

Steam Reforming of Dimethyl Ether over Solid Acid Catalyst Coupled with Cu-based Catalyst

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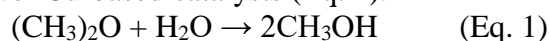
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Hydrogen fuel cells are considered to be among the most promising alternatives for next generation energy devices due to high energy density and zero harmful emissions. Steam reforming of natural gas, methanol, and gasoline can produce hydrogen. These raw materials have both advantages and drawbacks. Although infrastructure is well established for natural gas and gasoline, their reforming temperatures are high. Reforming of methanol proceeds at low temperatures (423–573 K); however, the cost of methanol as an energy source is relatively high; moreover it is biologically toxic. On the other hand, dimethyl ether (DME) is a candidate for a hydrogen energy carrier with excellent characteristics in storage and transportation. Similarly to methanol, dimethyl ether (DME) can be synthesized directly from syngas, and economically, DME synthesis is more profitable than methanol synthesis. Moreover, DME is relatively inert and non-toxic. In this study, steam reforming of DME was investigated over combined solid acid/Cu-based catalysts.

Cu/ZnO (CZ) and Cu/ZnO/Al₂O₃ (CZA) catalysts were prepared by coprecipitation (*cp*) [1]. ZSM-5, β-, Y-zeolites, Nb₂O₅, NbOPO₄, Nb₂O₅/Al₂O₃, and WO₃/Al₂O₃ were used as solid acid catalysts. The equal mass amounts of Cu-based catalyst and solid acid catalyst were used to test the effect of each catalyst component. Fig.1 shows the results of steam reforming of DME over CZA coupled with various solid acid catalysts. The reaction

proceeded via a successive two-steps mechanism: hydrolysis of DME to methanol over solid acids (Eq. 1), followed by steam reforming of methanol to produce H₂ and CO₂ over Cu-based catalysts (Eq. 2).



When HZSM-5(90) was used as solid acid catalyst, CZA (Cu/Zn/Al=45/45/10) showed higher H₂ production rate and DME conversion than those of CZ (Cu/Zn=50/50). This may be due to high Cu⁰ surface area of CZA. On NaZSM-5(90), no reaction took place, indicating an indispensable role of acid sites for DME steam reforming. The most preferable result was obtained over HZSM-5(90) coupled with CZA (45/45/10), on which high DME conversion as well as high rate of H₂ production was obtained. The rate of H₂ productions are poorly correlated with the amount of acid sites, suggesting that acid strength and hydrophobicity of solid acid catalysts are important for the effective DME steam reforming.

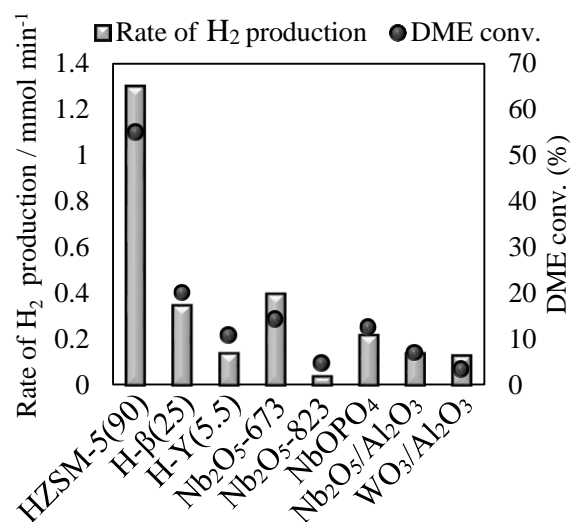


Fig.1 Effect of solid acid catalysts on the activity of steam reforming of DME over solid acid/CZA catalysts

The number in a parenthesis is SiO₂/Al₂O₃ ratio. Conditions: DME/H₂O/N₂=10/35/30, 100mg, 573K.

[1] a) T. Shishido, Y. Yamamoto, H. Morioka, K. Takaki, K. Takehira, *Appl. Catal. A-Gen.*, 263 (2004) 249. b) T. Kawabata, H. Matsuoka, T. Shishido, D.L. Li, Y. Tian, T. Sano, K. Takehira, *Appl. Catal. A-Gen.*, 308 (2006) 82