

# Notes

## Highly Water-Enhanced H-ZSM-5 Catalysts for Dehydration of Methanol to Dimethyl Ether

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Dimethyl ether (DME) has received attention as an alternative, clean diesel fuel due to its thermal efficiencies equivalent to traditional diesel fuel, lower NO<sub>x</sub> emission, near-zero smoke and less engine noise.<sup>1,2</sup> Consequently, the process of direct synthesis of DME from syngas has been investigated since Haldor Topsoe has developed a hybrid catalyst made of H-ZSM-5 and Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>.<sup>3,4</sup> The production of DME from CO<sub>2</sub> hydrogenation may provide the opportunity for a new CO<sub>2</sub> utilization technology. Compared with the process of DME production from syngas, CO<sub>2</sub> hydrogenation to DME requires the catalyst having high water-resistance because a large amount of water is produced in both methanol synthesis and reverse water gas shift reaction.<sup>5-8</sup> The objective of the present study is the evaluation of various zeolites for methanol dehydration to DME as part of the long-range goal of developing an integrated catalyst for producing DME directly from carbon dioxide and hydrogen. Water is believed to block the active sites for methanol consumption through competitive adsorption with methanol on the catalyst surface.<sup>2</sup> Therefore, it is necessary to develop the catalyst having a good resistance to the water produced from CO<sub>2</sub> hydrogenation or CO<sub>2</sub> rich syngas. Thus, we have investigated the water effect on catalytic dehydration of methanol to DME over  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and modified  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts to develop a suitable catalyst for one-step synthesis of DME from CO<sub>2</sub> hydrogenation.<sup>9</sup> However, these catalysts remarkably deactivated with the addition of water. To find out water-resistant methanol dehydration catalysts, therefore, we applied various zeolite catalysts as solid-acid catalysts to catalytic dehydration of methanol to DME. We report here that H-ZSM-5 catalysts have high water-resistance in methanol to DME reaction.

### Experimental Section

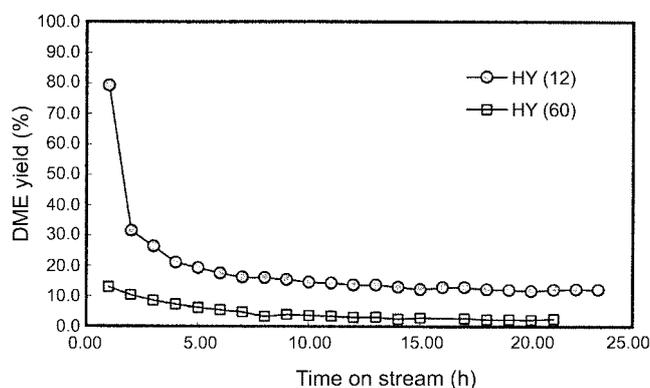
H-Y (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 12, 60) and H-ZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 30, 50, 80) were purchased from PQ Corporation. All the catalysts were calcined at 823 K for 4 h. Methanol dehydration was carried out in a fixed-bed reactor made of stainless steel tube.<sup>9</sup> Each catalyst (0.1 g, 50-70 mesh) mixed

with 1 g of quartz sand was loaded in the reactor. Before the reaction, the catalyst was activated in the stream of pure N<sub>2</sub> at 623 K for 4 h under atmospheric pressure. Reaction temperature was fixed at 523 K taking a typical methanol synthesis temperature. Methanol was introduced by a syringe pump. When a water effect was tested, water was also injected using a syringe pump. The products were analyzed by a gas chromatography equipped with thermal conductivity and flame ionization detectors. DME yield was defined as follows.

$$\text{DME yield} = \text{DME formed} / \text{CH}_3\text{OH fed} \quad (1)$$

### Results and Discussion

Methanol is dehydrated to form DME over acid-sites of zeolites. Figure 1 illustrates the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio effect on methanol dehydration over HY(x) zeolites. The value of x in HY(x) denotes the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of HY. HY(12) showed high initial activity, but quickly deactivated with time on stream. HY(60) showed very low yield from the first measurement. It is likely that HY(60) deactivated very rapidly within 1 h. In that case, the initial activity could not be measured correctly. Catalyst deactivation of HY zeolites



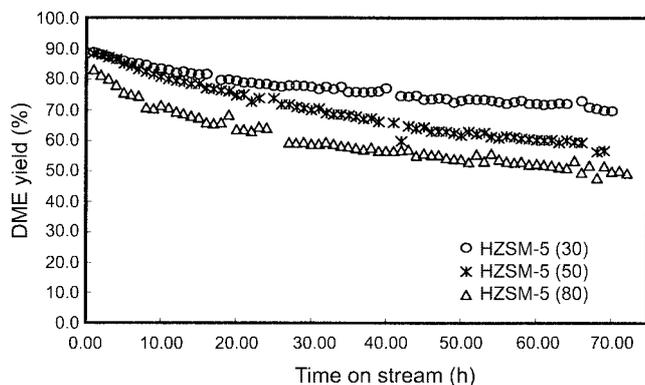
**Figure 1.** Stability test of HY zeolites (N<sub>2</sub> = 60 mL/min, P<sub>MeOH</sub> = 101.2 Torr, T = 523 K, catalyst loading = 0.1 g).

is due to the coke formation over strong acid sites resulting in the blockage of supercage. Strong acid sites are known to promote the polymerization of olefins and increase the rate of coke formation. Formation of coke on the catalyst surface subsequently blocks the active sites and shortens the lifetime of the catalyst. To survey the water effect on methanol dehydration over HY zeolites, water was added with methanol. However, addition of water could not regenerate HY zeolites. It is well known that coke formation on zeolites is a shape-selective process.<sup>10</sup> Under comparable conditions coke deposits much more slowly on medium-pore zeolites such as H-ZSM-5 than on large pore zeolites such as HY. Thus, It is most likely that the supercage of HY provides enough space for complete coking resulting in blocking the entrance of the supercage. As a result, water cannot enter the supercage of HY zeolites and has no opportunity to eliminate the carbon deposited on the active sites. As a consequence, catalyst deactivation of HY by carbon formation is irreversible.

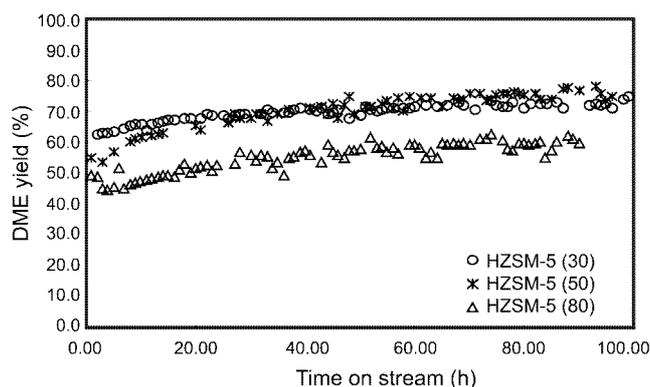
Unlike HY zeolites, ZSM-5 can be expected to inhibit coke formation in spite of the existence of strong acid-sites because there is no supercage. It can also be expected that ZSM-5 has water resistance due to hydrophobic properties resulting from high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio. Figure 2 shows catalytic dehydration of methanol over H-ZSM-5 catalysts having various  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios. H-ZSM-5 catalysts showed high catalytic activity, but slowly deactivated with time on stream. Methanol conversion increased with decreasing  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio, which may be due to the increase in the number of acid-sites with decreasing  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio.

In order to survey the water effect, water was injected simultaneously with methanol after the catalysts were used for 70 h. Figure 3 depicts methanol dehydration with water over H-ZSM-5 catalysts. Surprisingly, all H-ZSM-5 catalysts were regenerated by adding water. Furthermore, H-ZSM-5(30) and H-ZSM-5(50) reached almost equilibrium values in the condition that water and methanol were co-introduced. This is interpreted as the fact that water can remove the carbon deposited on the pore.

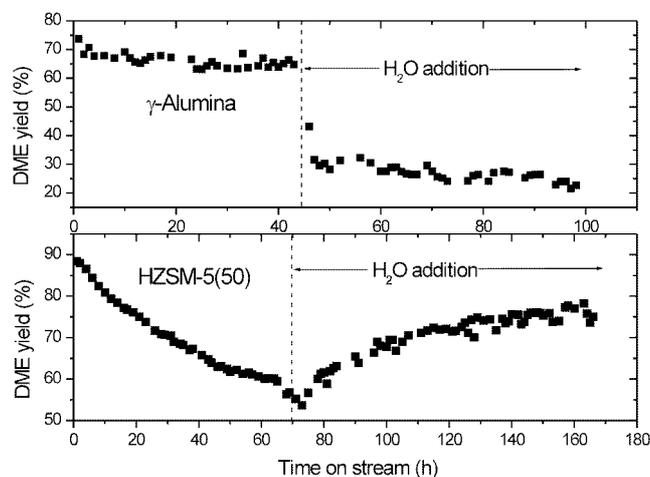
According to our previous results,<sup>9</sup> the activity of  $\gamma\text{-Al}_2\text{O}_3$  significantly decreased by the addition of water. Xu *et al.*<sup>2</sup> also reported that water has a poisoning effect on the



**Figure 2.** Stability test of H-ZSM-5 catalysts ( $\text{N}_2 = 60 \text{ mL/min}$ ,  $P_{\text{MeOH}} = 101.2 \text{ Torr}$ ,  $T = 523 \text{ K}$ , catalyst loading = 0.1 g).



**Figure 3.** The effect of water addition on methanol dehydration over H-ZSM-5 catalysts ( $\text{N}_2 = 60 \text{ mL/min}$ ,  $P_{\text{MeOH}} = 67.5 \text{ Torr}$ ,  $P_{\text{H}_2\text{O}} = 65.1 \text{ Torr}$ ;  $T = 523 \text{ K}$ , catalyst loading = 0.1 g).



**Figure 4.** Comparison of the effect of water addition over  $\gamma\text{-Al}_2\text{O}_3$  and H-ZSM-5 catalysts ( $\text{N}_2 = 60 \text{ mL/min}$ ,  $P_{\text{MeOH}} = 67.5 \text{ Torr}$ ,  $P_{\text{H}_2\text{O}} = 65.1 \text{ Torr}$ ;  $T = 523 \text{ K}$ , catalyst loading = 0.1 g).

catalytic activity for DME formation. Water molecules are known to preoccupy acid sites on catalyst and prevent methanol from being adsorbed onto the sites. Kinetic data confirms that the activation energy increases with the addition of water, possibly due to the blocking of the active sites by water. At high water coverage, the heat of water adsorption on  $\gamma\text{-Al}_2\text{O}_3$  is known to be approximately 16 kcal/mol,<sup>11</sup> consistent with the increase in activation energy for DME synthesis. Figure 4 shows the water effect on  $\gamma\text{-Al}_2\text{O}_3$  and H-ZSM-5 catalysts in order to compare both catalysts. In the case of  $\gamma\text{-Al}_2\text{O}_3$ , the catalyst was stable in the absence of water, but it rapidly deactivated with water addition. On the contrary, H-ZSM-5 catalyst was rather unstable in methanol dehydration without water, but it was very stable with co-feeding methanol and water. Therefore, it is promising that water has a positive effect on methanol dehydration over H-ZSM-5. Especially, in the case that DME is synthesized from  $\text{CO}_2$  and  $\text{H}_2$ , H-ZSM-5 can be the best candidate of catalyst because a large amount of water is formed during the reaction. Actually, we found that H-ZSM-5 catalysts were stable during DME synthesis from  $\text{CO}_2$  hydrogenation.<sup>8</sup>

### Conclusions

H-ZSM-5 catalysts show high initial activity but slowly deactivates with time on stream in methanol dehydration to DME. However, the catalysts can be regenerated by the addition of water resulting from removing carbon deposited on the catalysts. As a result, H-ZSM-5 can be considered as the best candidate for hybrid catalyst for the synthesis of DME from CO<sub>2</sub> and H<sub>2</sub>.

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