

Zirconium oxynitride as new support for Cu in methanol steam reforming

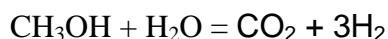
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Introduction

Supported copper catalysts have been used for steam reforming of methanol. This reaction could be potentially important for on-board systems which convert methanol and water to hydrogen for use in a fuel cell powered vehicle [1]:



ZrO₂ was used as a support for Cu in previous work of our group. Szizybalski et al. [2] suggested a different metal support interaction as compared to Cu/ZnO catalysts. In order to tune the support interaction by modifying the cation lattice, co-precipitated (Cu,Ce,Zr)O_{2-x} catalysts were synthesized. These catalysts showed varying interaction between Cu and (Ce,Zr)O₂ with increasing Cu content. Recently, we started to investigate the influence of modifying the anion lattice of ZrO₂ by substitution nitrogen. The aim of this study was to elucidate the implications of substitution in the anion lattice of ZrO₂ for the structural and catalytic properties of supported Cu catalysts.

Experimental

Yttrium-stabilized zirconia (YSZ) was prepared by co-precipitation. This sample was used to prepare by ammonolysis two zirconium oxynitride samples with different nitrogen contents, i.e. NYSZ-1 (3,4 wt%) and NYSZ-2 (2 wt%). Copper was supported on NYSZ-2 by two different preparation methods. First, by mixing with a Cu citrate solution (NYSZ-2A1) and, second, by mixing with a Cu nitrate solution (NYSZ-2B1). Drying was performed at 120 °C followed by calcination in air at 250 °C. The resulting samples are denoted NYSZ-2A2 and NYSZ-2B2, respectively.

X-ray diffraction (XRD) was used to characterize the intermediates after the various preparation steps. XRD patterns were collected in transmission between 5 and 100° (2θ). XAS data were collected in transmission mode at E4 and X1 at HASYLAB. Ex situ experiments were performed at Zr K and Y K edge. In situ experiments at Cu K edge were performed in a flow-through reactor at atmospheric pressure. Calcination, and reduction in hydrogen (2% in helium) at 250°C followed by steam reforming at 250°C were investigated.

Results

EXAFS refinement was performed to the Fourier transformed (FT) $\chi(k)$ of the Zr K and Y K edges of both samples YSZ and NYSZ-1. The analysis resulted in a very similar local structure with respect to metal-oxygen and metal-metal distances. Thus, as expected Y appears to be incorporated in the ZrO₂ lattice on Zr lattice sites. A constant ratio between the intensity of the FT peak of the metal-oxygen bond and that of the metal-metal bond was observed at the Y K edge (Fig.1). Conversely, this ratio decreased for the Zr K edge (Fig.2). Hence, nitrogen appears to be incorporated in the vicinity of the Y atoms while anion vacancies were created around the Zr atoms. Such a replacement mechanism was also described by Li et al. [3] for the incorporation of Y into the ZrO₂ lattice.

XRD revealed Gerhardtite ($\text{Cu}_2(\text{NO}_3)(\text{OH})_3$) as a Cu phase after mixing with the Cu nitrate solution (sample NYSZ-2B1). Accordingly, the EXAFS results showed an elongated Cu-Cu distances. In the calcined precursors, XANES and EXAFS indicated the presence of CuO as the copper containing phase. Compared to the Cu-citrate-route, higher crystallinity of CuO was detected by XRD in the material obtained by the Cu-nitrate-route.

XANES spectra collected during thermal treatment in hydrogen showed that the reduction of copper in NYSZ-2A2 proceeded at lower temperatures compared to that of NYSZ-2B2. This is in agreement with the increased size of the Cu crystallite resulting from the nitrate route. After reduction at 250 °C both catalyst samples exhibited a residual amount of Cu_2O . Apparently, the catalyst obtained by the citrate route (NYSZ-2A2) contained a higher amount of Cu_2O compared to the material obtained by the nitrate route (NYSZ-2B2).

XANES spectra measured during thermal treatment in methanol and steam (Fig.3 and 4) showed significant changes in the NYSZ-2A2 catalyst. Conversely, sample NYSZ-2B2 remained unaffected. Furthermore, the amount of hydrogen detected was higher for the NYSZ-2A2 catalyst. Szzybalski et al. [2] described a correlation between the oxygen content in copper particles and an increasing activity. A similar correlation with respect to an improved metal support interaction seems to hold for the copper catalysts obtained by the citrate route (NYSZ-2A2).

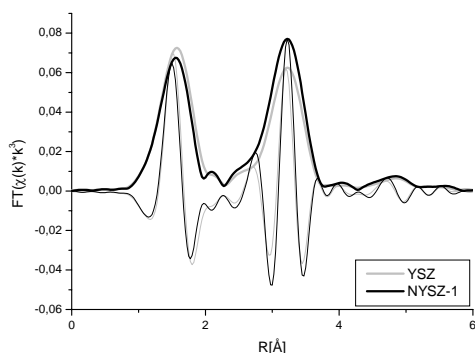


Figure 1: FT of YSZ and NYSZ-1 collected at Y K edge

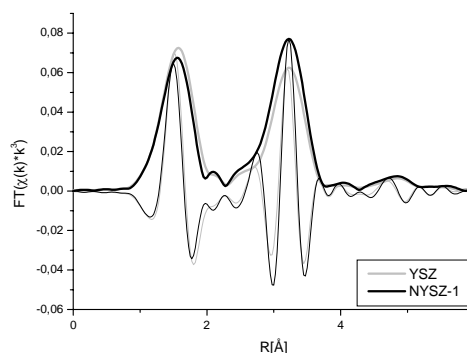


Figure 2: FT of YSZ and NYSZ-1 collected at Zr K edge

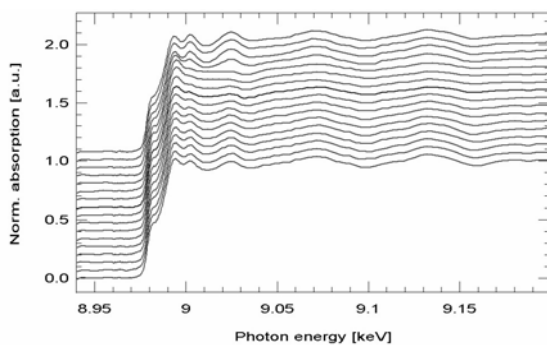


Figure 3: XANES spectra collected during heating ramp to 250°C in methanol steam for sample NYSZ-2A2

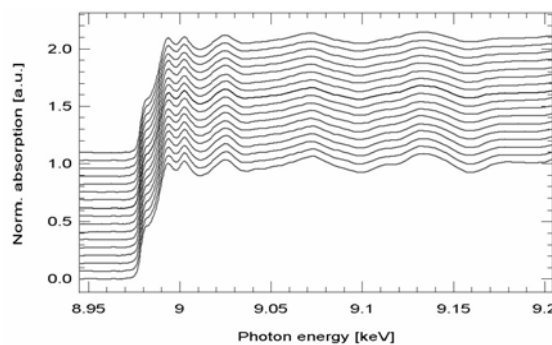


Figure 4: XANES spectra collected during heating ramp to 250°C in methanol steam for sample NYSZ-2B2



References

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