



Effect of Precipitate Ageing on the Microstructural Characteristics of Cu/ZnO Catalysts for Methanol Steam Reforming

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Introduction

Copper-zinc oxide catalysts are industrially relevant for the synthesis of methanol and can be also used for the catalytic conversion of methanol with water vapor (steam) to produce hydrogen (methanol steam reforming). The knowledge of the relationship between the catalytic activity, surface structure, and bulk structure of Cu/ZnO catalysts is necessary in order to elucidate synthesis pathways to new and improved catalysts. Recently, we were able to show that structural disorder in binary Cu/ZnO catalysts such as microstrain in copper nanoparticles affects the catalytic activity [1]. Here, we describe how microstructural characteristics of a “real catalyst” can be controlled by suitable preparation conditions. Ageing of freshly precipitated precursors leads to characteristic phase transformations [2] and enables designing a desired catalyst performance by modifying the precipitation conditions instead of varying the chemical composition.

Preparation and Experimental

Cu/ZnO catalyst (ratio Cu:Zn = 2:1) were prepared by co-precipitation with an aqueous solution of metal nitrates and sodium carbonate at constant pH (pH=7). The resulting precipitates were aged in their mother liquor for 0, 15, 30, 120 min, followed by washing (353 K, 80 ml H₂O), drying (383 K, 20h), calcinations (603 K, 3h) and reduction (2% H₂, 523 K) of the precursors. Changes in morphologie and nanostructure of the differently aged Cu/ZnO catalysts were observed by TEM (SEM). In situ X-ray diffraction (XRD) and in situ X-ray absorption spectroscopy (XAS) combined with on-line mass spectrometry for gas phase analysis elucidated microstructural characteristics of the four catalysts. Methanol steam reforming activity data (CH₃OH / H₂O ratio =1 at 523K and 1 bar) were correlated to detailed line profile analysis of the in situ XRD powder patterns (separation of particle size and strain) and to the refinement results of the in situ EXAFS measurements

performed at the Cu K-edge.

Results

The Cu/ZnO catalysts obtained from precursors aged for longer times (30 and 120 min) exhibited a much-increased H₂ production rate (Fig.1). The decreasing Cu particle size (110 Å = 0 min ageing to 70 Å = 120 min ageing) obtained from a detailed XRD line profile analysis and the resulting higher surface area alone cannot explain the increase in activity. However, the H₂ production rate in methanol steam reforming correlates well with the microstrain in the catalytically active copper phase. Ex-situ ⁶³Cu NMR investigations of freshly reduced catalysts are in good agreement with the in-situ XRD results concerning the microstrain in copper clusters. Analysis of the in-situ EXAFS spectra shows an increase in the amplitude of the first Cu-Cu shell as a function of ageing (Fig. 2), indicating that the Zn content in Cu clusters decreases with longer ageing times. This indicates, that the occupancy of Zn atoms on Cu lattice sites diminishes the transmission of strain, induced by an epitactical orientation of the copper on zincoxide. Furthermore, EXAFS analysis suggests an increasing structural disorder in the medium range order with increasing ageing time (e.g., microstrain). TEM investigations reveal an increasing content of nanostructured Cu/ZnO particles in the catalyst powder as function of ageing, which is in good agreement with increase in Copper particle size determined (Fig. 1).

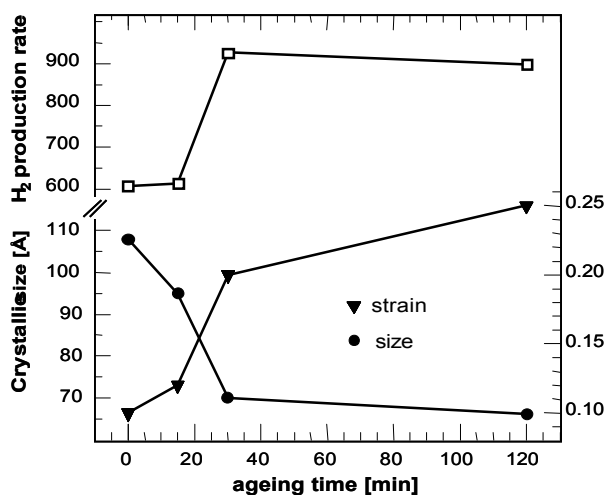


Fig. 1: H₂ production rate and particlesize vs. microstrain in copper as function of ageing

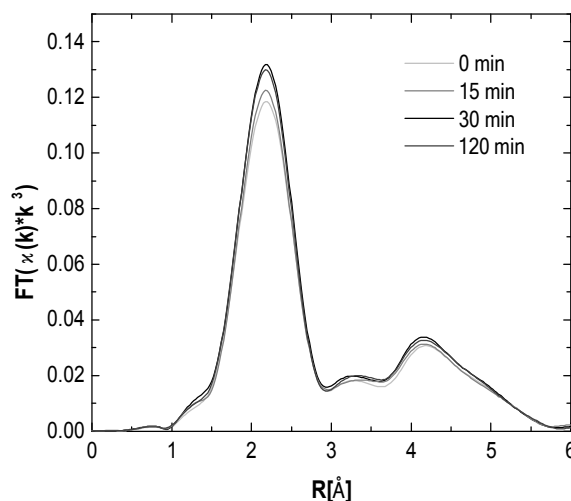


Fig.2: Cu EXAFS as function of precipitate ageing

- [1] M.M. Günter, T. Ressler, R.E. Jentoft, B.Bems, J. Catal. 203, **2001** 133-149 [2] B. Bems, M. Schur, A. Dassenoy, H. Junkes, D. Herein, R. Schlögl, Chem. Eur.J. 9 **2003** 2039-2052 [3] B.L. Kniep, T. Ressler, F. Girgsdies, A. Rabis, M. Baenitz, F. Steglich, R. Schlögl, Angewandte Chemie **2003**, accepted