edge were measured at beamline E4 and X1. Pellets of 5 mm or 13 mm were prepared by mixing the catalyst with boron nitride or polyethylen and pressing with a force of 1t. Spectra of Zr K-edge (17.998 keV) and Ce L3-edge (5.724 keV) are ex situ data. In situ experiments were performed at atmospheric pressure and temperatures up to 523 K under reduction conditions (2% H₂/He) in a flow-through catalysis cell. The evolution of the gas phase was monitored with a Pfeiffer QMS 200 mass spectrometer. The software package WinXAS v3.11 was used for analysis of the XAS data.

Results and discussion

In order to obtain better analysable data of the Ce L3-edge four single spectra were collected and added. The radial distribution functions obtained from XAS spectra measured at the Zr K-edge from the four catalysts with different copper content exhibit only minor differences (Fig. 1).

The reduction in H_2 was measured with XAS at the Cu K edge. Already the unreduced samples showed a different surrounding for the Cu atom. This could be identified as CuO for the most cases. The XANES investigations during the heating ramp from 298 K to 523 K at a heating rate of 6 K/min revealed for the samples with more than 5% Cu a higher reduction temperature with increasing Cu content. A principal component analysis (PCA) of this data showed Cu_2O as an intermediate phase during the reduction. The radial distribution functions at the end of the experiment indicate a different amount of oxygen in the copper phase (Fig.2). 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.

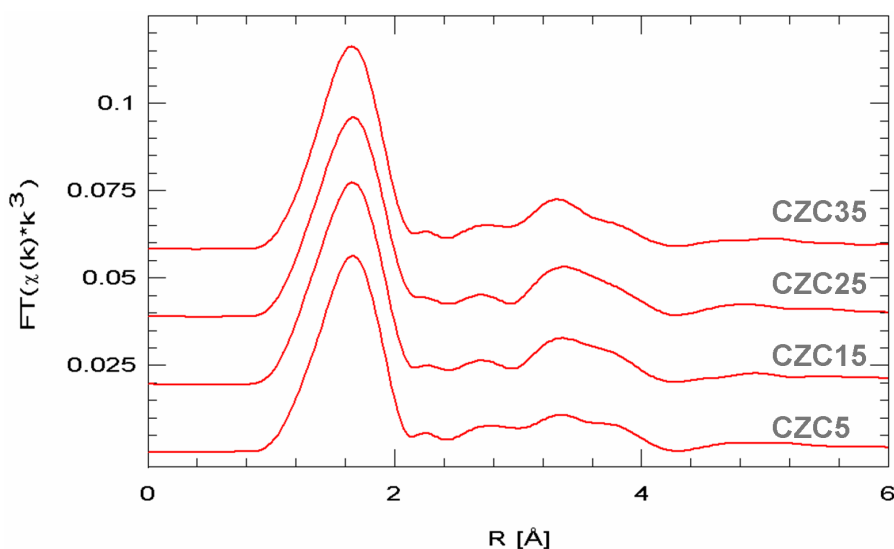


Figure 1: Zr K-edge radial distribution functions of various CZC catalysts.

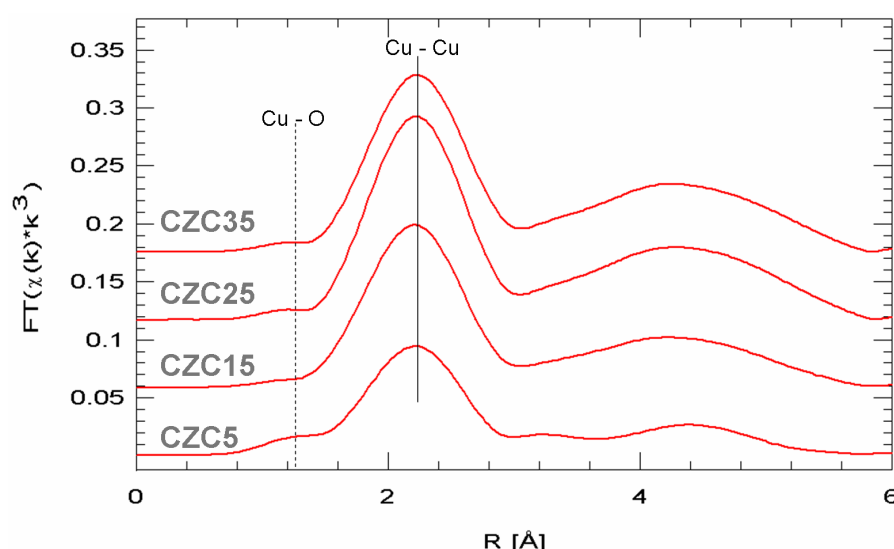


Figure 2: $FT(x(k) \cdot k^3)$ of the CZC catalysts after reduction in 2 % H_2/He .

References

- [1] P.J. de Wild, M.J.F.M. Verhaak, *Catal. Today* 60, 3 (2000).
- [2] A. Mastalir, B. Frank, A. Szizybalski, H. Soerijanto, A. Deshpande, M. Niederberger, R. Schomäcker, R. Schlögl, T. Ressler, J. *Catal.* 230, 464 (2005).