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Structural Modifications of Cu/ZnO-based Catalysts as a Function of Precipitate Ageing

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The preparation of new and improved Cu/ZnO based catalysts requires a detailed knowledge of the relationship between catalytic activity, surface structure, and bulk structure. Recently, we were able to show that in addition to the copper surface area, bulk structural parameters such as microstrain in copper particles correlate with the catalytic activity in methanol steam reforming.[1] Here we report on tailoring microstructural characteristics of "real catalysts" by appropriate ageing of freshly precipitated precursors [2,3]. Furthermore, we compare the effect of the precipitation agent (sodium carbonate or ammonium hydroxide) on the ageing process and the resulting microstructure of the catalyst.

Copper zinc oxide precursors, i.e. metal hydroxycarbonates or metal hydroxynitrates (70 mol-% Cu), were precipitated by simultaneous mixing of an aqueous solution of metal nitrates with sodium carbonate or ammonium hydroxide at constant pH (pH=7). The resulting precipitates were aged for 0, 15, 30 and 120 min, followed by washing, drying (120°C, 20h), calcination (330°C, 3h) and reduction (250°C, 2% H_2). The bulk structure, morphology, and catalytic activity of the Cu/ZnO catalysts under working conditions were characterized by in situ X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) in combination with on-line mass spectrometry, ex-situ nuclear magnetic resonance (NMR) and ex-situ high resolution transmission electron microscopy (HRTEM).

Precipitation using ammonium hydroxide leads to the formation of a single phase Cu,Zn hydroxynitrate precursor (HN), whereas the standard precipitation using sodium carbonate results in a mixture of several Cu,Zn-hydroxycarbonates (HC). In Figure 1 the methanol steam reforming activity of the catalysts obtained from HN, HC precursors aged for 0 and 120 min compared to pure CuO (prepared by precipitated malachite; $Cu_2(OH)_2(CO_3)$) is depicted as function of the copper particle size and microstrain (determined by detailed XRD line profile analysis). The increasing catalytic activity of the Cu/ZnO catalysts roughly correlates with the decreasing copper particle size and the resulting increased surface area.

The degree of microstrain in copper clusters can be neglected for the non-supported system (CuO), the HN prepared catalysts and the non-aged HC catalyst, whereas a significant degree of strain was determined for catalysts prepared from HC aged for 120 min. Detailed investigations of the Cu/ZnO catalysts obtained from hydroxycarbonates aged for 0, 15, 30 and 120 min (Fig.2) clearly demonstrate that the sudden increase in activity, accompanied by crystallization of the initially amorphous precipitates, can not be explained alone by an increase in specific Cu surface area (decrease in Cu particle size). Additionally, the H_2 production rate for methanol steam reforming correlates with the microstrain in the catalytically active Cu phase[3]. Ex-situ Cu^{63} NMR investigations of freshly reduced catalysts are in good agreement with in situ XRD results concerning microstrain in Cu clusters[2]. HRTEM investigations reveal an improved Cu/ZnO interface for the 30HC and 120HC catalyst resulting in strained Cu clusters [4]. It is assumed that strain is induced by an epitaxial orientation of Cu on ZnO. The active copper phase in Cu/ZnO catalysts exhibits a real microstructure that deviates significantly from that of bulk fcc copper metal. Ageing of hydroxycarbonate precipitates enables one to control microstructural parameters of "real Cu/ZnO" catalyst.

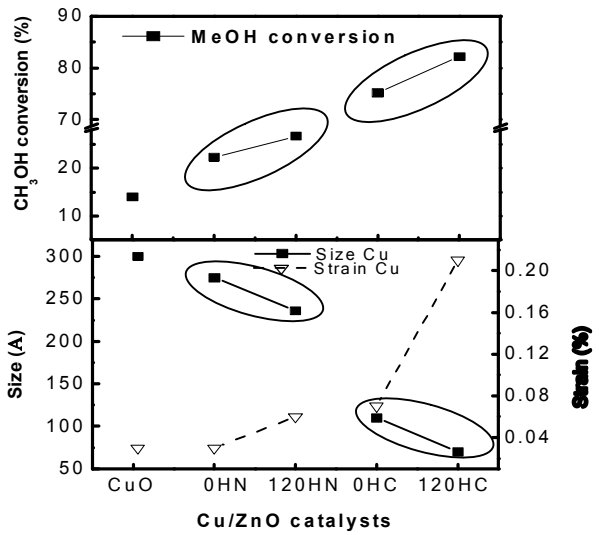

Fig.1 Catalytic activity, Cu particle size, and Cu microstrain for Cu/ZnO catalysts prepared from malachite, hydroxynitrate (HN) and hydroxy-carbonate precursors (HC) precipitates as function of ageing

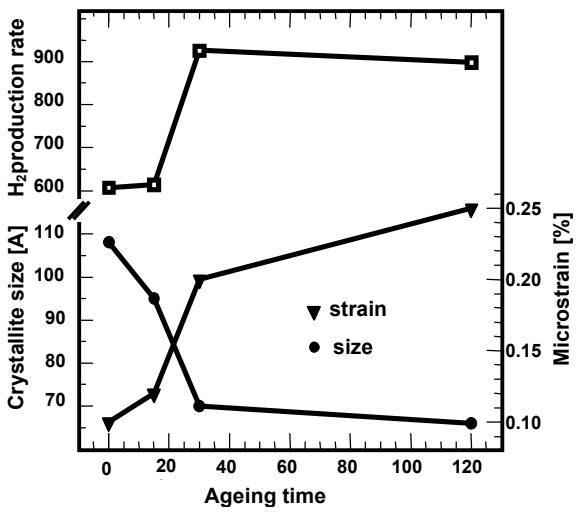

Fig.2 Catalytic activity, Cu particle size, and Cu microstrain for Cu/ZnO catalysts prepared by 0, 15, 30 and 120 min precipitate ageing of hydroxycarbonate precursors.

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