



Poster Abstract:

In situ XAS Studies on Cu/ZrO₂ Catalysts for Methanol Steam Reforming

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The production of hydrogen by steam reforming of methanol is of great interest for the development of fuel-cell powered engines, especially for mobile applications. The majority of known catalysts for this reaction are based on copper combined with a variety of supports and additives. But despite many years of extensive work in this field, neither the active state of copper nor the role of the support are completely understood. In extension of our work on the conventional Cu/ZnO catalysts [1-3], we started to investigate the properties of copper supported on nanostructured zirconia. Because of the small particle sizes and low copper loading, the use of X-ray diffraction (XRD) for this system is severely limited. Hence, ex situ and in situ X-ray absorption spectroscopy (XAS) was employed to obtain bulk structural information about the catalysts and their respective precursors.

The synthesis of the catalyst precursors involved the use of a polymer gel template [4-5]. The gel was soaked in a solution of zirconium (IV) propoxide and copper(II) acetylacetonate. The impregnated gel was exposed to aqueous conditions overnight for hydrolysis of the metal complexes. The hybrid material was dried at room temperature, and then calcined at 450 °C to remove the organic material. Samples with nominal copper loadings between 10 and 30 mol-% were prepared.

XAS experiments were performed at the beamline X1. Data was collected at the Cu K edge between 8.9 and 9.5 keV in the QEXAFS mode. For time-resolved in situ experiments a measuring time of 60 seconds per scan was used. The samples were diluted with boron nitride and pressed into 5 mm in diameter self-supporting pellets. In situ XAS experiments were carried out in the transmission mode in an in situ cell at atmospheric pressures. The evolution of the gas phase was monitored on-line with mass spectrometry. The software package WinXAS v2.0 [6] was used for analysis of the XAS data.

XRD analysis of the "as-prepared" materials (catalyst precursors) showed no trace of the copper containing phase even for high copper loading. In addition, the ZrO₂ support crystallized mainly in the tetragonal modification. Given that certain metal cations can stabilize tetragonal zirconia at room temperature, this may indicate an incorporation of copper into the zirconia lattice. However, the XANES and EXAFS show similarity with CuO (Figures 1+2). A XAFS refinement of a CuO model structure to the $FT(\chi(k) \cdot k^3)$ (Figure 3) afforded a very good agreement. Hence, the differences seen in the Figures 1 and 2 are caused by a strong amplitude damping, possibly because of extensive disorder in the CuO particles or a very small particle size. The latter may explain the "invisibility" of CuO in XRD. Furthermore, the quality of the XAFS fit allows to exclude the existence of significant amounts of other copper phases, including copper in ZrO₂.

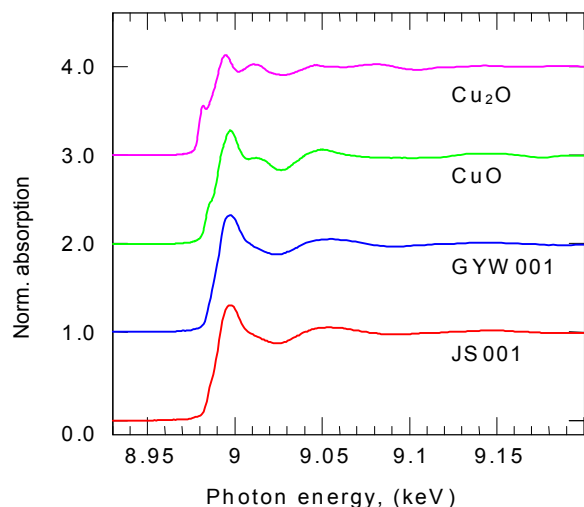


Figure 1: Normalized absorption of two catalyst precursor samples (JS001, GYW001) and two references (CuO, Cu₂O) at room temperature.

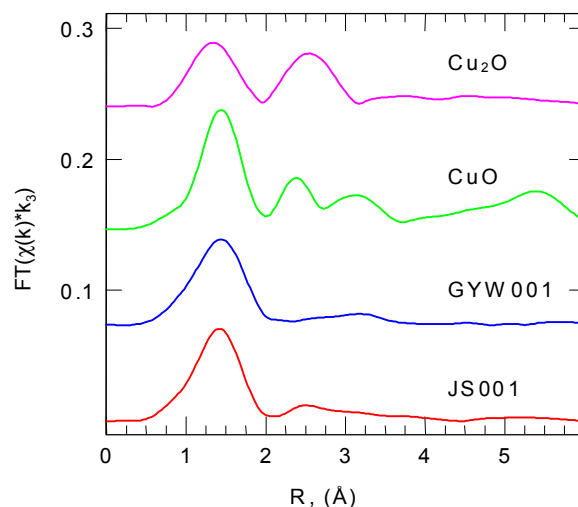


Figure 2: Radial distribution functions ($FT(\chi(k)*k^3)$) of the two catalyst precursors and the two references shown in Figure 1.

After temperature programmed reduction of the precursor in 2 vol-% H₂ atmosphere (Figure 4), only copper metal exhibiting strongly damped amplitudes in the $FT(\chi(k)*k^3)$ was detected. The amount of amplitude reduction cannot be explained as a temperature effect alone, again indicating very small Cu particles on the ZrO₂ support. Following reduction, the catalyst was exposed to steam reforming conditions and an activity similar to that of Cu/ZnO (10 wt-%) was measured by MS. Analysis of the absorption spectra obtained under catalytic conditions to reveal the structure of the “active” copper phase is underway.

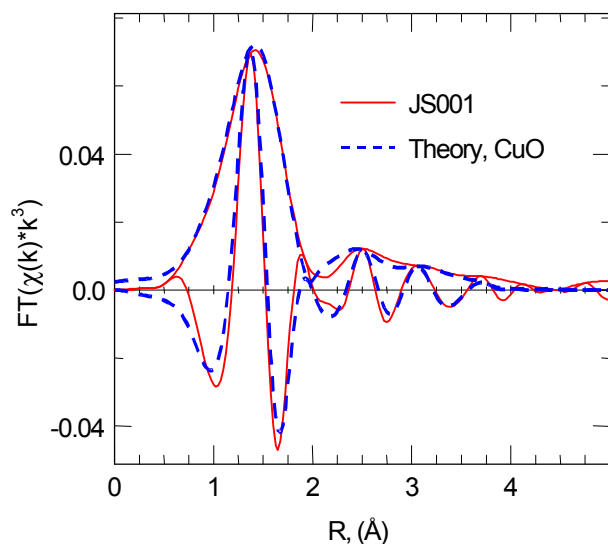


Figure 3: XAFS fit of a CuO model structure to the $FT(\chi(k)*k^3)$ of a CuO/ZrO₂ precursor.

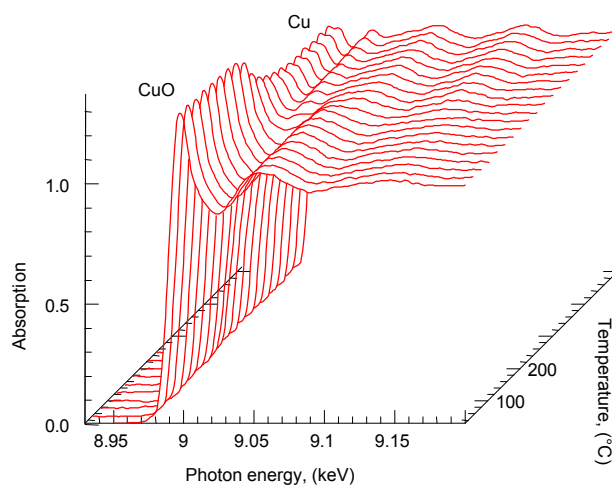


Figure 4: Temperature programmed reduction of CuO/ZrO₂ (precursor) to Cu/ZrO₂ (catalyst).

References

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