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Correlations between synthesis, precursor, and catalyst structure and activity of a large set of $CuO/ZnO/Al_2O_3$ catalysts for methanol synthesis

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ABSTRACT

Ternary $Cu/ZnO/Al_2O_3$ catalysts were systematically prepared via the coprecipitation route under strict control of parameters 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, CO_2, and H_2. 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 hydroxy 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 affect 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 $Cu/ZnO/Al_2O_3$ catalysts was observed for the following gas concentrations: 50–60% for H_2, 30–40% for CO, and 5–10% for CO_2, at 4.5 MPa and 245 °C.