Correlations between synthesis, precursor, and catalyst structure and activity of a large set of CuO/ZnO/Al2O3 catalysts for methanol synthesis

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Abstract

Ternary Cu/ZnO/Al2O3 catalysts were systematically prepared via the coprecipitation route under strictly controlled conditions such as pH, precipitation temperature, and calcination temperature. All catalysts were tested with respect to their methanol synthesis activity in a 49-fold multitubular high-throughput experimentation setup under conditions similar to the commercial methanol production route, using a syngas mixture of CO, CO2, and H2. Representative samples were chosen for a more detailed structure and morphology analysis to reveal correlations between the catalyst's "preparation history" and the methanol productivity. The best catalytic performance was observed for catalysts obtained from precursors precipitated in the pH range of 6–8 at 70 °C. XRD measurements allowed the "grouping" of catalysts based on their phases. It was found that a group of best-performing catalysts exhibited the characteristic XRD pattern of nondecomposed Cu/Zn hydroxide carbonate residues in the calcined precursors, leading to the assumption that carbonate species in this state may enhance productivity. Further investigations of these hydroxy carbonate-containing catalysts provided more detailed insight into the dynamic aging process and its effect on catalytic performance. The greatest methanol synthesis activity was observed for catalysts aged for 20–60 min after an initial phase formation time. The optimum calcination temperature was found to be in 250–300 °C. Under these conditions, the resulting Cu/Zn/Al hydroxy carbonates remained stable. In addition, the syngas feed composition was varied under reaction conditions and correlated to catalytic activities. The greatest methanol productivity over Cu/ZnO/Al2O3 catalysts was observed for the following gas concentrations: 50–60% for H2, 30–40% for CO, and 5–10% for CO2, at 4.5 MPa and 245 °C.

1. Introduction

Cu/ZnO/Al2O3 catalysts are used predominantly in the industrial low-pressure methanol synthesis process starting from synthesis gas, a mixture of H2, CO, and CO2. To date, the best catalytic performance has been achieved over Cu/ZnO/Al2O3 catalysts prepared by the coprecipitation method using nitrates of Cu, Zn, and Al and alkali carbonates or alkali bicarbonates as basic precipitating agents. The resulting hydroxy carbonates are converted to metal oxides by subsequent calcination at ca. 300–500 °C. The final active catalyst is obtained by reduction of CuO to metallic Cu under a diluted H2 flow before feeding the synthesis gas mixture [1–3]. Each step in the synthetic procedure may influence the activity of the final catalyst under reaction conditions, the structure of which may be different from that of a sample recovered after the reaction and analyzed ex situ. Numerous studies have evaluated sample sets covering a limited part of the parameter space or parts of the full catalyst synthesis sequence. Several of these studies focused on the binary Cu/ZnO system. Due to the somewhat fragmented data in the literature, it seemed worthwhile to undertake a more comprehensive study of the whole sequence from hydroxy carbonate precursor over oxide precursor to the reduced catalyst in the Cu/ZnO/Al2O3 system, and to attempt to elucidate the influence of the conditions and the structure of the solid after each step on the final activity of the catalyst.

The role of metallic copper in the reaction mechanism has been widely discussed in the literature over the past 20 years and remains a matter of debate. Today, it is widely accepted that metallic copper clusters are the active sites for the methanol synthesis reaction over Cu/ZnO-based catalysts [4,5]. The main function attributed to the ZnO is to increase Cu dispersion in the calcined sample, thus providing a large number of active sites exposed to the reaction gases [1]. In addition, however, ZnO may contribute to the high activity through some other effects, as discussed below.

Studies on the phases in the precipitate of Cu/Zn hydroxy carbonates in combination with aging effects have revealed that some precipitate phases seem to favor the dispersion of copper. For instance, in aurichalcite (CuZn)(CO3)2(OH)6, Cu is atomically dispersed in a zinc hydroxy carbonate matrix, whereas in zincian-