



Activity of Cu/ZnO Catalysts for Methanol Steam Reforming as a Function of the Ageing Conditions in Catalyst Preparation

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Introduction

Hydrogen as alternative power source for transportation (fuel cell application) can be produced by catalytic conversion of methanol with water vapor (steam) at reaction temperatures of 523 K. ZnO supported Cu catalysts are frequently used for methanol synthesis and are also known to be active for methanol steam reforming. For binary Cu/ZnO catalysts with varying molar ratios we were able to show that the methanol synthesis activity is strongly influenced by microstrain in the copper particles [1]. Here, we describe how microstructural characteristics such as structural disorder, impurities, microstrain, or particle size are determined by the preparation conditions (i.e. ageing of the precipitate).

Experimentals Section

In order to further investigate the influence of microstructural disorder and its implication for the catalytic activity in methanol steam reforming, Cu-Zn hydroxycarbonates with a Cu/Zn ratio of 70/30 mol % were prepared by coprecipitation from Cu nitrate and Zn nitrate solutions with Na₂CO₃ at constant pH (pH=7). Ageing of the precipitates in their pristine solutions results in a spontaneous crystallisation of the initially amorphous solids. The differently aged Cu-Zn hydroxycarbonates were dried, washed, and calcined for 3h in air at 603K.

Structural changes of the active catalyst under reaction conditions were elucidated by using the two complementary techniques in situ X-ray-diffraction (XRD) and in situ X-ray-absorption spectroscopy (XAS). Measurements were performed in an in situ XRD and an in situ XAS cell during methanol steam reforming (total flow of 100 ml/min and 44 ml/min, respectively, with a MeOH/H₂O ratio = 2 at 523K and 1 bar). The catalytic activity of the reduced Cu/ZnO catalysts was determined by monitoring the gas phase composition with on-line mass spectrometry. Activity data were correlated with the results of a detailed analysis of the crystallite size and strain of the reduced phase copper and ZnO using XRD line profile analysis. In addition to the information

of the long-range order structure obtained by XRD experiments, XAS measurements were performed to characterise microstructural changes in the medium-range order. The in situ XAS measurements were performed at the Cu K edge and the Zn K edge in the transmission mode.

Results and Discussion

The catalytic activity of four Cu/ZnO catalysts prepared with ageing times of 0, 15, 30 and 120 min was investigated during methanol steam reforming. By using a detailed XRD line profile analysis of the Cu (111) reflexes it was found that an increased ageing time of the precipitates leads to a decrease in copper particle size of the freshly reduced catalysts from 133 Å (0 min) to 104 Å (120 min) (Fig.1). In addition, analysis of the Cu (111) reflexes after reduction in hydrogen revealed a considerable microstrain in the copper phase (Fig.1). Apparently, the resulting higher Cu surface area alone cannot explain the sudden increase in the hydrogen

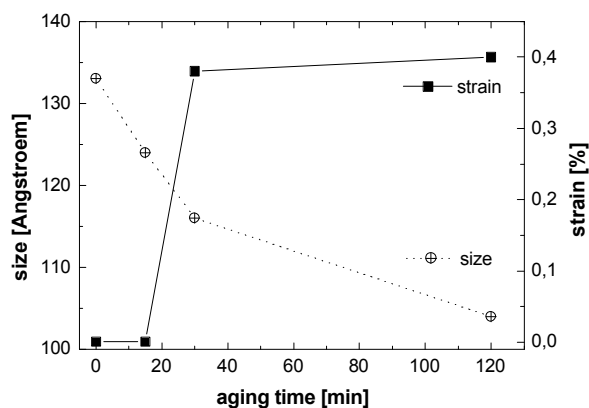


Figure 1. Evolution of size and strain from copper particles as function of aging time after reduction at 523K determined from Cu (111) reflex

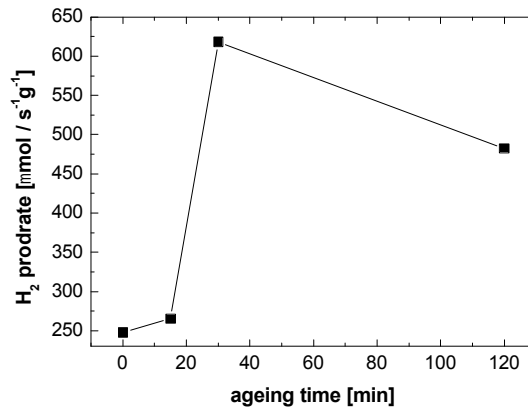


Figure 2. H₂ production rate during methanol steam reforming at 523K as function of ageing time

production rate between ageing times of 15 to 30 min (Fig.2). However, the H₂ production rate in methanol steam reforming correlates well with the microstrain in the catalytically active copper phase. The investigations have shown that microstructural features of ZnO supported Cu catalysts such as size and strain depends on the preparation conditions and the resulting composition and structure of the hydroxycarbonate precursors.



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[1] M.M. Günter, T. Ressler, B. Bems, C. Büschner, T. Genger, O. Hinrichsen, M. Muhler, R. Schlögl, *Catal. Lett.* **71** (1-2) (2001) 37-34.