Role of Al_2O_3 versus ZrO_2 in Cu/ZnO-based Catalysts in CO_2 Hydrogenation to Methanol

Jinsung Kim[1], Cheonwoo Jeong[1], Young-Woong Suh[1,2]*

[1]*Department of Chemical Engineering, Hanyang University, Seoul 04763, Republic of Korea*

[2]*Research Institute of Industrial Science, Hanyang University, Seoul 04763, Republic of Korea*

*E-mail: ywsuh@hanyang.ac.kr

CO_2 hydrogenation to methanol has been studied steadily because global warming by CO_2 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/Al_2O_3 in which Cu is an active metal for adsorption of CO and CO_2, and ZnO acts as a promoter. Although the role of Al_2O_3 as a support or promoter has been debated for several decades, Behrens et al. recently revealed structural and electronic promoter effects of Al_2O_3 for Cu/ZnO/Al_2O_3 catalysts of a fixed Cu/Zn ratio (7/3) and different Al_2O_3 contents up to 10 wt%, where the reactant was a CO/CO_2/H_2 mixture [1].

In this work the similar catalysts containing Al_2O_3 of 0–30 wt% were prepared and tested in CO_2 hydrogenation at 503 K and 30 barg. Figure 1 shows the methanol productivity of Cu/ZnO/Al_2O_3 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 g_{CH3OH} kg_{cat}^{-1} h^{-1}. In case of ternary Cu/ZnO/Al_2O_3, the activity results follow a volcano trend with the maximum at 4% Al (407.8 g_{CH3OH} kg_{cat}^{-1} h^{-1}). This means that the promoter effect of Al_2O_3 is also effective in CO_2 hydrogenation. Note that the activity decline for the catalysts containing Al higher than 4% (e.g., 225.3 g_{CH3OH} kg_{cat}^{-1} h^{-1} for 30% Al) results from the fact that the hydrotalcite phase (less active precursor structure) became dominant as Al content increased [3].

From the above results, we desired to know about the activity trend of Cu/ZnO/ZrO_2 catalysts because ZrO_2 is a very popular support material for Cu/ZnO in CO_2 hydrogenation [4]. As shown in Fig. 1, the CH_3OH productivity increased to 345.6 g_{CH3OH} kg_{cat}^{-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/Al_2O_3. It was found that the Cu/ZnO/ZrO_2 activity matches well with the specific Cu surface area (not shown here). This finding was already examined by our previous report that ZrO_2 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 Al_2O_3 is different from that of ZrO_2 in Cu/ZnO-based catalysts for CO or CO_2 hydrogenation. Different from this expectation, the compositions of Al_2O_3 and ZrO_2 are very random in the quaternary Cu/ZnO/Al_2O_3/ZrO_2 catalysts studied so far in the literature. The activity results of such catalysts having the optimized Al_2O_3 and ZrO_2 contents will be presented.

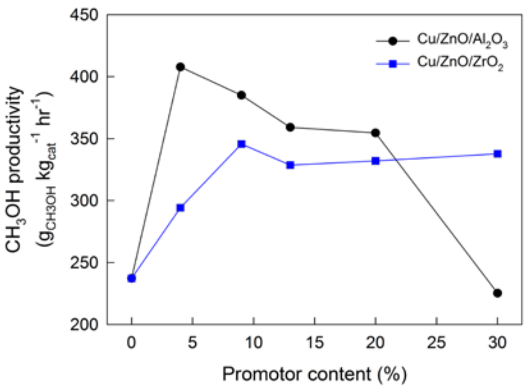

Fig.1 CH_3OH productivity as a function of Al (black, circle) and Zr (blue, square) contents.

REFERENCES

[1] M. Behrens, S. Zander, P. Kurr, N. Jacobsen, J. Senker, G. Koch, T. Resseler, R.W. Fischer and R. Schlögl, J. Am. Chem. Soc., 135 (2013) 6061.

[2] M.M. Günter, B. Bems, C. Büscher, T. Genger, O. Hinrichsen, M. Muhle and R. Schlögl, Catal. Lett., 71 (2001) 37.

[3] M. Beherns, I. Kasatkin S. Kühl and G. Weinberg, Chem. Mater., 22 (2010) 386.

[4] G. Bonura, M. Cordaro, C. Cannilla, F. Arena and F. Frusteri, Appl. Catal. B, 152 (2014) 152.

[5] C. Jeong and Y-W. Suh, Catal. Today, 265 (2016) 254.