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

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Introduction

Cu/ZnO catalysts are frequently used for methanol synthesis and are also known to be active for the catalytic conversion of methanol with water vapor (steam reforming). Previously, we have shown that the methanol synthesis activity of binary Cu/ZnO catalysts with varying molar ratios is strongly influenced by microstrain in the copper particles [1]. In order to further investigate such microstructural characteristics and its implication for the catalytic activity in methanol steam reforming, Cu-Zn hydroxcarbonate precursors (ratio Cu/Zn = 70/30 mol-%) were prepared by coprecipitation from metal nitrate and sodium carbonate solutions at constant pH (pH = 7). The precipitates were aged in their pristine solutions at times of 0, 15, 30, and 120 min. After reduction, structural changes of the four Cu/ZnO catalysts obtained during methanol steam reforming ($MeOH/H_2O$ ratio of ~ 1 at 523K at 1 bar) were monitored by in-situ X-ray-diffraction (XRD) and in-situ X-ray-absorption spectroscopy (XAS). The catalytic activity was determined by measuring the gas phase composition with on-line mass spectrometry.

Results

It was found that Cu/ZnO catalysts obtained from precipitates that were aged for longer times (30 min and 120 min) exhibited a much-increased H_2 production rate. The copper particle size of the freshly reduced catalyst (obtained by detailed XRD line profile analysis of the Cu (111) peak) decreases with increasing ageing time of the precipitates. However, the resulting higher Cu surface area alone cannot explain the sudden increase in H_2 production. Analysis of Cu (111) peak after reduction in hydrogen revealed a considerable microstrain in the catalytically active copper phase after ageing times of the precipitates of 30 min which correlates well with the increased H_2 production rate in methanol steam reforming. The investigations have shown that microstructural features of ZnO supported Cu catalysts such as size and strain depend on the preparation conditions, and the resulting composition and structure of the hydroxycarbonate precursors.

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