Microstructure of ternary $Cu/ZnO/Al_2O_3$ catalysts and their catalytic performance in methanol steam reforming

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Introduction

Cu-catalysts supported on $ZnO-Al_2O_3$ mixed oxides are of considerable industrial interest for low pressure methanol synthesis and water gas shift reaction. They are also known to be active in methanol steam reforming. Methanol, as a chemical source of hydrogen, applied in fuel cells is a promising alternative for petroleum based fuels. In order to achieve a rational-derived catalyst synthesis a fundamental knowledge of the implication of the microstructure on the activity is required. Recent publications on the "real structure" of copper based catalysts pointed out that besides the Cu surface area bulk structural parameters, e.g. microstrain in the Cu particles, correlate with the activity in methanol steam reforming [1-4]. Here, we report structure-activity relationships of various $Cu/ZnO/Al_2O_3$ catalysts in methanol steam reforming.

Preparation and Experimental

A set of CuZnAl- mixed oxide precursors for methanol synthesis were prepared according to patented procedures implying precipitation of hydroxycarbonates from metal nitrate solutions and subsequently washing, drying and calcination. Reduction characteristics of the oxide precursors were examined using conventional TPR, in situ X-ray diffraction (XRD) and in situ X-ray absorption spectroscopy (XAS). Catalytic activity in steam reforming of methanol obtained from in situ experiments was correlated to microstructural properties of the catalysts investigated.

Results

Different preparation conditions affect the microstructure of the catalytically active copper phase ("chemical memory") in a variety of ways. Thus, the investigated catalysts show significant differences in their catalytic performance in methanol steam reforming (Fig. 1). The catalytic activity is mainly determined by the specific copper surface area. The presence of strained copper particles as the result of an advanced Cu-ZnO interface was determined only for the most active $Cu/ZnO/Al_2O_3$ catalyst (CZA01). Conventional TPR and ex situ TEM investigations confirm a homogeneous microstructure of Cu and ZnO particles with a narrow particle size distribution for this catalyst (CZA01). Conversely, a heterogeneous microstructure with large Cu particles and a pronounced bimodal particle size distribution was identified for the less active catalysts (CZA02-06). Thus, similar to the binary Cu/ZnO system microstrain in the copper nanoparticles is an indicator for a homogeneous microstructure of superior $Cu/ZnO/Al_2O_3$ catalyst for methanol chemistry [2, 4].

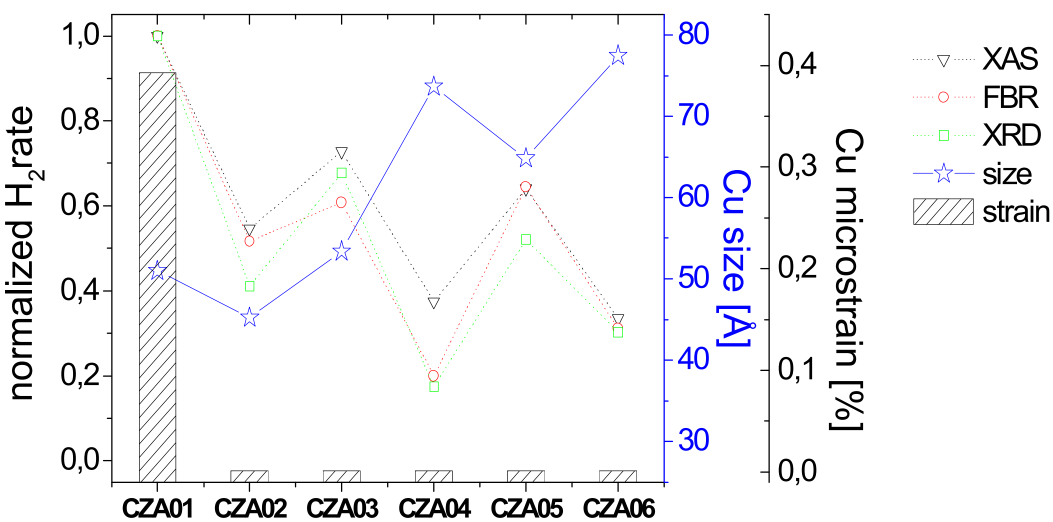

Figure1: normalized H_2 rate obtained from in situ experiments (XRD, XAS) and measured in a fixed bed micro-reactor (FBR) compared with Cu crystallite size and microstrain

Reference

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[4] Kniep *et. al.*, J. Catal., 236, **2005**, 34-44