

Promotional effect of water on direct dimethyl ether synthesis from carbon monoxide and hydrogen over Cu-Zn/Al₂O₃ catalysts prepared by using the sol-gel method

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We have developed excellent catalysts for direct synthesis of dimethyl ether (DME) by using the sol-gel method. The Cu-Zn/Al₂O₃ catalysts prepared using the sol-gel method have higher activity and higher selectivity for direct DME synthesis from syngas (mixed gas of CO and H₂) than usual direct DME synthesis catalysts, mixed catalysts of methanol synthesis catalysts and methanol dehydration catalysts [1-2]. This time, effects of water on direct DME synthesis from syngas under the atmospheric pressure and under 0.9 MPaG have investigated.

Cu-Zn(15-15 wt%)/Al₂O₃ catalysts prepared by the consecutive sol-gel method were used for CO hydrogenation. Ratio of reaction gases was H₂/CO/Ar = 5.0/5.0/1.0 ml min⁻¹, and the amount of catalyst was 1.0 g. Some water vapor, or steam of water, was added through the H₂/CO/Ar gas using a water bubbler in some constant temperature bath or using a cold trap controlled under some temperature through after a water vaporizer. Reaction pressure was maintained under the atmospheric pressure and 0.9 MPaG, absolute pressure 1.0 MPa. Online gas chromatographs with TCD and FID were used for the analysis of reactants and the products, and Ar gas was used for the internal standard gas.

The relation between the steam concentration and DME production rate was obtained. There was the most optimum concentration of water vapor amount in the reactant gas for direct DME synthesis. The steam concentration was 0.66 mol.% and the DME production rate was 9.8 μmol g_{-cat}⁻¹ h⁻¹ at the reaction temperature 220 °C. On the other hand, production rate of DME at 220 °C from the reaction gas with less steam (0.07 mol.%) was 4.2 μmol g_{-cat}⁻¹ h⁻¹. Water vapor activated the direct DME synthesis. However, more

amount of CO₂ was produced from 47 μmol g_{-cat}⁻¹ h⁻¹ to 280 μmol g_{-cat}⁻¹ h⁻¹ with depending on the increase of the steam concentration from 0.07 mol.% to 0.66 mol.%. Water gas shift reaction (WGS) occurred well, and more amount of steam than 1 mol.% deactivated the direct DME synthesis.

Under the 0.9 MPaG, water vapor also activated direct DME synthesis, but the range of the water activation for DME synthesis was very narrow. The most optimum amount of steam was 0.09 mol.%, and the production rate was 486 μmol g_{-cat}⁻¹ h⁻¹ at the reaction temperature 220 °C. It meant that the DME yield was 8.0 %; very high yield even under the low pressure. On the other hand, production rate of DME at 220 °C from the reaction gas with less water (0.08 mol.%) was 377 μmol g_{-cat}⁻¹ h⁻¹. Even under high pressure, water affected for better DME production, but this promotional effect was in the narrow range of water amount. More amount of steam also worked for WGS and main product was changed to CO₂ from DME.

XPS analysis suggested that copper on the catalyst were oxidized to Cu²⁺, and FT-IR analyses showed that the peak area of IR spectra of CO adsorbed to Cu⁺ was significantly increased after the water/steam treatment. Water/steam in the reaction gas oxidized copper on the catalyst like the water/steam treatment [3-4]. Probably, in the case with water in the reactant gas, Cu⁰ on the catalysts were oxidized to Cu⁺ and Cu²⁺, and these Cu^{δ+} promoted methanol synthesis, and then DME production rate was increased.

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