Quantitative Correlation Between the Acidity and the Catalytic Activity for the Methanol Dehydration

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Dimethyl ether (DME) has attracted much attention because it can be utilized as a fuel in a diesel engine through well-distributed LPG stations. Compared with a diesel fuel, DME can evolve the less amounts of air pollutants such as NO_x, SO_x and particulate matters. It can also be reformed to hydrogen at low temperatures for the fuel cell. Conventionally, DME can be produced through the dehydration of methanol. Other routes such as direct synthesis from CO and H_2 or CH_4 and steam have been sought. In any case, the incorporation of acid catalysts is indispensable for the DME synthesis. Until now, several sold acid catalysts such as Alumina, Silica-alumina, and Zeolites have been examined for this reaction. However, the quantitative correlation between the acidity and the catalytic activity has not been reported over a wide range of solid acid catalysts. In this work, we conducted the dehydration of methanol into DME over various solid acid catalysts such as g-Al_2O_3, Silica-alumina, H-ZSM-5, NaH-ZSM-5, Mordenite, H-Y and Beta. The amounts of acid sites and the acid strength were monitored with NH_3-TPD (temperature-programmed desorption).

NaH-ZSM-5 catalysts were prepared by impregnating $NaNO_3$ on H-ZSM-5 catalyst (Zeolyst, SiO_2/Al_2O_3 =23). The activity of each catalyst was examined using a fixed-bed reactor at the reaction pressure of 1 atm. The steady-state methanol conversion was obtained from 473 to 593 K. 11 vol% methanol in He was utilized as a feed and the gas hourly space velocity (GHSV) was 30000 h^{-1}. The effluent gas composition was analyzed with an on-line gas chromatography.

The catalytic activity increased over H-ZSM-5 with decreasing the ratio between SiO_2 and Al_2O_3 from 150 to 23. For all tested catalysts, the activity decreased in the following order: H-ZSM-5(23), H-Mor(20) > H-ZSM-5(30), H-Beta(18) > H-ZSM-5(60), g-Al2O3, H-Y(5.1) > H-ZSM-5(150), Silica-alumina. In the case of NaH-ZSM-5, the catalytic activity decreased with increasing amounts of Na on H-ZSM-5. The catalytic stability was also examined over H-ZSM-5(23), 25%Na-H-ZSM-5(23), and H-Mor(18) at 593 K. For all catalysts, the stable methanol conversion was observed. However, the amount of accumulated carbon was affected by the kinds of catalyst. The NaH-ZSM-5 showed the least amount of carbon formation during the stability test. The acidity of catalysts was measured with NH_3-TPD. For all TPD patterns, two peaks were observed at low and high temperature regions which can be assigned to weak and strong acid sites, respectively. The amount of strong acid sites appeared to be closely related to the catalytic activity for all solid acid catalysts. The general correlation plot can be made for all solid acid catalysts.