Catalysts prepared by using the sol-gel method and their pretreatments for direct synthesis of dimethyl ether

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Abstract: We had developed excellent catalysts for direct synthesis of dimethyl ether (DME) by using the sol-gel method. The $Cu\text{-}Zn/Al_2O_3$ catalysts prepared using the sol-gel method have higher activity and selectivity for direct DME synthesis from syngas than usual direct DME synthesis catalysts, mixed catalysts of methanol synthesis catalysts and methanol dehydration catalysts. This time, we have improved DME production rate and selectivity by increasing temperature for calcination and reduction of the catalysts prepared by the sol-gel method. The fastest DME production rate was 627 $\mu mol\, g_{cat}^{-1}\, h^{-1}$ and the selectivity was 97 *C*.% at 240 °C and under 0.9 MPaG.

Keywords: Dimethyl ether (DME), CO hydrogenation, sol-gel method

1. Introduction

Dimethyl ether (DME) is slightly expensive because it is produced by dehydration of methanol, and the price of DME will be almost twice of that of methanol. DME burns without particulate matter (PM) and SOx, and the emission of NOx is less than those of other fuels such as diesel oil and LPG. DME will be a clean substitute of diesel oil and LPG. Also, DME can be a hydrogen/energy carrier and storage [1-3]. DME can be produced economically by the direct DME synthesis from syngas (mixed gas of CO and H_2). We have developed excellent catalysts for direct DME synthesis by using the sol-gel method. The $Cu\text{-}Zn/Al_2O_3$ catalysts prepared using the sol-gel method have higher activity and selectivity for direct DME synthesis from syngas than usual catalysts for direct DME synthesis, mixed catalysts of methanol synthesis catalysts and methanol dehydration catalysts [2-4]. This time, effects of catalyst pretreatment, such as calcination and reduction temperatures, were determined for better DME synthesis activity and selectivity.

2. Experimental

Cu-Zn(15-15 wt.%)/Al_2O_3 catalysts were prepared by the consecutive sol-gel method. The catalysts were used in single, without mixing of acid catalyst such as alumina and zeolite, for hydrogenation of CO. The prepared catalysts in the dried gel state were crushed to smaller than 150 μm, 100 mesh. The crushed catalyst powder were calcined in air and reduced by H_2 flow for 5 h, respectively. The temperature of the calcination and the reduction were changed from 350 to 750 °C for each catalyst pretreatment. Ratio of reaction gases was $H_2/CO/Ar = 5.0/5.0/1.0$ ml min^{-1}, the weight of catalyst was 1.0 g, and the reaction pressure was under 0.9 MPaG, absolute pressure 1.0 MPa. Online gas chromatographs with TCD and FID were used for the analysis of reactants and products, and Ar gas was used for the GC internal standard gas.

3. Results and discussion

In the case of the catalysts calcined at 500 °C, the fastest DME production rate was obtained over the catalyst reduced at 500 °C. The rate was 510 $\mu mol\, g_{cat}^{-1}\, h^{-1}$ and the DME selectivity was 95 *C*.% at 240 °C reaction temperature. On the other hand, over the catalyst calcined at 600 °C gave lower activity and selectivity at 500 °C and 600 °C. However, DME activity and selectivity were increased with increase of the reduction temperature. The fastest DME production rate was obtained over the catalyst reduced at 750 °C. (*Cf*. Figure 1) The rate was 627 $\mu mol\, g_{cat}^{-1}\, h^{-1}$ and the selectivity was 97 *C*.% at 240 °C reaction temperature, and the higher turnover frequency (TOF) also was obtained.

Some results of X-ray diffraction (XRD) analyses of the catalysts are shown in Figure 2. ZnO peaks (2θ = 32.1°, 37.3°), Cu peaks (2θ = 43.4°, 50.5°, 74.0°), and CuO peaks (2θ = 45.6°) were detected. Also, $CuAl_2O_4$ peak (2θ = 60.1°) was detected. Higher temperature calcination formed the spinel structure, $CuAl_2O_4$. These XRD results, TEM analysis, and previous reports [5, 6] suggested that the higher temperature calcination treatment triggered copper and aluminum to form $CuAl_2O_4$ spinel type composite, and this composite was reduced at higher reduction temperature, and fine copper particles were produced and dispersed well. These phenomena led the higher DME synthesis activity and selectivity.

4. Conclusions

We have improved DME production rate and selectivity by increasing temperature for calcination and reduction pretreatments. The fastest DME production rate was 627 μmol g_{cat}^{-1} h^{-1}, and the selectivity was 97 *C*.%, and the DME yield was 10% at 240 °C reaction temperature under 0.9 MPaG, absolute pressure 1.0 MPa.

Acknowledgements

This research was supported by Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency (JST). The project title was "Co-electrolysis of CO_2 and H_2O for DME synthesis" in the project of "Development of Innovative Technology for Energy-Carrier Synthesis using Novel Solid Oxide Electrolysis Cell" (JPMJCR1343).

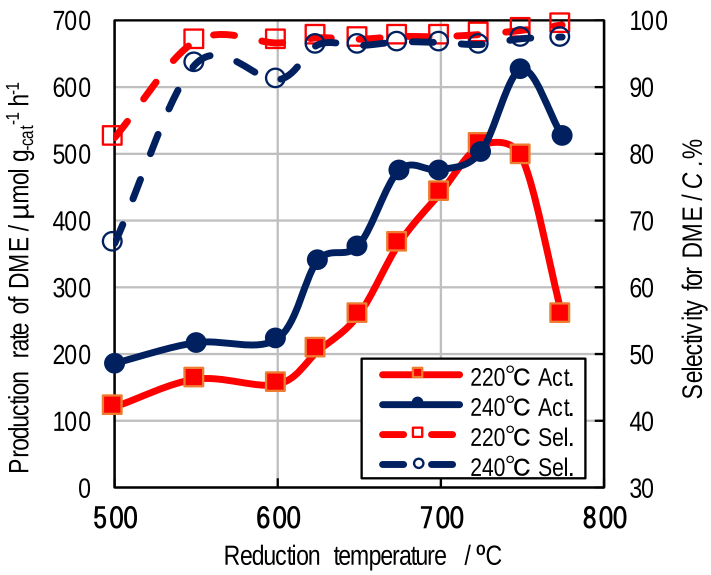

Figure 1. Production rate of DME and selectivity for DME of CO hydrogenation over Cu-Zn(15-15 wt.%)/Al_2O_3 catalysts prepared using the consecutive sol-gel method calcined at 600 °C.

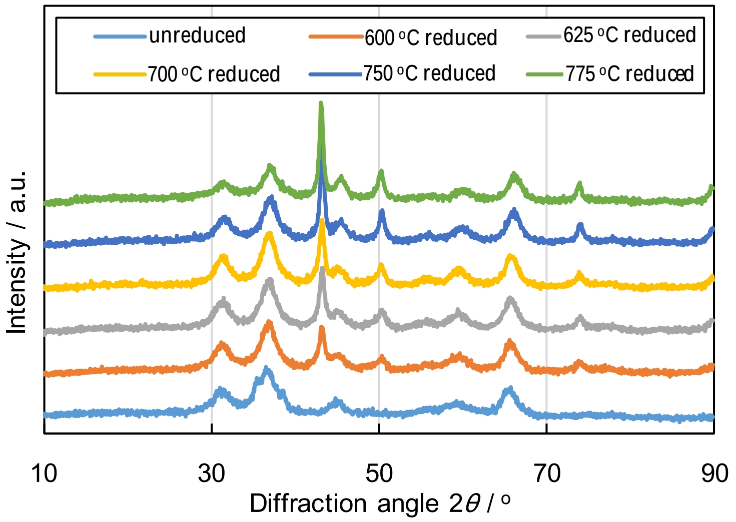

Figure 2. XRD pattern of the Cu-Zn(15-15 wt.%)/Al_2O_3 catalysts prepared using the consecutive sol-gel method, calcined at 600 °C for 5 h, and reduced at respective temperature for 5 h.

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