Dehydration of Methanol to Dimethyl Ether over ZSM-5 Zeolite

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Methanol dehydration to dimethyl ether (DME) has been investigated over ZSM-5 zeolites and compared with that of γ-Al_2O_3. Although the catalytic activity was decreased with an increase in silica/alumina ratio, the DME selectivity increased. H-ZSM-5 and NaH-ZSM-5 zeolites were more active for conversion of methanol to DME than γ-Al_2O_3. Na^+ ion-exchanged H-ZSM-5 (NaH-ZSM-5) shows higher DME selectivity than H-ZSM-5 due to the selective removal of strong acid sites.

Key Words : Dehydration, DME, Methanol, ZSM-5 zeolite

Introduction

Dimethyl ether (DME) is a useful chemical intermediate for the preparation of many important chemicals, such as dimethyl sulfate and high-value oxygenated compounds.[1-3] Recently, it has received much attention as an alternative diesel fuel due to its low NO emission, near-zero smoke and less engine noise compared with those of traditional diesel fuels.[45] In addition, it has been used as an aerosol propellant to replace chlorofluoro carbonswhich can destroy the ozone layer of the atmosphere.[6] DME has been produced by catalytic dehydration of methanol over a solid-acid catalyst. As an alternating process, the direct synthesis of DME from syngas was proposed over bifunctional catalysts,[7] which had two kinds of active sites: one is for methanol formation and the other for methanol dehydration.[8] This process is more favorable in view of thermodynamics and economy.[9]

The process of methanol production from synthesis gas has been used successfully for several decades, and the reaction mechanism and the role of each active ingredient in catalyst have been well studied. In contrast to methanol synthesis, the catalytic dehydration of methanol to DME has received less attention. Woodhouse *et al*. patented that methanol dehydration takes place readily on pure or phosphoric acid modified Al_2O_3 catalysts;[10] however, water produced in the reaction process blocked active sites for methanol dehydration through competitive adsorption with methanol on catalyst surface.[4]

Concerning DME formation in methanol dehydration, different mechanisms have been proposed. Bandiera and Naccache[11] suggested the reaction of methanol occurs at the Brønsted acid and its adjacent Lewis basic sites with formation of the two surface species $[CH_3\cdot OH_2]^+$ and $[CH_3O]^-$ which upon condensation give DME and water. Kubelková *et al.*[12] reported that methanol is initially adsorbed at the zeolite. With transference of the zeolitic proton the methoxonium ion, $H_3COH_2^+$, is formed. This dehydrates leaving a methyl group bonded to the zeolite surface. Later on, those surface methoxy groups can react with another methanol molecule to form dimethyl ether. However, Blaszkowski *et al.* proposed that the two parallel reaction pathways for the production of DME are possible.[13]

In this paper we have studied the role of acid property in the methanol dehydration process. The purpose of the present study is to evaluate the H-ZSM-5 and modified H-ZSM-5 catalysts to develop a suitable catalyst for an integrated process of producing DME directly from syngas. For comparison, γ-Al_2O_3 catalyst also has been investigated.

Experimental Section

Catalyst preparation. γ-Al_2O_3 used commercial grade (Strem Chemicals, 99.7%). The ZSM-5 catalyts was obtained from P.Q Corporation. The ZSM-5 sample was supplied under ammonium form and transformed into the hydrogen form by calcining in flowing air at 823 K for 10 h with heating rate 10 K/min. H-ZSM-5 was treated with 1 M $NaNO_3$ at reflux, washed three times with de-ioned water, dried at 393 K for 2 h and then calcined in flowing air at 823 K for 10 h with heating rate 10 K/min to generate NaH-ZSM-5. The Na content was quantitatively analyzed by an atomic absorption spectrometer. The degree of ion exchange was 36% (H/Al = 0.64, Na/Al = 0.36).

Characterization of acidity. The strength and distribution of acid sites were tested by NH_3-TPD technique, which were performed on a conventional apparatus consisting of a cylindrical quartz micro-reactor, a vertical furnace and a thermal conductivity detector (TCD) of a DS-6200 gas chromatograph. Typically, a 0.1 g zeolite sample was placed

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in the fixed bed reactor of 1.5 cm thick bed and was heated up to 873 K with a temperature program of 10 K/min under He flow of 50-60 mL/min, and then the sample was further heated for 2 h at isothermal temperature. Adsorption of ammonia was carried out at 353 K for 10 min under atmospheric pressure. Prior to desorption, the samples were flushed with He for l h at 353 K to remove the physically adsorbed ammonia. Desorption of ammonia was done at a heating rate of 10 K min^{-1} from 353 K up to 873 K under a He flow (25 mL/min). The desorbed ammonia was detected by the TCD detector.

Reaction system. Methanol dehydration was carried out in a fixed-bed reactor (4 mm inner diameter, 30 cm length) made of stainless steel tube. In a typical experiment, each catalyst (0.2 g, 20-40 mesh) was loaded in the reactor. Before the reaction, the catalyst was activated in a stream of pure N_2 at 773 K for 4 h under atmospheric pressure. Methanol was injected by a syringe pump. The products were analyzed by a gas chromatography equipped with thermal conductivity and flame ionization detectors.

Results and Discussion

In Figure 1, the results of methanol dehydration to DME over different acid catalysts are presented. As shown in Figure 1(A), the activity of catalyst increases in the following sequence: H-ZSM-5(30) > NaH-ZSM-5(30) > γ-Al_2O_3. The value in bracket denotes the SiO_2/Al_2O_3 ratio. The conversion of methanol dehydration to DME over NaH-ZSM-5(30) zeolite almost didn't change with time on stream. However, the conversion of methanol over H-ZSM-5 decreased slightly in 500 min, which might be due to the coke formation over strong acid sites.[4] Although decreasing slightly at beginning, the conversion on γ-Al_2O_3 stabilized from 50 min. This indicates that water, which is one of reaction products, initially blocked the active sites on the surface of catalyst for methanol consumption.[4] The change of the DME selectivity with time on steam in methanol dehydration over several acid catalysts is illustrated in Figure 1(B). The DME selectivity over NaH-ZSM-5(30) catalyst did not change during 500 min. In cases of γ-Al_2O_3 and H-ZSM-5(30), DME selectivity decreased with time on stream, but the decreasing rate of DME selectivity over H-ZSM-5(30) was more steep than that over γ-Al_2O_3.

It should be noted that there are significant differences in conversion and selectivity between NaH-ZSM-5(30) and H-ZSM-5(30) catalysts. NaH-ZSM-5(30) obtained from H-ZSM-5(30) by performing ion exchange with aqueous $NaNO_3$ was found to have much reduced the number of acid sites and, especially, eliminated the strong acid sites (see Figure 3 and Table 1). Therefore, subsequent reactions of DME over strong acid sites to form light olefins were reduced by sodium ion exchange.[14] Thus, NaH-ZSM-5(30) gave a higher selectivity for DME.

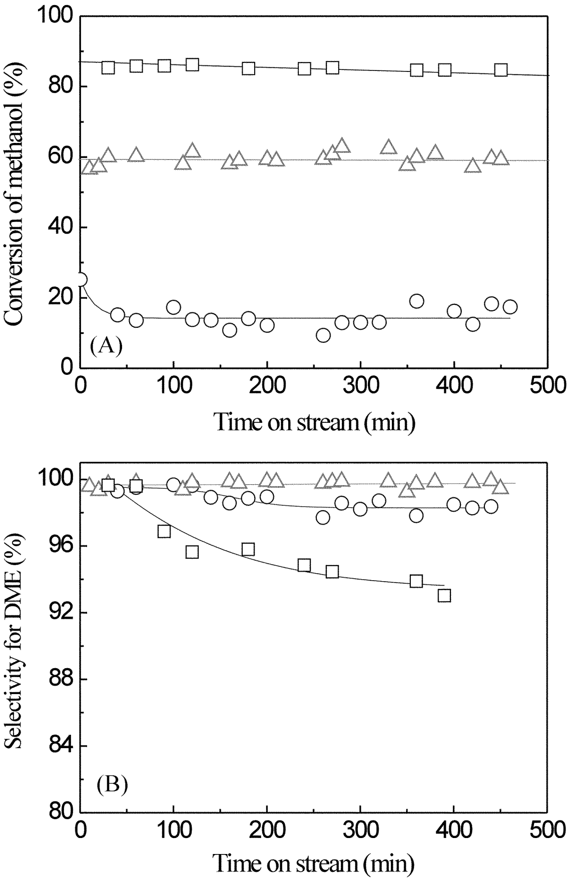

Figure 1. The results of methanol dehydration over various solid acid catalysts. (Catalyst loading = 0.2 g, 20-40 mesh; N_2 flow rate = 360 mL/h; WHSV = 4 h^{-1}; T = 523 K). (□) H-ZSM-5(30); (△) NaH-ZSM-5(30); (○) γ-Al_2O_3.

The influence of the reaction temperature against the conversion of methanol and selectivity for DME over acid catalysts is shown in Figure 2. The conversion over NaH-ZSM-5(30) catalyst increased with an increase in temperature from 473 K to 598 K. The conversion rather decreased at the higher temperature than 598 K. The deactivation of NaH-ZSM-5(30) could be ascribed to coke or water at high temperature.[5] Those results obtained over γ-Al_2O_3 was similar to those over NaH-ZSM-5(30), but the cause of deactivation was different with that for NaH-ZSM-5(30) catalyst. The decrease of methanol conversion over γ-Al_2O_3 at temperature beyond 598 K was due to reaching thermodynamically limiting regime at 598 K. Since the reaction of methanol dehydration to DME is exothermic, reaction equilibrium will move to left by further increasing of temperature. These reasons can also be applied to explain the results of H-ZSM-5(30).

H-ZSM-5(30) and NaH-ZSM-5(30) zeolite possess Lewis and Brönsted acid sites,[15,16] however, the former has stronger acidity and much more acid site density (see Figure 3 and Table 1). So H-ZSM-5(30) catalyst exhibits higher catalytic activity for methanol dehydration, compared to that of NaH-ZSM-5(30) zeolite. For example, a conversion level of 78% was achieved at temperature as low as 473 K and conversion of methanol reached thermodynamic equilibrium at 498 K. Unlike NaH-ZSM-5(30) zeolite, γ-Al_2O_3 exhibits only Lewis acidity,[15,16] Hence, it seemed that the catalytic activity

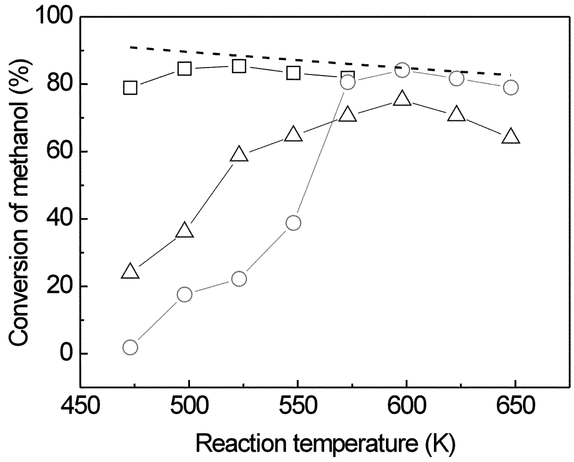

Figure 2 Effect of reaction temperature on methanol dehydration (Catalyst loading = 0.2 g, 20-40 mesh; N_2 flow rate = 360 mL/h; WHSV = 4 h^{-1}). (□) H-ZSM-5(30); (△) NaH-ZSM-5(30); (○) γ-Al_2O_3; (---) Equilibrium conversion.

of γ-Al_2O_3 in the case of high reaction temperature over 575K was significantly higher than that of NaH-ZSM-5(30), as shown in Figure 2.

Methanol dehydration is considered to occur on the acid sites of catalyst surface.[17] The properties of acid sites have been studied by NH_3-TPD and the results are shown in Figure 3 and Table 1. It can be noticed that for H-ZSM-5(30) catalyst two main bands can be observed around 460 K and 690 K, in good agreement with other previous reports.[18] However, there is only one peak appeared in the NH_3-TPD profile of γ-Al_2O_3 and NaH-ZSM-5(30). The area below the TPD curves, which indicates the total number of acid sites on the surface of catalyst, decreases in the order of H-ZSM-5(30) > NaH-ZSM-5(30) > γ-Al_2O_3. This fact is in good agreement with the activity sequence (Figure 1(A)). The peak center of NaH-ZSM-5(30) almost appear at same position as γ-Al_2O_3, indicating that these two catalysts has similar acid strength. On the other hand, the acid sites density of NaH-ZSM-5(30) is about two times higher than that of γ-Al_2O_3(Table 1). However, the dehydration activity of NaH-ZSM-5(30) is much higher than that of γ-Al_2O_3 (Figure 1(A)). It can be ascribed that water has a positive effect on methanol dehydration over NaH-ZSM-5 while a negative effect over γ-Al_2O_3.[4]

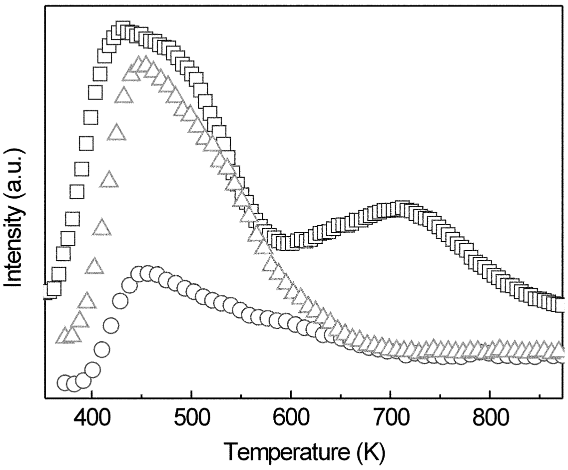

Figure 3. NH_3-TPD profiles of various solid acid catalysts (Samples were dried at 873 K for 2 h in He stream. NH_3 was adsorbed for 10 min. After desorption of physisorbed NH_3 at 353 K for 1 h, TPD was measured from 353 K to 873 K). (□) H-ZSM-5(30); (△) NaH-ZSM-5(30); (○) γ-Al_2O_3.

As mentioned above, acid property of catalyst has an apparent effect on methanol dehydration. And it is well known that H-ZSM-5 zeolite having different silica/alumina ratio possesses different acid property. Therefore, the catalytic dehydration of methanol over H-ZSM-5 catalysts having various SiO_2/Al_2O_3 ratios has been studied (depicted in Figure 4). H-ZSM-5(30) has been found to be the most active among these three catalysts, but it gave lower DME selectivity. H-ZSM-5(50) and H-ZSM-5(140) gave almost same catalytic activity and the DME selectivity (>99%), although they have so much different acid properties (See Figure 5).

The acidity of the three zeolites measured by NH_3-TPD is presented in Figure 5. The TPD profiles show two peaks at 460 K and 695 K, a high and a low temperature peak corresponding to strong and weak acid sites, respectively.[19] The area below the TPD curve decreased with increasing of SiO_2/Al_2O_3 ratio. It shows that the higher SiO_2/Al_2O_3 ratio H-ZSM-5 has, the lower total number of acid sites it possesses. It should be noted that LT (low temperature) and HT (high temperature) peak centers shift to low temperature synchronously as the SiO_2/Al_2O_3 ratio increases. The results indicate that an increase in SiO_2/Al_2O_3 ratio from 30 to 140 come to decrease the strength of both types of acid sites (weak and strong acid sites). Since zeolites having a higher SiO_2/Al_2O_3 ratio possess less strong acid sites, fewer DME dehydration to olefin generates on these zeolites.[18] As a result, it seems that the higher selectivity for DME is obtained.

Table 1. Results of the NH_3-TPD experiments

Catalyst	H-ZSM-5(30)		γ-Al_2O_3	NaH-ZSM-5(30)
Peak type*	LT	HT		
Temperature of peak center (K)	461	694	456	454
Area (a.u.) (×10^6)	6.58	2.87	3.01	6.98
Total area (a.u.) (×10^6)	9.45			

Note: Samples were dried at 873 K for 2 h in an He stream. NH_3 was adsorbed for 10 min. After desorption of physisorbed NH_3 at 353 K for 1 h, TPD was measured from 353 K to 873 K. *LT: Low temperature peak; HT: High temperature peak.

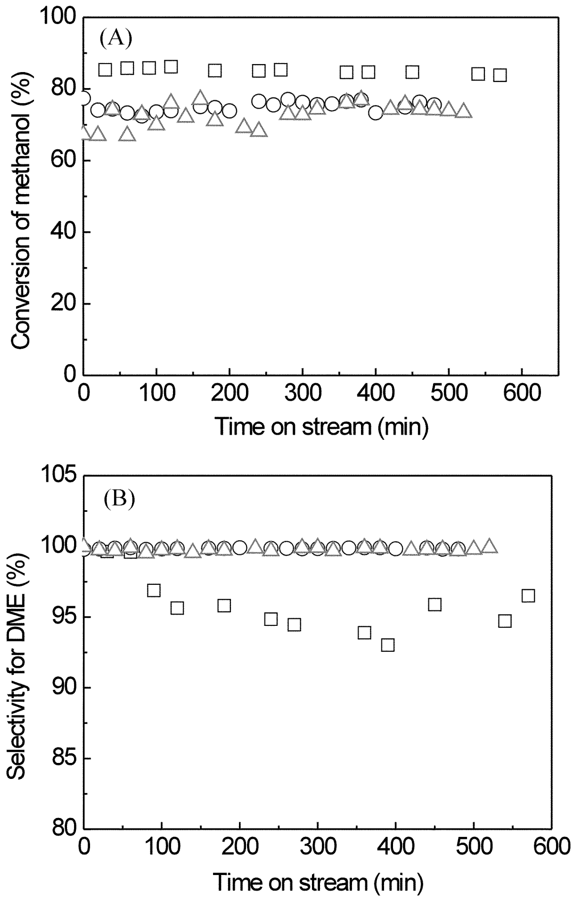

Figure 4. Effect of SiO_2/Al_2O_3 ratio of H-ZSM-5 on methanol dehydration. (Catalyst loading = 0.2 g, 20-40 mesh; N_2 flow rate = 360 mL/h; WHSV = 4 h^{-1}; T = 523 K). (□) H-ZSM-5(30); (○) H-ZSM-5(50); (△) H-ZSM-5(140).

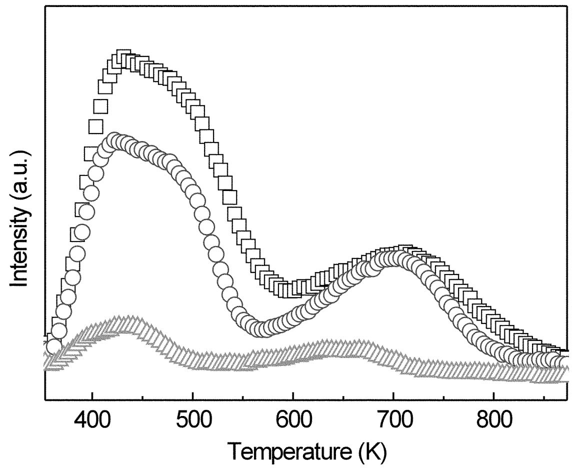

Figure 5. NH_3-TPD profiles of H-ZSM-5 zeolites (Samples were dried at 873 K for 2h in He stream. NH_3 was adsorbed for 10 min. After desorption of physisorbed NH_3 at 353 K for 1 h, TPD was measured from 353 K to 873 K). (□) H-ZSM-5(30); (○) H-ZSM-5(50); (△) H-ZSM-5(140).

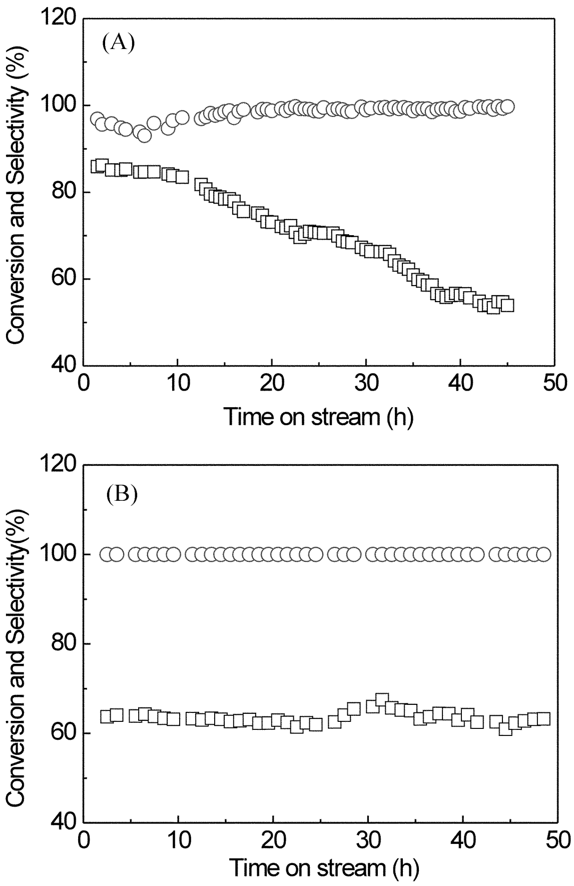

Figure 6. Methanol conversion and DME selectivity versus time on stream. (A) H-ZSM-5(30); (B) NaH-ZSM-5(30). (Catalyst loading = 0.2 g, 20-40 mesh; N_2 flow rate = 360 mL/h; WHSV = 4 h^{-1}; T = 523 K). (□) Conversion of methanol; (○) Selectivity for DME.

As discussed in previous part, Na^+ ion-exchange of H-ZSM-5(30) has a notable effect on its acidity. The methanol dehydration to DME is mainly controlled by acid sites of catalyst. Thus, it could be expected that stability of NaH-ZSM-5(30) was different from H-ZSM-5(30). Figure 6 shows the methanol conversion and selectivity for DME as a function of time on stream at 523 K. Catalyst NaH-ZSM-5(30) was indeed more stable than H-ZSM-5(30). The methanol conversion over H-ZSM-5(30) zeolite decreased from 86% to 72% during a dehydration period of *ca.* 20 h, while that over NaH-ZSM-5(30) decreased slightly. This might show that the deactivation probably due to coke more quickly over H-ZSM-5(30) than NaH-ZSM-5(30).

It should be noted that the DME selectivity over H-ZSM-5(30) was low in the initial time and soon reached a stable level. Initially, H-ZSM-5(30) has strong acid sites (see Figure 3), which catalyzed the DME to olefins.[14] Thus the DME selectivity was transiently decreased. With the reaction proceeding, coke deposition reduced the acidity on the surface of H-ZSM-5(30). Consequently the DME selectivity over H-ZSM-5(30) was recovered during 8 h. This results demonstrate that NaH-ZSM-5(30) is a promising catalyst for methanol dehydration to DME.

Conclusions

All the H-ZSM-5 catalysts in this study were active and selective for methanol dehydration to DME. NaH-ZSM-5 zeolite was moderately active and highly stable for methanol dehydration to DME, compared with γ-Al_2O_3. The catalytic activity was decreased with an increase in a silica/alumina ratio, whereas the DME selectivity was increased. H-ZSM-5 modified by Na^+ ion-exchange (NaH-ZSM-5) was found to have much reduced the number of acid sites and eliminated the strong acid sites especially. As a consequence, very robust DME catalyst can be developed by eliminating the strong acid sites of H-ZSM-5 zeolite, and moreover it can be achieved not only long-term stability but also the 100% DME selectivity.

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