

CuO-ZrO₂ catalysts in mesoporous silica: CO₂ hydrogenation to methanol

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With the emerging interest of mitigating the increase concentrations of CO₂, a greenhouse gas, while storing energy as liquid fuels, the direct hydrogenation of CO₂ in place of CO into methanol has become a very active field of research. [1] For the industrialization of the title reaction's plants, new catalysts only for the CO₂ hydrogenation to methanol should be developed. CO₂ hydrogenation to methanol is exothermic and the number of mole of products is lower than that of the educts ($\text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O}$, $\Delta_r H$ (298 K, 50 bar) = $-40.9 \text{ kJ mol}^{-1}$). The endothermic reverse water gas shift reaction (RWGS reaction, $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$, $\Delta_r H$ (298 K, 50 bar) = 49.8 kJ mol^{-1}), converting CO₂ into CO, can compete in particular at high temperatures. We reported that Cu/ZrO₂ catalysts exhibited high activity and selectivity in the title reaction. [2] For further improvement of the catalytic activity, enhancement of Cu dispersion should be promising. Herein, CuO/ZrO₂ catalysts were deposited in interior of KIT-6 (one of mesoporous silica), and then the effect of preparation conditions of CuO/ZrO₂/KIT-6 on the CO₂ hydrogenation was investigated.

The CuO/ZrO₂/KIT-6 was prepared by a stepwise impregnation method. The KIT-6 was prepared according to a reported procedure. [3] The KIT-6 was impregnated with an aqueous solution of ZrO(NO₃)₂·xH₂O (Wako), dried at 110 °C overnight, and calcined at desired temperatures (400, 600, and 800 °C) for 4 h. Next, the crude materials were impregnated with an aqueous solution of Cu(NO₃)₂·3H₂O (Wako), dried at 110 °C overnight, and calcined at 350 °C for 2 h. The loadings of Cu and ZrO₂ were 13 and 44 wt%, respectively.

The CO₂ hydrogenation was conducted in a fixed-bed tubular reactor at 10 bars. Fig. 1 shows the methanol production rate for the

catalysts. With decreasing the calcination temperature, the methanol synthesis rate increased. Fig. 2 shows PXRD patterns for the three CuO/ZrO₂/KIT-6 catalysts after activity test. When ZrO₂/KIT-6 was calcined at 400 °C, metallic Cu peak at *ca.* 43° was hardly observed, resulting in formation of smaller Cu particles than PXRD detection limitation. When ZrO₂/KIT-6 was calcined at 600 and 800 °C, the Cu sharp peak appeared. This indicates aggregation of Cu particles deposited on KIT-6 surface, not in the mesopore of the KIT-6. Thus, small Cu particles seem to work as main active species for the CO₂ hydrogenation to methanol.

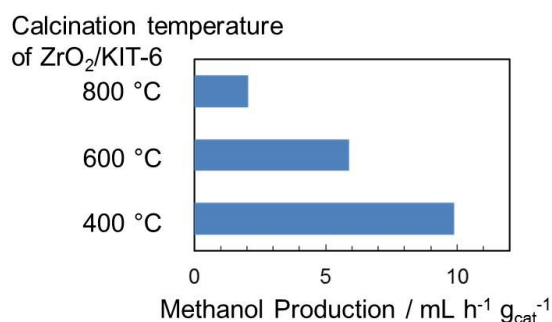


Fig. 1 MeOH production of CuO/ZrO₂/KIT-6. Reaction condition: CO₂/H₂/N₂ = 1/3/1, catalyst loading = 500 mg, W/F = 1000 mg_{cat} s mL⁻¹, temperature = 230 °C, pressure = 10 bar.

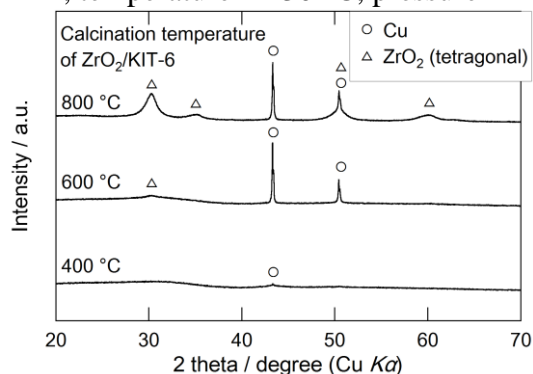


Fig. 2 XRD patterns of CuO/ZrO₂/KIT-6 after activity test.

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Acknowledgements

This work was supported by the Japan Society of the Promotion of Science (JSPS, No. 15J10157).