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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 nano particles affects the catalytic activity [1,2]. 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 [3] and enables designing a desired catalyst performance by modifying the precipitation conditions instead of varying the chemical composition.

Preparation

Four Cu/ZnO catalyst (molar ratio Cu:Zn = 70:30) were prepared by co-precipitation of mixed copper zinc hydroxy carbonates at constant pH (pH=7). The precipitates were aged under constant stirring in their mother liquor for 0 min, 15 min, 30 min and 120 min. The resulting precursors were washed (353 K, 80 ml H_2O), dried (383 K, 20h) and calcined (603 K, 3 h, static air) under the same conditions. Bulk structural changes of the four differently aged catalysts in steam reforming gas mixture were investigated by using the two complementary method in situ X-ray diffraction (XRD) and in situ X-ray adsorption spectroscopy (XAS) combined with on-line mass spectrometry (MS). Phase transitions and kinetics during reduction obtained from in-situ XAS experiments (523 K, heating ramp: 6K/min; 2 vol% H_2 in He) were compared to TG/MS results. Microstrucutral characteristics of the catalysts as function of precipitate ageing were performed in an in-situ XRD and in situ XAS cell in methanol steam reforming gas mixture (total flow of 160 ml/min and 40 ml/min, respectively, with a MeOH/H_2O ratio = 1 at 523K and 1 bar). Activity data were correlated to detailed line profile anaylsis of the XRD powder patterns (separation of particle size and microstrain) and to the refinement results of the EXAFS measurements performed at the Cu-Kedge. In addition, ex situ ^{63}Cu nuclear spin resonance (NMR) measurements of the freshly reduced catalysts were performed at room temperature. Changes in morphologie and surface structure as function of precipitate ageing were investigated by using ex situ transmission electron microscopy (TEM) of the reduced catalysts and in-situ X-ray photoelectron spectroscopy (XPS).

Results

A sequential two-step reduction process (CuO $\Rightarrow$ Cu_2O $\Rightarrow$ Cu) was found for the CuO/ZnO precursors. With increasing ageing time the onset of reduction is shifted from 462 K to 444 K, accompanied by a decrease in particle size from 130 Å (0 min) to 70 Å (120 min) obtained from detailed line profile analysis. The Cu/ZnO catalysts prepared from precursors aged for longer times (30 and 120 min) exhibit a much-increased H_2 production rate (Fig1). The higher Cu surface area alone of the freshly reduced catalysts (estimated from the particle size and determined by N_2O decompostion) cannot explain the strong increase in catalytic activity between 15 and 30 min ageing time. However, a positive correlation between microstrain in copper particles and catalytic activity was found. In addition, EXAFS refinement of the Cu K-edge spectrum revealed an increase in Debye-Waller factors in the medium range order as function of ageing time, which is in good agreement with the observed microstrain obtained by XRD line profile analysis. Similar to the X-ray diffraction, the line profile and line breadth of the ^{63}Cu NMR signal is affected by the particle size and microstrain of the copper particles (Fig. 2). Precursors aged for 0 min and 15 min revealed a symmetric line broadening due to less strained and larger Cu particles whereas precursors aged for 30 min and 120 min exhibited an asymmetric line broadening due to strained and smaller Cu nano particles. Furthermore, it was found that continuous precipitate ageing leads to a decreasing amount of Zn occupying Cu lattice sites (determined by EXAFS analysis) in the active copper phase. This indicates, that the occupancy of Zn atoms on Cu lattice diminishes the transmission of strain, induced by an epitactical orientation of copper on zincoxide. TEM investigations reveal the complex morphological arrangement of the catalyst as function of ageing. However, the amount of nanostructured Cu/ZnO particles in the catalyst powder increases with increasing ageing time, which is in good agreement with the copper particle size evolution determined by XRD line profile analysis. The better interaction of copper and ZnO in nanostructured particles leads to microstrain in copper particles and thus, to an increase in catalytic activity.

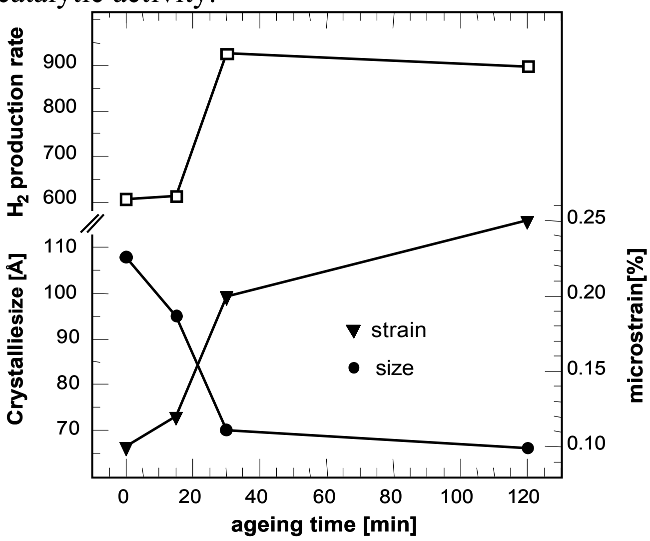

Fig. 1: H_2 production rate and particlesize vs. microtrstrain of copper as function of precipitate ageing

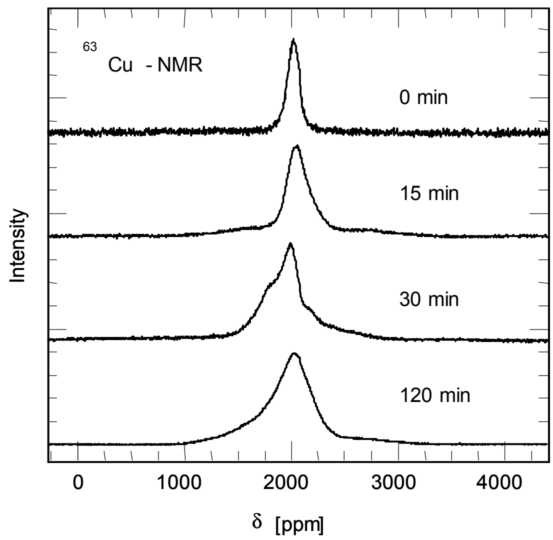

Fig. 2: ^{63}Cu NMR of the freshly reduced Cu/ZnO catalysts as function of precipitate ageing

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