

Cu/ZrO₂ catalysts for methanol steam reforming

A. Szzybalski¹, F. Girgsdies¹, T. Ressler¹, J.H. Schattka², Y.Wang², R.A. Caruso²

¹*Fritz-Haber-Institute of the MPG, Department of Inorganic Chemistry,
Faradayweg 4-6, 14195 Berlin, Germany;*

²*Colloid Department, Max-Planck-Institut of Kolloid- und Grenzflächenforschung,
Am Mühlentberg, Haus 2, 14476 Golm, Germany*

Introduction

Hydrogen powered fuel cells appear to be a promising replacement for conventional combustion engines. However, problems arise concerning the storage of hydrogen. Therefore, research has recently been focused on methanol steam reforming (MSR) to produce hydrogen on board. Because the conventional Cu/ZnO^{1,2} catalysts are not particularly stable under rapidly changing reaction conditions, new materials need to be studied, that exhibit an improved long-term stability and selectivity. In this work, nanostructured Cu/ZrO₂ systems prepared by various templating techniques have been investigated to elucidate correlations between activity and stability, and structural changes under reaction conditions.

Experimental

The Cu/ZrO₂ catalysts investigated can be divided into three groups. First, Cu/ZrO₂ nanopowders were synthesized for instance, by the addition of a Cu(NO₃)₂ solution to a solution of Zr(OPr)₄ and tetramethylammoniumhydroxid followed by subsequent heating at 80°C for 20h. The precursors were calcined at 500°C for 12h. Second, mesoporous ZrO₂ structures were obtained from a blockcopolymer soaked with a mixture of zirconium(IV)propylat and acetylacetonate. Subsequently, copper acetate was dissolved in the polymer solution. The precursors were calcined in air at 450°C. Third, macroporous ZrO₂ was prepared from a polymer gel template^{4,5}. The template was impregnated with a solution containing Zr(OC₃H₇)₄, copper acetylacetonate, and propanol and left standing for several hours. Calcination in oxygen at 500°C resulted in the mesoporous ZrO₂.

Transmission X-ray absorption spectra measured at beamline E4 and X1 in combination with on-line mass spectrometry (*Pfeiffer QMS 200*) were used to characterize the relationship between the local structure and activity. Pellets (5 mm in diameter) of catalyst, pressed (1t) together with boron nitride (mass ratio catalyst : BN=1:3) were analysed at the Cu K- edge (8.979 keV) at atmospheric pressure, temperatures up to 400°C and a total flow of maximum 34 ml/min. Because some of the catalysts are almost amorphous for x- ray diffraction analysis, the precursor materials were also investigated at the Zr K- edge (17.998 keV) at beamline X1 to determine the constitutive zirconia phases. One in situ experiment has been performed at this energy to investigate the structural changes around Zr under reaction conditions. The software package WinXAS⁵ v2.1 was used for analysis of the XAS data.

Results and discussion

For most of the catalysts studied, reduction of the precursor material (CuO/ZrO_2) in 2 vol-% H_2/He resulted in Cu/ZrO_2 . The initial low activity for MSR could be significantly improved by a suitable activation procedure. No significant changes in the long-range or short-range order structure of Cu and ZrO_2 during extended under methanol steam reforming conditions were detected. The radial distribution functions obtained from XAS spectra measured at the Zr K-edge from eight differently prepared catalysts exhibit only minor differences (Fig. 1). Samples denoted as GYW008 and HR60N seem to consist of mixtures of tetragonal, monoclinic, or amorphous ZrO_2 . The analysis of these data is underway.

In situ TPR experiments were performed at the Cu K edge in 2 vol-% H_2/He at a heating rate of 10K/min. The various catalysts show a different reduction behaviour with increasing reaction temperature (Fig. 2) These differences roughly correlate with the cluster sizes (different preparation methods) and copper content of the corresponding Cu/ZrO_2 systems.

Furthermore, a more reliable way to determine the content of copper in the Cu/ZrO_2 catalysts was developed. Because hafnium is a natural impurity in ZrO_2 , the absorption edge of Hf (Hf L_{3-} edge (9.561 keV) (Fig. 3)) can be measured together with the Cu K-edge. From the ratio of the edge-jump of the copper edge and the hafnium edge, the copper content can be estimated.

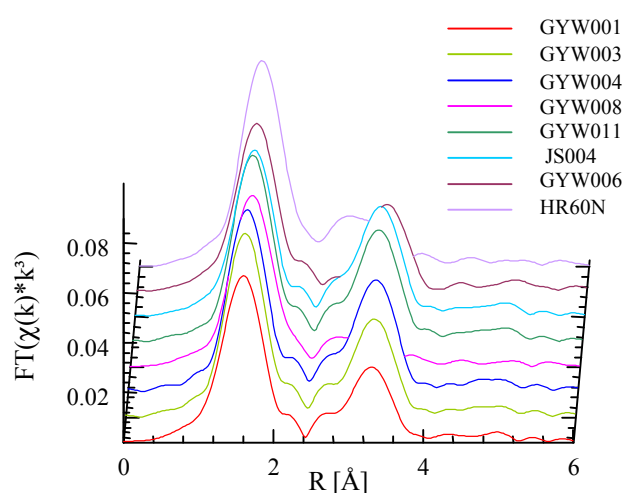


Fig. 1 Zr K edge rRadial distribution functions of various Cu/ZrO_2 catalysts, ex situ (Zr K-edge).

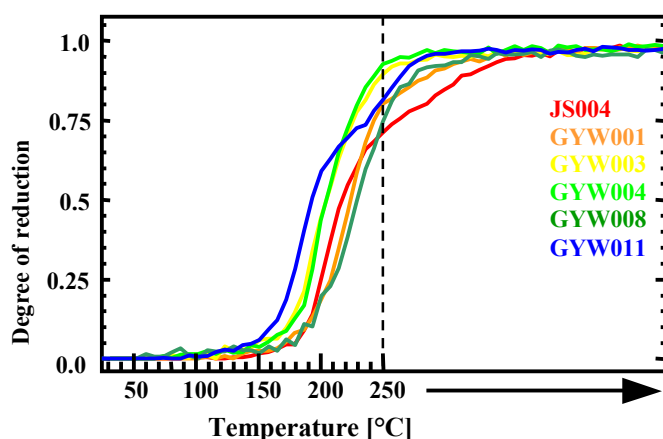


Fig. 2 In situ Cu K XANES measured during TPR: Reducibility of Cu in differently prepared Cu/ZrO_2 catalysts (Cu K-edge), heating rate 10K/min, 2 vol-% H_2/He .

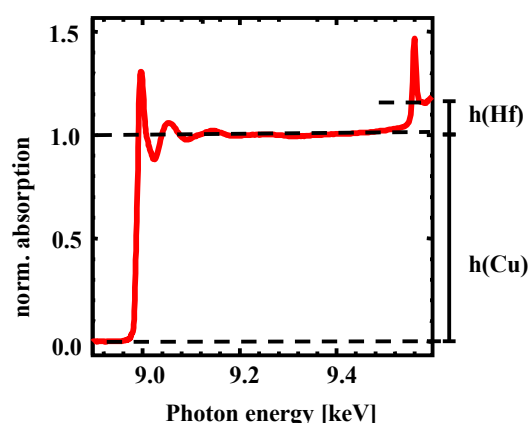


Fig. 3 Normalized Cu K edge absorption spectra of Cu/ZrO_2 at the Cu K-edge together with the Hf L_{3-}



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