Catalytic Dehydration of Methanol to Dimethyl Ether (DME) over Solid-Acid Catalysts

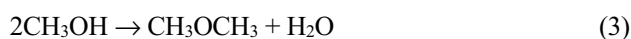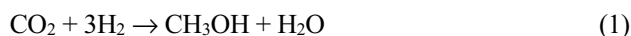**Ki-Won Jun,[*] Hye-Soon Lee, Hyun-Seog Roh, and Sang-Eon Park[*]**

Catalysis Center for Molecular Engineering, Korea Research Institute of Chemical Technology,
P.O. Box 107, Yuseong, Daejeon 305-600, Korea
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The conversion of methanol to dimethyl ether (DME) has been carried out over γ-alumina, silica-alumina, and modified γ-alumina catalysts. Especially, the water effect has been investigated on purpose to develop a suitable catalyst for one-step synthesis of DME from CO_2 hydrogenation. The γ-Al_2O_3 modified with 1 wt% silica is more active and less deactivated by water than unmodified one. CO_2 has no effect on catalytic dehydration of methanol to DME.

Keywords : Methanol, Dehydration, Dimethylether, Solid-acid catalyst.

Introduction

In recent years, DME has received attention as an alternative, clean diesel fuel because of its thermal efficiencies equivalent to traditional diesel fuel, lower NO_x emission, near-zero smoke and less engine noise.[1,2] DME is also used as a raw material for making chemicals and aerosol propellant such as hair spray, shaving cream to replace ozone-destroying chlorofluorocarbons (CFC).[2] Recently, the process of direct synthesis of DME from syngas has received much attention during twenty years and researchers at Haldor Topsoe have developed a hybrid catalyst by the addition of specially treated H-ZSM-5 to the traditional $Cu/ZnO/Al_2O_3$ methanol synthesis catalyst.[3,4] In contrast to the process of DME production from syngas, since CO_2 hydrogenation to DME produces a large amount of water in both methanol synthesis and CO synthesis (reaction 1, 2),[5-8] the water can deactivate the catalyst.

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \tag{1}$$

$$CO_2 + H_2 \rightarrow CO + H_2O \tag{2}$$

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \tag{3}$$

Xu *et al.* reported that most of the tested solid-acids deactivated in the presence of water during methanol to DME reaction.[2] Water is believed to block the active sites for methanol consumption through competitive adsorption with methanol on the catalyst surface.[2] Therefore, it is necessary to develop the catalyst having good resistance to the water produced from CO_2 hydrogenation or CO_2 rich syngas. The aim of the present study is to evaluate the various solid-acid catalysts to develop a suitable catalyst for one-step synthesis of dimethylether from CO_2 hydrogenation, especially stable for high partial pressure of water.

[*]To whom all correspondence should be addressed. e-mail: kwjun @krict.re.kr or separk@krict.re.kr

Experimental Section

Catalyst preparation. Two kinds of γ-alumina were used in this study. One was commercial-grade (strem chemicals, 97.7%) and the other was prepared by using Boehmite (CATAPAL-B). These alumina catalysts were calcined at 823 K under flowing dry air for 4 h. Commercial SiO_2-Al_2O_3 catalyst (Aldrich, 24 wt% SiO_2) was also used. Modified γ-Al_2O_3 catalysts were prepared by the impregnation method with the appropriate amount of H_3BO_4 (Shinyo pure chemicals, 99.5%), $ZrO(NO_3)_2 \cdot 6H_2O$ (Aldrich, 98%), and colloidal silica (Aldrich, 40 wt% SiO_2 solution), respectively. The resultant materials were dried at 393 K overnight followed by calcination in air at 823 K for 4 h.

Reactor system. Methanol dehydration was carried out in a fixed-bed reactor (8 mm inner diameter, 30 cm length) made of stainless steel tube. In a typical experiment, 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 a stream of pure N_2 at 623 K for 4 h under atmospheric pressure. Methanol was introduced by a syringe pump. The products were analyzed by a gas chromatography equipped with thermal conductivity and flame ionization detectors.

Results and Discussion

Characteristics. Table 1 summarizes the specific BET surface areas, pore volumes and pore diameters of the catalysts employed in this study. The prepared γ-Al_2O_3 has higher surface area than commercial one. The commercial γ-Al_2O_3 catalysts modified with B_2O_3, ZrO_2, or SiO_2 have somewhat lower BET surface areas than the original one. However, the modified γ-Al_2O_3 catalysts prepared using boehmite have relatively higher BET surface areas than the unmodified γ-Al_2O_3 catalyst prepared from boehmite. It was confirmed that all the γ-Al_2O_3 and modified γ-Al_2O_3 catalysts have the same XRD patterns.

Catalytic reaction. From the industrial point of view,

Table 1. The BET surface area of γ-alumina and modified γ-alumina catalysts

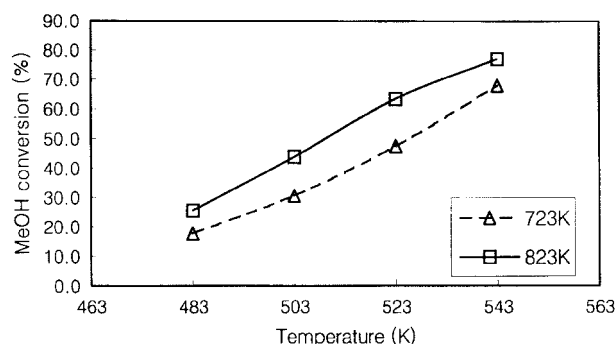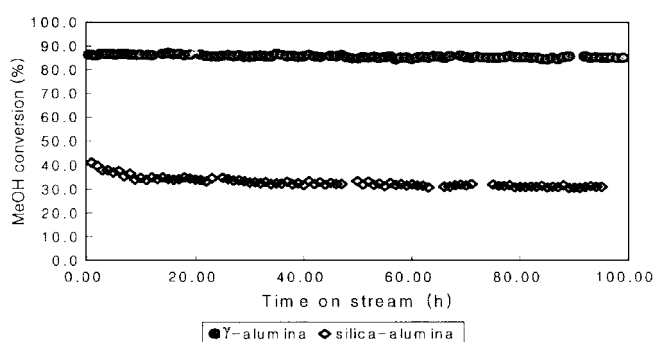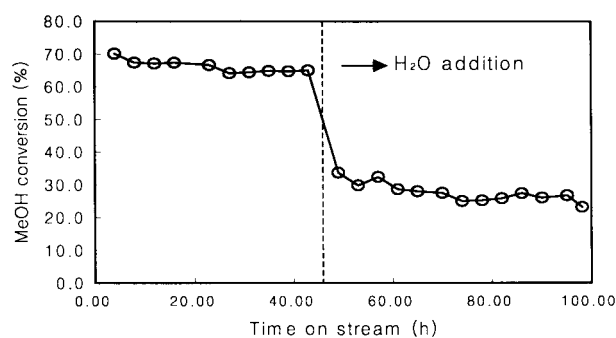| Catalyst	Surface area (m²/g)	Pore volume (cc/g)	Pore diameter (Å)
γ-Al₂O₃ (S)	161.5	0.478	118.3
γ-Al₂O₃ (B)	179.4	0.507	112.9
B₂O₃/γ-Al₂O₃ (S)	155.7	0.458	117.6
B₂O₃/γ-Al₂O₃ (B)	217.7	0.356	65.6
ZrO₂/γ-Al₂O₃ (S)	159.0	0.453	113.9
ZrO₂/γ-Al₂O₃ (B)	253.4	0.451	71.1
SiO₂/γ-Al₂O₃ (S)	160.3	0.475	118.6
SiO₂/γ-Al₂O₃ (B)	206.8	0.472	91.2

S: denotes commercial γ-Al₂O₃ purchased from Strem. B: denotes γ-Al₂O₃ prepared from Boehmite.
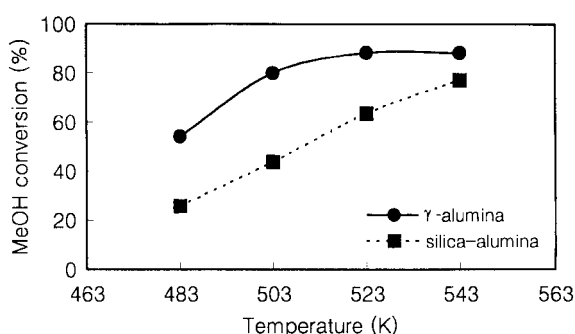
Figure 1. Methanol conversion *vs.* reaction temperature over γ-Al₂O₃ and SiO₂/Al₂O₃ (N₂ = 60 mL/min, P$_{MeOH}$ = 101.2 Torr, catalyst loading = 0.5 g).

Figure 2. The effect of calcination temperature on methanol dehydration over SiO₂/Al₂O₃ (N₂ = 60 mL/min, P$_{MeOH}$ = 101.2 Torr, catalyst loading = 0.5 g).

Figure 3. Catalytic stability test of γ-Al₂O₃ and SiO₂/Al₂O₃ (N₂ = 60 mL/min, P$_{MeOH}$ = 101.2 Torr, T = 523 K, catalyst loading = 0.5 g).

Figure 4. The effect of water on methanol dehydration over γ-Al₂O₃ (N₂ = 60 mL/min, P$_{MeOH}$ = 101.2 Torr without water; P$_{MeOH}$ = 67.5 Torr, P$_{H2O}$ = 65.1 Torr; T = 523 K, catalyst loading = 0.1 g).

γ-Al₂O₃ and SiO₂-Al₂O₃ are easily available among the solid-acid catalysts. Consequently, these two catalysts were employed in methanol dehydration reaction. Figure 1 shows the methanol dehydration reaction at different temperatures over γ-Al₂O₃ and 24 wt% SiO₂/Al₂O₃. The partial pressure of methanol was fixed at *ca*. 101.2 Torr. The methanol conversion increased with increasing temperature from 483 K to 543 K. In the case of commercial γ-Al₂O₃ catalyst, methanol conversion reaches the equilibrium value at 523 K.

It is well known that the acidity of SiO₂-Al₂O₃ depends on the calcination temperature. To investigate the effect of the calcination temperature, the reaction was conducted over commercial 24% SiO₂-Al₂O₃ catalysts at different calcination temperatures (Figure 2). It was confirmed that better activity was obtained at higher calcination temperature. This is possibly due to the change of both hydrophilicity and acidity. Generally, dehydroxylated SiO₂-Al₂O₃ becomes rather hydrophobic resulting in the decrease of sorption capacity of water.[2] Water blocks the active sites for methanol dehydration through competitive adsorption with methanol on the catalyst surface.[2] This is why the catalyst calcined at lower temperature showed lower activity. Besides, the high temperature calcination may change the strength of the acidity.

To test the stability with time on stream, methanol dehydration reaction was conducted over two commercial catalysts for 100 h. As shown in Figure 3, γ-Al₂O₃ exhibited stable activity for 100 h at 523 K. In the case of SiO₂-Al₂O₃,

methanol conversion slightly decreased in the initial stage, but the stable activity was maintained after 10 h. Xu *et al.*[2] reported that γ-Al₂O₃ showed an initial deactivation in the first 10 h. This result is different from ours. This is likely due to the difference in the kind of the commercial γ-Al₂O₃ catalysts used.

To survey the effect of water on the catalytic activity of γ-Al₂O₃, water was introduced to the reactant with the partial pressure of 65 Torr. As shown in Figure 4, the activity of γ-Al₂O₃ significantly decreased by the addition of water. These results are consistent with others. Xu *et al.* reported that water has a poisoning effect on the catalytic activity for
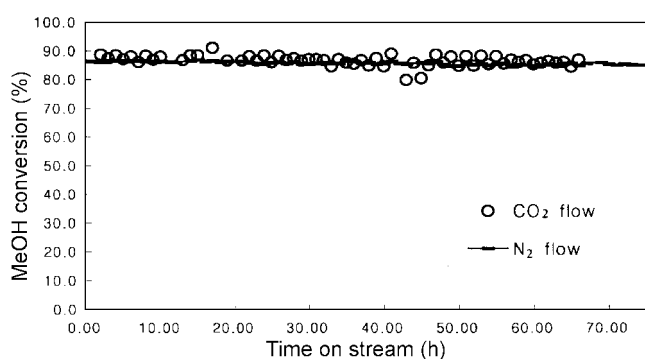
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Figure 5. The effect of CO_2 on methanol dehydration over γ-Al_2O_3 (N_2 = 60 mL/min, P_{MeOH} = 101.2 Torr, T = 523 K, catalyst loading = 0.5 g).

DME formation.[2] Water molecules seem to preoccupy acid sites on catalyst and prevent methanol from being adsorbed onto the sites. Lewis acid-site can be changed to Brönsted acid-site in the presence of water. It is also known that Brönsted acid-site on γ-Al_2O_3 is very weak.[9] Moreover, kinetic data confirm that 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 γ-Al_2O_3 is known to be approximately 16 kcal/mol,[10] consistent with the increase in activation energy for DME synthesis. In addition, when water is added to the reaction system, the equilibrium shifts backward. Therefore, the presence of large amount of water will clearly retard the methanol dehydration activity.

To investigate the effect of CO_2, a weak acid, on the catalytic activity of γ-Al_2O_3, CO_2 was used as a carrier gas instead of N_2. As shown in Figure 5, CO_2 has no effect on methanol dehydration over γ-Al_2O_3. This result suggests the absence of high basic, active sites on the surface, in good agreement with Xu *et al.*'s result.[2]

To see the effect of contact time, methanol dehydration reaction was carried out with the change of catalyst amount at 523 K. According to Figure 6, it is clear that γ-Al_2O_3 reaches the thermodynamic equilibrium above the catalyst amount of 0.5 g. In the presence of water (water pressure = 65 Torr), more than 1 g catalyst is necessary to reach the
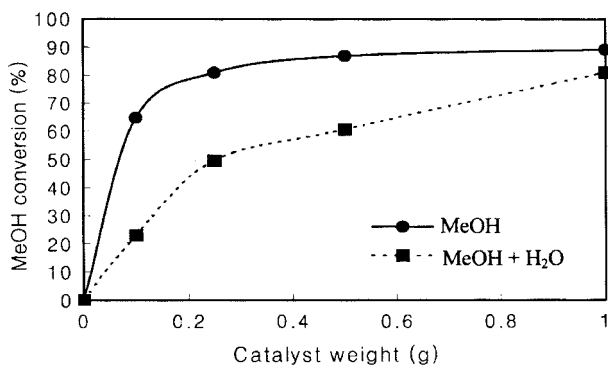
equilibrium conversion. In other words, methanol conversion increases with increasing the amount of catalyst and does not reach the equilibrium value in the presence of water. This suggests that the decrease of methanol conversion in the presence of water is not due to the equilibrium limit but mainly due to the catalyst deactivation.

According to the above results, it can be expected that the amount of water adsorbed should be decreased to achieve better activity over γ-Al_2O_3. Thus, γ-Al_2O_3 was *in-situ* pre-treated at 623 K for 4 h under N_2 atmosphere to remove the water adsorbed on the catalyst surface before the reaction. Temperature was fixed at 623 K because the temperature is the high limit allowable in DME synthesis, over which temperature the formation of hydrocarbons as by-products is inevitable. Table 2 summarizes the results. In the absence of water, the conversion of pretreated catalyst was 22% higher than that of untreated catalyst. Also in the presence of water, the conversion of pretreated catalyst was higher than that of untreated catalyst by 9%.

Modification of γ-Al_2O_3. To improve the catalytic performance, the commercial γ-Al_2O_3 was modified with B, Zr, and Si, respectively. The prepared γ-Al_2O_3 from Boehmite was also modified with the same component. Table 3 summarizes the activity comparison over various modified γ-Al_2O_3 catalysts. B_2O_3-modified catalysts showed rather lower activities but ZrO_2-modified catalysts showed almost similar performances in comparison with unmodified γ-Al_2O_3. However, SiO_2-modified catalysts showed better performance

Table 2. The effect of pretreatment on methanol dehydration over γ-alumina

	Methanol conversion (%)		Activity loss
	Without H_2O (A)	With H_2O (B)	1-B/A (%)
Pretreated* (C)	65.1	23.1	64.5
Untreated (D)	43.1	13.7	68.2
D/C (%)	66.2	59.3	

Conditions: N_2 flow rate = 60 mL/min, P_{MeOH} = 101.2 Torr (with H_2O addition: P_{MeOH} = 67.5 Torr, P_{H2O} = 65.1 Torr), catalyst loading = 0.1 g, T = 523 K. *in-situ* pretreatment at 623 K for 4 h under N_2 atmosphere.

Table 3. Methanol dehydration over γ-alumina and modified γ-alumina catalysts

Catalyst	Methanol conversion (%)	
	Without H_2O	With H_2O
γ-Al_2O_3 (S)	63.7	22.4
γ-Al_2O_3 (B)	60.4	22.2
5% ZrO_2/γ-Al_2O_3 (S)	60.3	20.5
5% ZrO_2/γ-Al_2O_3 (B)	62.8	19.5
5% B_2O_3/γ-Al_2O_3 (S)	49.1	20.7
5% B_2O_3/γ-Al_2O_3 (B)	50.4	15.5
5% SiO_2/γ-Al_2O_3 (S)	72.0	29.5
5% SiO_2/γ-Al_2O_3 (B)	69.7	22.7

Conditions: N_2 flow rate = 60 ml/min, P_{MeOH} = 101.2 Torr (with H_2O addition: P_{MeOH} = 67.5 Torr, P_{H2O} = 65.1 Torr), catalyst loading = 0.1 g, T = 523 K.

Figure 6. The effect of contact time on methanol dehydration over γ-Al_2O_3 (N_2 = 60 mL/min, P_{MeOH} = 101.2 Torr without water; P_{MeOH} = 67.5 Torr, P_{H2O} = 65.1 Torr; T = 523 K).

Table 4. Methanol dehydration over silica-modified γ-alumina catalysts

Catalyst	Methanol conversion (%)	
	Without H_2O	With H_2O
γ-Al$_2$O$_3$(S)	63.7	22.4
γ-Al$_2$O$_3$ (B)	60.4	22.2
1% SiO$_2$/γ-Al$_2$O$_3$ (S)	74.4	37.5
1% SiO$_2$/γ-Al$_2$O$_3$ (B)	70.0	28.4
5% SiO$_2$/γ-Al$_2$O$_3$ (S)	72.0	29.5
5% SiO$_2$/γ-Al$_2$O$_3$(B)	69.7	22.7
10% SiO$_2$/γ-Al$_2$O$_3$(S)	71.7	27.1
10% SiO$_2$/γ-Al$_2$O$_3$(B)	55.8	21.7

Conditions: N_2 flow rate = 60 mL/min, P_{MeOH} = 101.2 Torr (with H_2O addition: P_{MeOH} = 67.5 Torr, P_{H2O} = 65.1 Torr), catalyst loading = 0.1 g, T = 523 K.

than the untreated γ-Al$_2$O$_3$ in terms of methanol conversion and water resistance. Therefore, the effect of SiO$_2$ content was studied to find out the optimum SiO$_2$ content and the results are summarized in Table 4. Among the SiO$_2$modified γ-Al$_2$O$_3$ catalysts, 1 wt% SiO$_2$/γ-Al$_2$O$_3$ exhibited the best conversion irrespective of the presence of water. As a result, it was found that 1 wt% SiO$_2$/γ-Al$_2$O$_3$ has improved catalytic performance as well as water resistance.

Conclusions

The γ-Al$_2$O$_3$ catalyst is active and stable in methanol dehydration to DME. The presence of water significantly deactivates γ-Al$_2$O$_3$, possibly due to blocking the active sites by water. The catalytic performance of γ-Al$_2$O$_3$ can be improved by the pretreatment at high temperature in N_2 atmosphere by removing water adsorbed on the surface. CO_2 has no effect in catalytic dehydration of methanol. Among the modified γ-Al$_2$O$_3$ catalysts, SiO$_2$-modified catalyst shows the improved catalytic performance. Especially, 1 wt% SiO$_2$/γ-Al$_2$O$_3$ exhibits the best methanol conversion as well as improved water resistance.

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