

Microstructural optimization in metal/oxide catalysts: Higher intrinsic activity of copper by partial embedding of Cu nanoparticles

Malte Behrens* and Robert Schlögl,

Fritz Haber Institute, Max Planck Society, Inorganic Chemistry Department,
Faradayweg 4-6, 14195 Berlin (Germany)

*behrens@fhi-berlin.mpg.de

Introduction

Cu/ZnO/(Al₂O₃) catalysts are active in industrial methanol synthesis and a Cu/ZnO synergy is discussed in literature, the nature of which is still under debate [1-3]. However, it seems clear that synergetic effects should have their origin in the Cu-ZnO interface region. The catalytic properties are, thus, not only determined by the amount of Cu surface area (S_{Cu}) but also by the nature of Cu-ZnO interface contacts. As a result of the latter effect, deviations of S_{Cu} -activity correlations from linearity can be observed [4]. Usually, the amount of S_{Cu} is regarded as the dominating effect and a catalyst of considerably lower S_{Cu} would be estimated to exhibit inferior activity compared to a high S_{Cu} sample of the same Cu loading. The potential of intrinsic or synergistic effects, which are responsible for different specific activities of Cu, is not easily determined because surface and interface area are interrelated by morphology and microstructure, which are difficult to control during preparation of applied Cu/ZnO/(Al₂O₃) systems. For modern catalysts, the optimization of Cu dispersion can be regarded as widely advanced, while optimization of the Cu-oxide interface contact, i.e. the microstructural arrangement of the components, presents further unexplored room for improvement.

Materials and Methods

In our contribution, we present two types of Cu/Zn/Al₂O₃ catalysts. One was prepared according to the technically applied synthesis route (co-precipitation from mixed CuZnAl nitrate solution with sodium carbonate at constant pH 7, 65°C, ageing, washing, calcination at 330°C and reduction) and is denoted catalyst B. The other one, catalyst A, is a novel type of catalyst prepared accordingly, but with two important modifications: (i) Instead of pure sodium carbonate solution and mixed CuZnAl-nitrate solution, a combination of sodium aluminate and carbonate solution was used as precipitating agent for a CuZn-nitrate solution during coprecipitation, (ii) the ageing period was suppressed by realizing a continuous process with direct spray-drying of the fresh precipitate suspension. The precursors were subjected to the same treatments during preparation. It is important to note that both samples exhibit exactly the same industrially relevant metal composition of Cu:Zn:Al = 60:25:15 and, thus, experimentally observed differences can be related to a different microstructure.

Results and Discussion

The characterization of the samples A and B using XRD, FTIR, TGA, BET, and (HR)TEM, includes investigation of the microstructure of the final reduced catalysts. For both samples approximately 90 % of the spherically shaped Cu particles fall into a size range of 4–9 nm (mean diameter 8.1 ± 2.4 and 7.2 ± 2.2 nm for catalyst A and B). Considering the similarity of Cu particle size and shape, we assume that differences in the catalytic performance of the two materials are related to the different microstructure of the ZnO/Al₂O₃ component and its interface contact to Cu. Hence, these two samples allow studying the microstructural effects on

the catalytic properties without decisive contributions of average composition and Cu particle size. As shown in Figure 1, in catalyst A individual separated oxide particles are hardly observed. The Cu particles are partly embedded in an amorphous oxide matrix. This arrangement results in an intimate interface contact of metal particles and the continuous Cu depleted oxide. In typical areas of catalyst B on the other hand Cu and ZnO particles are observed in an alternating arrangement forming a porous framework.

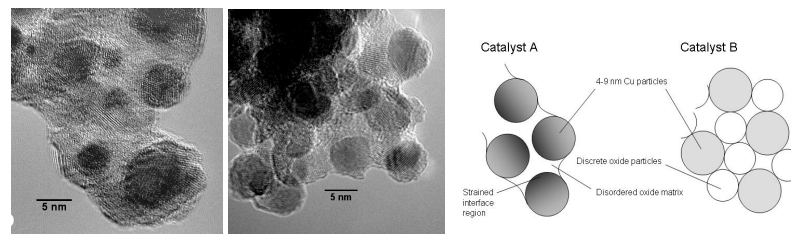


Figure 1. Typical HRTEM images of catalysts A (left) and B (middle) and schematic illustration of the microstructure (right).

S_{Cu} was determined for both samples by N₂O chemisorption and amounts to 24.8 ± 1.2 and $36.1 \pm 1 \text{ m}^2 \text{ g}^{-1}$ for catalyst A and B, respectively. This difference can be rationalized considering the partly embedded nature of the Cu particles in catalyst A. However, the catalytic activity in methanol synthesis of this catalyst was $13.1 \pm 0.7 \text{ mmol g}^{-1} \text{ h}^{-1}$ in our test (10 bar, 220°C), which is higher than the activity of $11.6 \pm 0.6 \text{ mmol g}^{-1} \text{ h}^{-1}$ determined for catalyst B. It is noted that the activity of a commercial catalyst, provided by Süd-Chemie AG, showed an activity in the same range. According to these results, the intrinsic activity of Cu (normalized to S_{Cu}) in catalyst A was more than 50% higher. The enhanced Cu-oxide interface contact leads to an unavoidable decrease of S_{Cu} , but, at the same time, seems to beneficially affect the remaining exposed fraction of the Cu surface. In case of the novel catalyst A, this positive effect outweighs the loss of S_{Cu} , demonstrating clearly the unexpectedly high degree of adjustability of intrinsic activity by the interplay of interface and surface for copper nanoparticles of similar size. In our contribution, we will present comprehensive analytical data of the preparation processes and discuss possible models for Cu/ZnO synergy.

Significance

These results demonstrate the importance of the microstructure, i.e. the interplay of Cu-oxide interface and Cu surface area, and can be seen as an encouraging example of the potential of novel synthesis methods aiming at tailoring the Cu/oxide arrangement to further optimize the catalytic performance of Cu based methanol synthesis catalysts.

References

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