

Microstructural Characteristics of Cu/ZnO Catalysts as Function of Precipitate Ageing

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Introduction

A detailed knowledge of the relationship between catalytic activity, surface structure, and bulk structure of Cu/ZnO catalysts is required to prepare new and improved catalysts. In addition to the copper surface area, the catalytic activity of binary Cu/ZnO catalysts in methanol steam reforming correlates with the microstrain in the bulk of the copper particles. [1] Recently, we were able to show that microstructural characteristics of a “real catalyst” such as microstrain can be controlled by ageing of freshly precipitated precursors. [2, 3] Here, we compare the effect of precursor ageing on the microstructural characteristics of Cu/ZnO catalysts prepared by using either sodium carbonate or ammonium hydroxide as precipitating agent.

Preparation and Experimental

The precursors for Cu/ZnO catalysts were precipitated at constant pH (pH=7) by simultaneous mixing of an aqueous solution of metal nitrates with (a) sodium carbonate or (b) ammonium hydroxide (1.2 M). The resulting precipitates were aged in their mother liquor for 0 and 120 min, followed by washing and drying. Calcination and reduction of the precursor obtained from ammonium hydroxide were investigated using X-ray diffraction (XRD), thermogravimetry combined with mass spectrometry (TG/MS) and electron microscopy (EM). The bulk structure, morphology, and catalytic activity of the Cu/ZnO catalysts under working conditions were characterized by in situ XRD and X-ray absorption spectroscopy (XAS) in combination with on-line mass spectrometry, ex-situ nuclear magnetic resonance (NMR) and ex-situ EM.

Results

Precipitation using ammonium hydroxide leads to the formation of a single phase hydroxynitrate precursor (HN), whereas the standard precipitation method using sodium carbonate results in a mixture of several hydroxycarbonates (HC). The characteristic crystallization during ageing of hydroxycarbonates and the accompanying increase in catalytic activity was not observed for the Cu/ZnO catalysts obtained from aged hydroxynitrate precipitates. The lower catalytic activity of Cu/ZnO catalysts obtained

from HN precursors compared to the catalysts prepared by HC precursors roughly correlates with the larger copper particle size (determined by detailed XRD line profile analysis) and the resulting lower copper surface area (Fig 1.). The specific copper surface area exposed to the gas mixture mainly determines the catalytic activity. However, bulk structural characteristics such as microstrain can enhance the catalytic activity of the copper surface [1,2,3]. The higher degree of strain in the catalyst prepared by 120 min ageing of hydroxycarbonates (120HC, Fig.1) clearly indicates, that distinct interface between Cu and ZnO is necessary to obtain strained copper particles. NMR and EXAFS results (Fig. 2) reveal a more ideal copper bulk structure for the Cu/ZnO catalysts obtained from hydroxynitrates compared to those obtained from hydroxycarbonates. The more defect rich character of the copper particles prepared via the hydroxycarbonate route is in good agreement with HRTEM investigations comparing both series of catalysts. Upon addition of oxygen to the feed gas followed by re-reduction of the catalyst, an increase in catalytic activity was observed for both series of catalysts (HN and HC). The higher catalytic activity appears to correlate with minor structural changes in the medium range order of Cu and ZnO rather than an increase in copper surface area, microstrain or oxygen in copper clusters as previously reported [4].

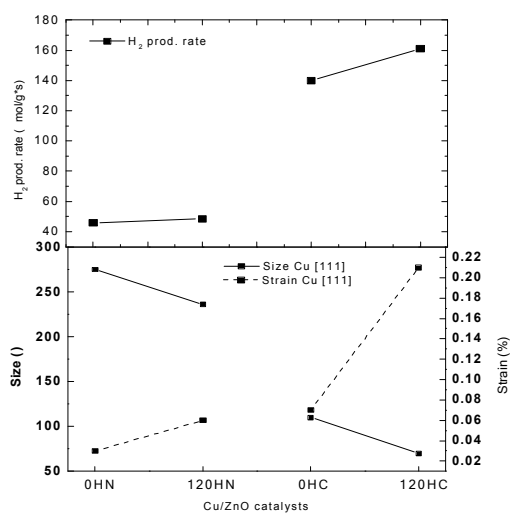


Fig. 1: H₂ production rate and particle size vs. microstrain in copper as function of ageing

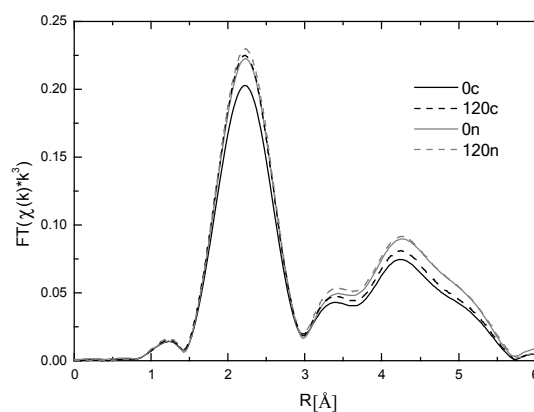


Fig. 2: Cu EXAFS of Cu/ZnO from HC and HN as a function of precipitate ageing.

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