Role of Al2O3 versus ZrO2 in Cu/ZnO-based Catalysts in CO2 Hydrogenation to Methanol

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CO2 hydrogenation to methanol has been studied steadily because global warming by CO2 emission is a major concern worldwide and methanol can be used as a building block for various chemicals. The industrial methanol synthesis catalyst is Cu/ZnO/Al2O3 in which Cu is an active metal for adsorption of CO and CO2, and ZnO acts as a promoter. Although the role of Al2O3 as a support or promoter has been debated for several decades, Behrens et al. recently revealed structural and electronic promoter effects of Al2O3 for Cu/ZnO/Al2O3 catalysts of a fixed Cu/Zn ratio (7/3) and different Al2O3 contents up to 10 wt%, where the reactant was a CO/CO2/H2 mixture [1].

In this work the similar catalysts containing Al2O3 of 0–30 wt% were prepared and tested in CO2 hydrogenation at 503 K and 30 barg. Figure 1 shows the methanol productivity of Cu/ZnO/Al2O3 catalysts. Surprisingly, the activity trend is very similar to the results of Behrens et al. [1]. Binary Cu/ZnO, derived from zincian malachite precursor [2], exhibited 237.2 gCH3OH kgcat⁻¹ h⁻¹. In case of ternary Cu/ZnO/Al2O3, the activity results follow a volcano trend with the maximum at 4% Al (407.8 gCH3OH kgcat⁻¹ h⁻¹) and different Al2O3 contents up to 10 wt%, where the reactant was a CO/CO2/H2 mixture [1].

From the above results, we desired to know about the activity trend of Cu/ZnO/ZrO2 catalysts because ZrO2 is a very popular support material for Cu/ZnO in CO2 hydrogenation [4]. As shown in Fig. 1, the CH3OH productivity increased to 345.6 gCH3OH kgcat⁻¹ h⁻¹ to 9% Zr and was then changed little up to 30% Zr, which is very different from the case of Cu/ZnO/Al2O3. It was found that the Cu/ZnO/ZrO2 activity matches well with the specific Cu surface area (not shown here). This finding was already examined by our previous report that ZrO2 acts as a nano-spacer between Cu/ZnO particles in the hydrogenolysis of butyl butyrate [5]. Therefore, the similar methanol productivities in the 9–30% Zr window is a trade-off between lower Cu loading and smaller Cu particles with Zr content increasing.

Based upon our results, one may expect that the optimal content of Al2O3 is different from that of ZrO2 in Cu/ZnO-based catalysts for CO or CO2 hydrogenation. Different from this expectation, the compositions of Al2O3 and ZrO2 are very random in the quaternary Cu/ZnO/Al2O3/ZrO2 catalysts studied so far in the literature. The activity results of such catalysts having the optimized Al2O3 and ZrO2 contents will be presented.

Fig.1 CH3OH productivity as a function of Al (black, circle) and Zr (blue, square) contents.

REFERENCES