



Zirconium oxynitride as novel 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 liquid methanol and water to hydrogen for use in a fuel cell to power a vehicle [1]:



ZrO₂ was used as a support for Cu in previous work of our group. Szzybalski 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. Here, we investigated the influence of modifying the anion lattice of ZrO₂ by nitrogen ($3\text{O}^{\times} + \text{N}_2 \rightarrow 2\text{N}_\text{O}^{\cdot} + \text{V}_\text{O}^{\circ\circ} + 3/2\text{O}_2$).

The aim of this study was to elucidate the implications of substitution in the anion lattice of ZrO₂ on the structural and catalytic properties of the supported Cu.

Preparation

Two different supports with different nitrogen-content were used. The first one was prepared by ammonolysis of ZrO₂ stabilized with 6 mol% Y₂O₃, which was prepared by co-precipitation. The second one was prepared by ammonolysis of commercial ZrO₂ [3]. These materials were loaded with Cu by impregnation with either Cu citrate or Cu nitrate solution. Drying was performed at 120 °C followed by calcination in air at 250 °C.

Results

The products and intermediates were characterized by X-ray diffraction (XRD), BET, infrared spectroscopy (IR), X-ray absorption spectroscopy (XAS), hot-gas extraction,

temperature programmed reduction (TPR), and thermogravimetry. Furthermore, activity tests for methanol steam reforming were performed.

XAS of the support showed that Y was incorporated at the Zr lattice position. Incorporation of nitrogen took place in the vicinity of the Y atoms and caused vacancies around the Zr atoms.

Thermogravimetry showed that conversion of the Cu precursors to CuO was complete at 250 °C. Above 400 °C nitrogen was detected by mass spectrometry. A concurrent increase in mass was observed, which is consistent with incorporation of oxygen by replacing the nitrogen.

XRD revealed Gerhardtite ($\text{Cu}_2(\text{NO}_3)(\text{OH})_3$) as a Cu phase after the impregnation with Cu-nitrate, which was in agreement with IR results. In the calcined precursors, CuO was found as the copper containing phase. Compared to the Cu-citrate-route, higher crystallinity of CuO was detected in the material obtained by the Cu-nitrate-route. In addition, the BET surface area of the calcined nitrate-derived catalyst is lower compared to the ZrON

support, whereas an increase of the BET surface area was observed during the Cu-citrate-route.

TPR traces of the calcined samples showed either two (Cu-citrat-route) or three (Cu-nitrate-route) peaks (Fig.1), indicating different particle size distributions of CuO in the calcined catalysts. In

either case, the reduction was complete below 250 °C. Thus, reduction and steam reforming of methanol were performed at 250 °C. The results of the catalytic testing and the corresponding structure activity relationships will be discussed.

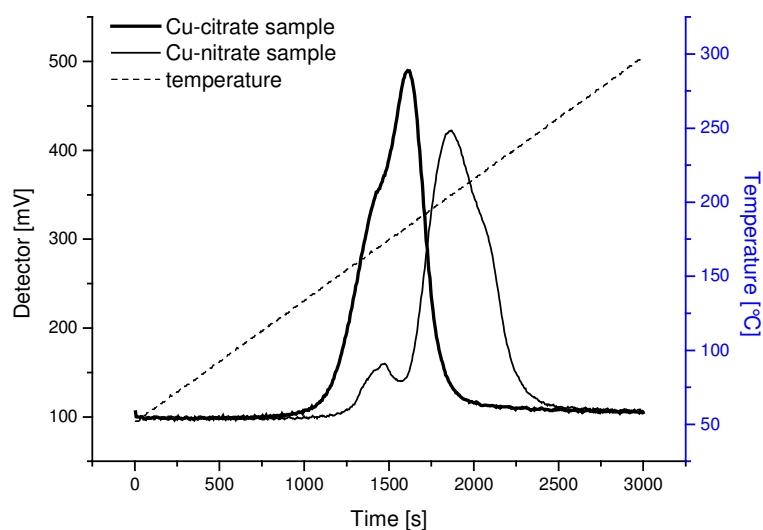


Figure 1: TPR traces collected with 5% H_2 in He

References:

- [1] P.J. de Wild, M.J.F.M. Verhaak, *Catal. Today* 60 (2000) 3-10.
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