

# Cu on Zirconia and Zirconium Oxynitride as Catalyst for Methanol Steam Reforming

A. Dennstedt<sup>1,2</sup>, N. Frenzel<sup>2</sup>, M. Behrens<sup>1</sup>, A. Trunschke<sup>1</sup>, R. Schlögl<sup>1</sup>, M. Lerch<sup>2</sup> and T. Ressler<sup>2</sup>

<sup>1</sup>Department of Inorganic Chemistry, Fritz-Haber Institute of the MPG, Faradayweg 4-6, 14195 Berlin, Germany

<sup>2</sup>Institut für Chemie, TU-Berlin, Sekr. C2, Straße des 17. Juni 135, 10623 Berlin, Germany

## Introduction

Hydrogen can be used in fuel cells to provide energy. For mobile applications methanol may be employed as hydrogen source instead of pure hydrogen. Hence, hydrogen is obtained by steam reforming of methanol (MSR) resulting in the formation of hydrogen and carbon dioxide. Cu containing catalysts have been shown to be sufficiently active and selective for MSR. By using Cu on ZrO<sub>2</sub> as support, H. Purnama [1] obtained an improved activity and selectivity compared to a commercial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst. A. Szizybalski [2] showed that the activity of these catalysts correlated with a residual amount of oxygen in the reduced Cu phase. Modifying the cation lattice of the ZrO<sub>2</sub> support by incorporation of metals may vary the properties of these catalysts. Moreover, in this contribution we report on modification of the anion lattice of ZrO<sub>2</sub> by incorporation of nitrogen. Therefore, the aim of this study was to investigate the influence of nitrogen incorporation and, in addition, of different calcination atmospheres on the structure of the Cu containing phase.

## Experimental

Commercial ZrO<sub>2</sub> was used both as support and as raw material for zirconium oxynitrides which were also used as support for copper catalysts. Zirconium oxynitrides containing 7 wt% N were prepared by ammonolysis at 1100°C. Copper was supported by impregnation with a Cu citrate solution. Afterwards the samples were dried for 24h at 120°C. Calcination at 250°C was performed in 20% O<sub>2</sub> in helium or 20% CO<sub>2</sub> in helium.

X-ray diffraction (XRD) experiments were conducted in reflection geometry on a STOE Theta/theta diffractometer using a XRK 900 high temperature cell for in situ measurements. X-ray absorption spectroscopy (XAS) data were collected in transmission at both Cu K edge and Zr K edge. The experiments were performed at beamlines E4 and X1 at HASYLAB in a flow-through reactor at atmospheric pressure. Both calcinations and reduction in hydrogen (2% H<sub>2</sub> in helium) followed by steam reforming (1.5% H<sub>2</sub>O and 1.5% CH<sub>3</sub>OH in helium) including an oxygen treatment were performed at 250°C. The composition of the atmosphere was monitored by online mass spectrometry.

## Results

The commercial ZrO<sub>2</sub> showed a monoclinic structure. The as-prepared zirconium oxynitride contains mainly Zr<sub>7</sub>O<sub>8</sub>N<sub>4</sub> (β-phase). Furthermore Zr<sub>2</sub>ON<sub>2</sub> (γ-phase) and residual amounts of monoclinic ZrO<sub>2</sub> were found in this sample. After impregnation no change in the structure of the supports was detected. The Cu phase obtained was not detectable by XRD. In the EXAFS analysis both samples showed the same coordination of Cu which could be simulated by 4 oxygen neighbors.

During XAS experiments of calcinations in O<sub>2</sub>/He a similar change of the Cu phases was observed. The support seemed to play no role during this step. Calcination of zirconium oxynitride supported samples in CO<sub>2</sub>/He showed a different behaviour which also depended

on the experimental setup. During XRD Cu crystallites were detected, but during XAS a mixture of different copper oxides was observed. In all samples prepared in the rotary furnace the Cu containing phase observed by XAS was CuO.

Cu was obtained after reduction in 2% H<sub>2</sub>/He. ZrO<sub>2</sub> supported catalysts showed no methanol steam reforming activity. By XAS and XRD Cu was observed in methanol steam atmosphere before the oxygen treatment. During the treatment both methods showed the formation of CuO. After the oxygen treatment a mixture of Cu and Cu<sub>2</sub>O was detected by XAS.

The as prepared supported zirconium oxynitride catalyst calcined in O<sub>2</sub>/He was active in the Steam reforming of methanol. In contrast the catalyst calcined in CO<sub>2</sub>/He showed activity only after the oxygen treatment. Both XAS and XRD indicated a phase change of the support during this step (Figure 1): a decrease of  $\beta$ -phase was accompanied by an increase of tetragonal ZrO<sub>2</sub>. Cu was observed in both zirconium oxynitride samples in methanol steam atmosphere at 250°C. During the oxygen treatment of both samples Cu<sub>2</sub>O was observed by XAS and XRD. After the treatment Cu was formed again.

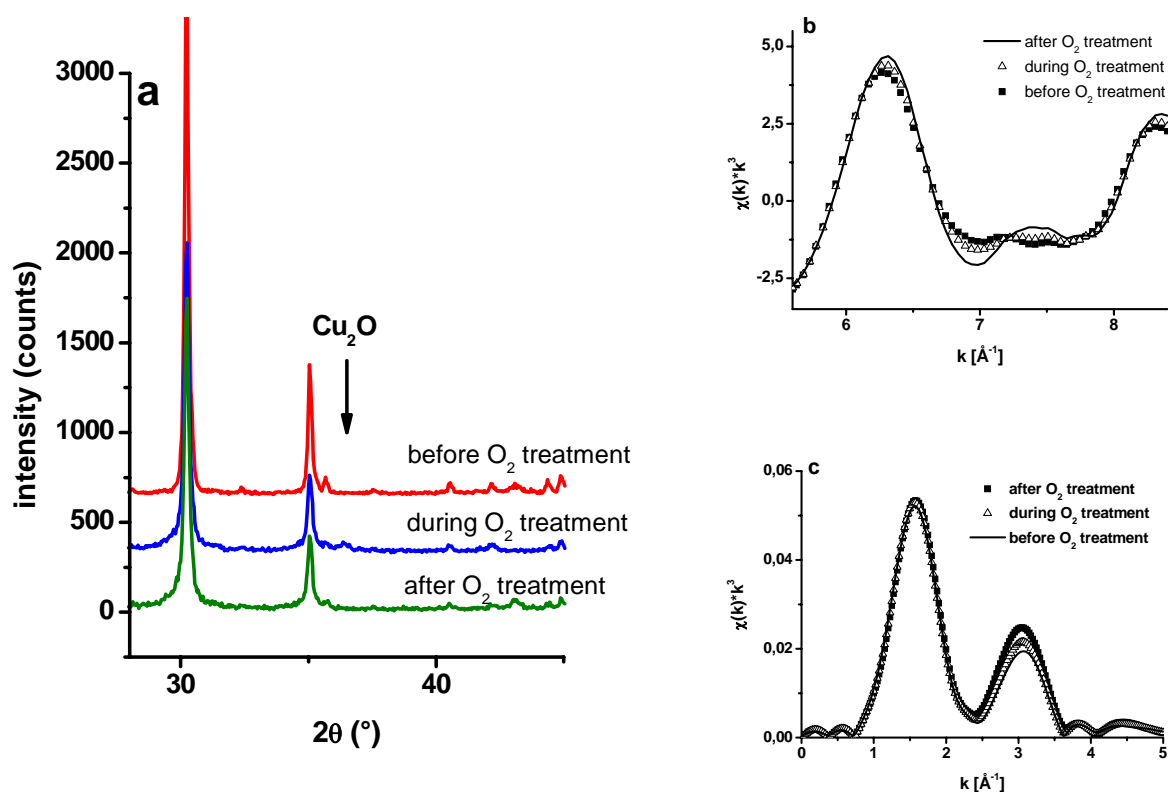


Figure 1: change of zirconium oxynitride support during O<sub>2</sub> treatment: a) shows X-ray diffractogram with decreasing amount of oxynitrides and formation of Cu<sub>2</sub>O during the step, b) shows the region of  $\chi(k)$  with the biggest differences, and c) shows the influence to the Fourier transformed of this  $\chi(k)$ .

The nitrogen incorporation prevents a stronger oxidation of the deposited Cu during the oxygen treatment. Furthermore a new Zr containing phase is observed which may influence the performance of the catalyst. The CO<sub>2</sub> containing calcination atmosphere prevents a change of the support which also avoids the methanol steam reforming directly after the reduction.

## References

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- [2] A. Szizybalski, F. Girgsdies, A. Rabis, Y. Wang, M. Niederberger, and T. Ressler, *J. Catal.* 233, 297 (2005)