

In situ investigations of Cu/ZnO catalysts during calcination in different gas atmospheres

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Introduction

Calcination of appropriate Cu/Zn hydroxycarbonates to the mixed oxides is a crucial step in the catalysts preparation of Cu/ZnO catalysts. Conventionally, calcination is performed in the presence of oxygen. It is assumed that during calcination at mild temperatures CuO and ZnO are modified by ad-mixed OH⁻ and CO₃²⁻ groups^[1, 2]. These ad-mixed groups may serve as growth inhibitors of defect rich Cu particles in the final catalyst required for superior activity in methanol steam reforming. Therefore, calcination in the presence of CO₂ may retain some particular ad-mixed carboxyl groups in the working Cu/ZnO catalyst in methanol steam reforming. Here, bulk structural investigation during calcination in different gas atmospheres (O₂, CO₂, He) on the microstructure of Cu/ZnO catalysts were investigated by using two complementary methods in situ X-ray diffraction (XRD) and in situ X-ray absorption spectroscopy (XAS) combined with online mass spectrometry.

Experimental

A Cu/ZnO catalyst with a molar ratio of Cu:Zn = 70:30 was prepared by co-precipitation of (Cu,Zn) hydroxycarbonates from metal nitrate solution. Therefore, 500 ml of a premixed Cu/Zn nitrate solution (total 1.0 M) and a 1.6 M Na₂CO₃ solution were dosed simultaneously to 400 ml H₂O (25 ml min⁻¹). The pH-value during the precipitation process at 338 K was adjusted to 7.0 by controlling the dosing rate of the precipitation agent. The precipitate was aged in the mother liquid for 2 hrs, filtered off, washed until the absence of sodium in the solution was achieved, and dried in a drying oven at 393 K for 20 hrs. Combined in situ XRD/MS experiments were performed on a STOE Theta/theta diffractometer equipped with a XRK 900 high temperature cell and a mass spectrometer for online gas analysis. In situ XAS/MS experiments of the catalysts were carried out at beamline E4 at the Cu K edge (E=8979 eV) in transmission mode in an in situ cell at atmospheric pressure. 2 mg of the catalyst precursor and 30 mg BN were physically mixed and pressed at a force of 1 t into a pellet with 5 mm (i.d.). The amounts of material in the pellets were calculated to give an absorber optical thickness close to 1.5 absorption lengths. Calcination was conducted at a total flow of 20 ml min⁻¹ with an identical temperature program (heating rate: 5 K min⁻¹, 603 K for 3 hrs) in (a) 20% O₂/He, (b) 20% CO₂/He, and (c) He. Afterwards, the oxide precursors were reduced in situ (5% H₂ in He, heating rate: 6 K min⁻¹, 523 K for 1 hour).

Results and Discussion

The precipitated catalyst precursor contained a mixture of several crystalline phases (i.e. Rosasite {(Cu,Zn)₂(OH)₂CO₃}, Aurichalcite {(Cu,Zn)₅(OH)₆(CO₃)₂}, CuO and ZnO). Bulk structural analysis by XRD indicates that independent of the gas phase composition applied the hydroxycarbonates were transformed into the bivalent oxides (Figure 1). The lattice cell volume of CuO obtained after calcination in CO₂ (82.1 Å³) and in inert gas (81.8 Å³) was considerably enlarged compared to calcination in oxygen (79.0 Å³). The largest crystallite

sizes of CuO were identified for the samples calcined without oxygen (48-50 Å) compared to the sample calcined in O₂ containing atmosphere (30 Å). Conversely, the lattice spacing and crystallite sizes of ZnO were less affected by the different calcination conditions employed. Complementary analysis by XAS at the Cu K edge revealed a different coordinative environment of copper in the case of calcination in CO₂ containing atmosphere. This sample presents a totally different structure in the medium range order (>2 Å) with a shell at 2.17 Å (Figure 1). This shell does not belong to any copper oxide structure but corresponds to a typical Cu-C distance of Malachite (Cu₂(OH)₂CO₃). In contrast, calcination in O₂ and in inert gas resulted in a short and medium range order structure which is characteristic for CuO. Time resolved TPR-XANES investigations during the reduction process revealed a sequential reduction pathway from CuO to an intermediate and metastable phase Cu₂O and finally to Cu metal which is in good agreement with previous investigations^[3]. Reduction of the catalyst previously calcined in inert gas exhibited larger Cu crystallites (46 Å) than calcination in O₂ (36 Å) and CO₂ (37 Å). Considering the CuO crystallite sizes calculated after calcination sintering by thermal degradation occurred for all samples investigated. Apparently, degradation is less pronounced for the sample calcined in CO₂. This indicates a higher degree of interaction of the Cu particles in the ZnO matrix. However, the in CO₂/He calcined catalyst exhibits a considerable lower reduction temperature (T_{max}=490 K) than the catalyst calcined in 20% O₂/N₂ (T_{max}=495 K) indicating that the reduction kinetic is not only affected by the CuO crystallite size.

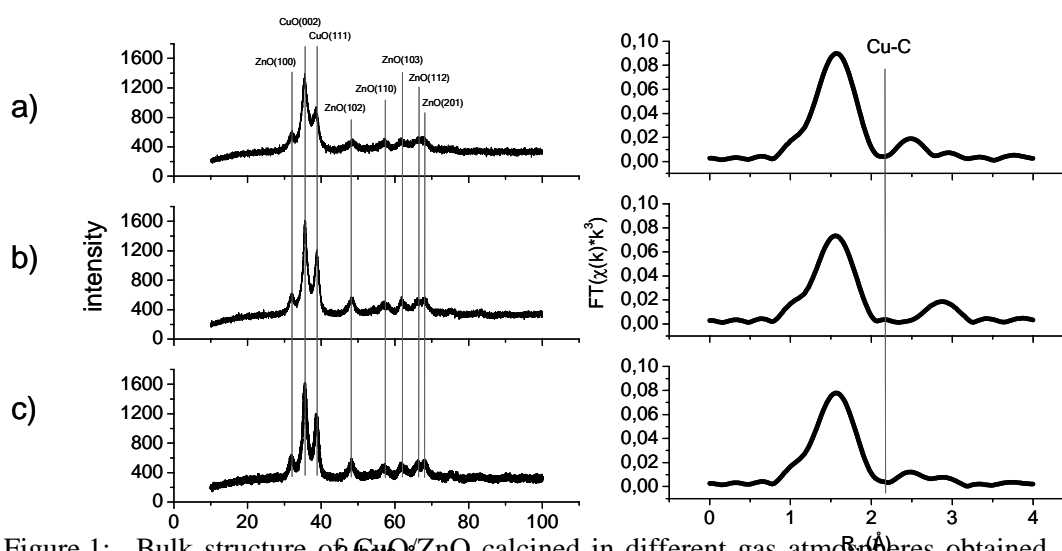


Figure 1: Bulk structure of CuO/ZnO calcined in different gas atmospheres obtained from in situ experiments (XRD, XAS measured at the Cu K edge); a) calcined in 20% O₂/He; b) calcined in 20% CO₂/He, and c) calcined in He.

Calcination in different gas atmospheres (O₂, CO₂, and He) has an impact on the microstructure (phase composition, texture, morphology) of Cu/ZnO catalysts. Hence, calcination of (Cu,Zn) hydroxycarbonates in an adequate mixture of O₂ and CO₂ may result in an enhanced catalytic activity in methanol steam reforming.

References

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- [3] Günther et. al. J. Synch. Rad. 8 (2001)