Modification of H-ZSM-5 and γ-Alumina with Formaldehyde and Its Application to the Synthesis of Dimethyl Ether from Syn-gas

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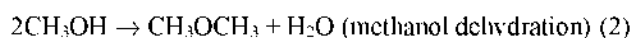
H-ZSM-5 and γ-alumina were treated with formaldehyde and sodium carbonate. The treatment increased the amounts of weak acid sites, removing strong acid sites. The maximum temperature of weak acid sites in their ammonia TPD spectra shifted in the direction of high temperature. The modified H-ZSM-5 and γ-alumina were mixed with the methanol synthesis catalyst to perform dimethyl ether synthesis from syn-gas. The modified catalysts showed better selectivity to dimethyl ether, minimizing the reforming reaction to carbon dioxide. The maximum yield of 53.3% to dimethyl ether was achieved under the reaction conditions of 54.4 atm, 523 K, and the feed rate of 4500 L·hr^{-1}·g$_{cat}$$^{-1}$.

Key words : Dimethyl ether, Syn-gas, H-ZSM-5, γ-Al$_2$O$_3$

Introduction

Modification of solid acids has been an issue from the viewpoint of both academic and industrial applications.[1-6] A typical acid catalyzed reaction, the synthesis of dimethyl ether from syn-gas, was investigated by the modification of solid acid with formaldehyde. Dimethyl ether has excellent properties for a propellant and a clean fuel as a diesel alternative.[7,8] The physical mixture of the methanol synthesis catalyst and the solid acid catalyst was used for the synthesis of dimethyl ether from syn-gas. H-ZSM-5 and γ-alumina have been employed as solid acids.[9-11] However, their strong acidity deteriorates the yield and selectivity to dimethyl ether because of the water reforming reaction of methanol/dimethyl ether producing carbon dioxide and hydrogen. The modification of these solid acids is a key step to maximize the yield and selectivity to dimethyl ether from syn-gas. Herein, we have developed an effective and convenient method to modify solid acids. The treatment of formaldehyde increased the amounts of weak acid sites of solid acid, removing strong acid sites. The modified H-ZSM-5 and γ-alumina with formaldehyde were applied to the methanol dehydration reaction to form dimethyl ether. The dimethyl ether was synthesized in a single step reaction from syn-gas in the presence of the hybrid catalyst of the methanol synthesis catalyst and the modified solid acid (Eq. 1, 2).[12]

$$CO + H_2 \rightarrow CH_3OH \qquad \text{(methanol synthesis)} \qquad (1)$$

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \text{ (methanol dehydration) } (2)$$

Experimental Section

Solid acids (2 g, alumina or H-ZSM-5) were placed in an

aqueous solution of Na$_2$CO$_3$ (1 N, 100 mL). Formaldehyde (8.4 mL, 37% solution) was added and stirred for 4 h at the room temperature. The solid acids were filtered and washed with distilled water until no Na$^+$ ion was extracted, and dried overnight at 423 K. For the ammonia TPD (Temperature-Programmed Desorption), the solid acid (500 mg) was placed in a quartz reactor and pretreated under the helium atmosphere at 773 K for 1 h. Ammonia gas was introduced to the reactor for 10 min after the catalyst bed temperature lowered to 473 K. The system was, then, purged with helium for 1 h at the same temperature of 473 K. The TPD spectra were obtained with the helium carrier gas (50 mL/min) at the heating rate of 10 K/min. The peak at m/e = 16 (the molecular peak of ammonia at m/e = 17 overlaps with the peak from water) was monitored by a quadupole mass detector (Balzers, MS-Cube 200). The hybrid catalysts were prepared by the mixing of a commercial methanol synthesis catalyst (CuO/ZnO/Al$_2$O$_3$ = 6 : 3 : 1) and solid acids (1 : 1 w/w). The hybrid catalysts (500 mg) were placed in a vertical fixed bed reactor (3/8 inch OD) and reduced by hydrogen (5% in helium) in situ at 523 K for 1.5 h. The one step dimethyl ether synthesis from syn-gas (CO : H$_2$ = 1 : 1.2) was performed under the reaction conditions of 54.4 atm, the feed rate of 4500 mL·hr^{-1}·g$_{cat}$$^{-1}$, and the temperatures of 523 K and 533 K. The reaction products were *in situ* analyzed by an on-line GC (Gow-Mac 600; FID detector, Carbosphere, 1/8 inch × 2 m; TCD detector, Porapak Q, 1/8 inch × 2 m).

Results and Discussion

The ammonia TPD experiment was performed to monitor the acid strength and the amounts of acid sites on the H-ZSM-5. As shown in Figure 1, the unmodified H-ZSM-5 showed typical ammonia TPD spectrum with two maximum peaks (1-2). The high temperature peak at 783 K was attributed to strong acid sites, and the one at 573 K to weak

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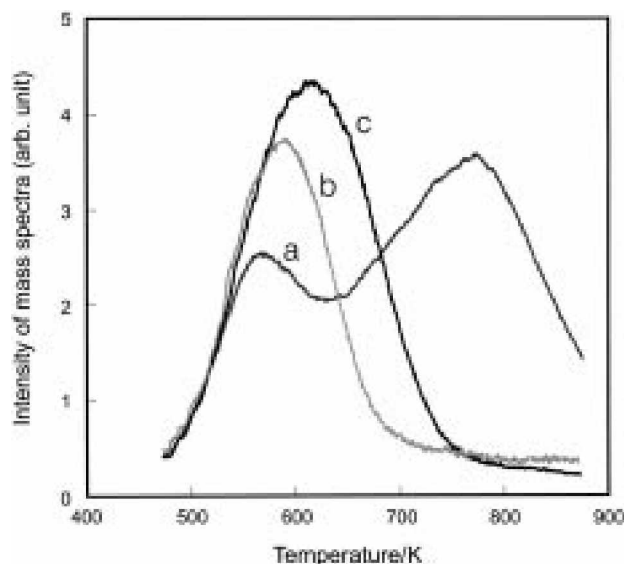
Figure 1. Ammonia TPD spectra on H-ZSM-5. a: without treatment. b: Na₂CO₃ treatment. c: formaldehyde + Na₂CO₃ treatment.

acid sites. The deconvolution of the TPD spectrum gave the area ratio of 210:633 (arbitrary unit) of the low and high temperature peaks.

With the treatment of formaldehyde and sodium carbonate. the high temperature peak completely disappeared. and the low temperature peak became larger (integration area from 210 to 626 in arbitrary unit) with the temperature shift of 56 K to the high temperature region. The TPD patterns showed that the strength and the amounts of acid sites were effectively modified by the treatment of formaldehyde. The treatment of sodium carbonate without formaldehyde removed the high temperature peak. too. The addition of formaldehyde with sodium carbonate. however. exhibited synergistic effects to maximize the amounts of weak acid sites on H-ZSM-5. The formaldehyde modified H-ZSM-5 was physically mixed with the copper-containing methanol-synthesis catalyst and applied to the formation of dimethyl ether from syn-gas (Table 1).

The major product on unmodified H-ZSM-5 was carbon dioxide. The water reforming reaction of methanol/dimethyl ether forming carbon dioxide and hydrogen would be a predominant reaction. The selectivity and yield to dimethyl ether were poor. 13.3 and 5.7%, respectively. Carbon dioxide was the only by-product. The low selectivity would be

attributed to the reforming reaction catalyzed by strong acid sites.

The treatment of formaldehyde and sodium carbonate eliminated the strong acid sites. increasing weak acid sites (Figure 1). The acidity modification did not affect the conversion of CO, which suggests that the CO conversion catalyzed by the copper-containing catalyst is the rate-determining step. After the formation of methanol. the acid catalyst catalyzed both dehydration to form dimethyl ether and water reforming reaction to form carbon dioxide and hydrogen. The selectivity to dimethyl ether increased from 13.3 to 59.7%, more than 4 times. and the yield of dimethyl ether increased from 5.7 to 26.7%. The elimination of strong acid sites minimized the reforming reaction. increasing the selectivity of dehydration reaction. The addition of sodium carbonate without formaldehyde also increased the yield of dimethyl ether as expected from the ammonia TPD experiment. Nonetheless. there was a good synergistic effect to maximize dimethyl ether production with the treatment of formaldehyde and sodium carbonate at the same time (32% yield increase). The reaction pattern at 533 K was similar to that of 523 K.

The effects of formaldehyde treatment were further monitored on γ-alumina. As shown in Figure 2. the γ-alumina had a low temperature peak as a major one with a small shoulder
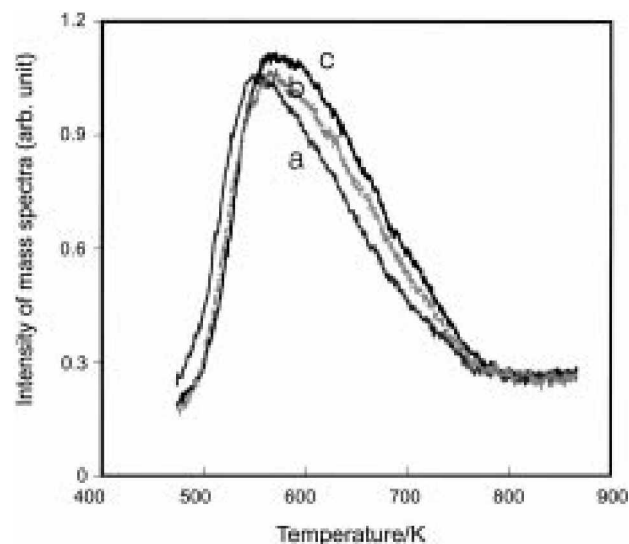

Figure 2. Ammonia TPD spectra on γ-alumina. a: without treatment. b: Na₂CO₃ treatment. c: formaldehyde + Na₂CO₃ treatment.

Table 1. Dimethyl ether synthesis from syn-gas. Reaction conditions: 54.4 atm, the feed rate of 4500 mL·hr⁻¹·g_cat⁻¹, CO : H₂ = 1 : 1.2, methanol-synthesis catalyst : H-ZSM-5 = 1 : 1 (w/w)

Reaction temp. (K)		Without treatment	Treatment with Na₂CO₃ only	Treatment with Na₂CO₃ + HCHO
523	conversion of CO (%)	42.8	34.0	41.5
	Selectivity of CH₃OCH₃ (%)	13.3	59.7	64.5
	yield of CH₃OCH₃ (%)	5.7	20.2	26.7
533	conversion of CO (%)	46.1	38.8	45.2
	selectivity of CH₃OCH₃ (%)	18.0	62.5	66.8
	yield of CH₃OCH₃ (%)	8.3	24.0	30.2

Table 2. Dimethyl ether synthesis from syn-gas. Reaction conditions: 54.4 atm, the feed rate of 4500 mL·hr^{-1}·g$_{cat}^{-1}$, CO : H$_2$ = 1 : 1.2, methanol synthesis catalyst: γ-alumina = 1 : 1 (w/w)

Reaction temp. (K)		Without treatment	Treatment with Na$_2$CO$_3$ only	Treatment with Na$_2$CO$_3$ + HCHO
523	conversion of CO (%)	52.8	53.0	67.0
	selectivity of CH$_3$OCH$_3$ (%)	64.1	66.0	79.5
	yield of CH$_3$OCH$_3$ (%)	33.8	34.8	53.3
533	conversion of CO (%)	49.3	48.8	61.1
	selectivity of CH$_3$OCH$_3$ (%)	63.6	66.9	78.6
	yield of CH$_3$OCH$_3$ (%)	31.1	32.06	48.4

at high temperature. The addition of formaldehyde increased the amounts of the weak acid sites on the γ-alumina. The integration of low temperature peaks showed 17% increase in the weak acid sites. The maximum peak was also 19 K shifted toward the higher temperature region as is the case with H-ZSM-5. The formaldehyde treatment changed the amounts of the weak acid sites and their acidity. The treatment of sodium carbonate gave only small change of temperature shift without the area change in the TPD spectrum. The treatment of other bases, such as NaOH or NH$_4$OH, gave the same modification effects as those of sodium carbonate. The same dimethyl ether synthesis reaction was performed with the modified g-alumina (Eq. 2, Table 2).

Similar to the reaction of H-ZSM-5, the selectivity increased from 64.1 to 79.5%. There was also a conversion increase from 52.8 to 67.0% with the formaldehyde treatment. As a result, the yield to dimethyl ether increased from 33.8 to 53.3%. The relative selectivity increment on the γ-alumina was smaller than that on the H-ZSM-5 due to the small amounts of strong acid sites on the untreated γ-alumina and a minor reforming reaction. Nevertheless, there was a conversion and yield increase. Because the amounts of weak acid sites on the γ-alumina were smaller than on the H-ZSM-5, the dehydration reaction might be a rate-determining step on the γ-alumina/copper-containing catalyst. The increment of weak acid sites could increase the overall reaction rate and the conversion of carbon monoxide. Meanwhile, the sodium carbonate treatment of the γ-alumina did not show any improvement on the conversion and the selectivity. Sodium carbonate treatment without formaldehyde did not give integration area change in the ammonia TPD spectra (Figure 2), which can be correlated to the similar reactivity of the treated and untreated g-alumina.

Conclusion

In summary, the formaldehyde treatment has modified the acidity of the H-ZSM-5 and the g-alumina, efficiently and conveniently. The maximum temperature of the weak acid

sites at the ammonia TPD spectra increased 56 K on the H-ZSM-5 and 19 K on the γ-alumina. The dehydration of methanol to form dimethyl ether was a typical acidity dependent reaction. The H-ZSM-5 exhibited a poor selectivity to dimethyl ether due to the reforming reaction catalyzed by strong acid sites. The formaldehyde treatment increased the amounts of weak acid sites and decreased those of strong acid sites, which effectively controlled the selectivity to dimethyl ether and increased the yield almost four times on the H-ZSM-5. The formaldehyde treatment on the γ-alumina increased acidity and amounts of weak acid sites, too. The excellent yield of dimethyl ether, 53.3%, was accomplished with the hybrid catalyst of the methanol-synthesis catalyst and the γ-alumina treated with formaldehyde.

References

1. Van Hooff, J. H. C.; Roelofsen, J. W. *Stud. Surf. Sci. Catal.* **1990**, *58*, 241.
2. Reschetilowski, W.; Unger, B.; Wendlandt, K. P. *J. Chem. Soc. Farad. Trans.* **1989**, *85*, 2941.
3. Woolery, G. L.; Kuehl, G. H.; Timken, H. C.; Chester, A. W. *Proc. 11th International Zeolite Conference*, RP 61, 1996.
4. Timken, H. C.; Kuehl, G. H. *Proc. 11th International Zeolite Conference*, RP 62, 1996.
5. Kwak, B. S.; Sachtler, W. M. H. *J. Catal.* **1994**, *145*, 456.
6. Mastoshi, N.; Kenji, K.; Shinzo, O. *Catal. Today* **1997**, *35*, 393.
7. Paul, K.; Herwig, O. *S.4E Technical Paper 950062*: 1995.
8. John, B. H.; Bodil, V.; Finn, J.; Inga, D. S. *S.4E Technical Paper 950063*; 1995.
9. James, J. S. *Chem. Eng. Comm.* **1991**, *110*, 123.
10. Li, J. L.; Zhang, X. G.; Inui, T. *Appl. Catal. A: General* **1996**, *147*, 23.
11. Allan, S.; Lyngby, J. R.; Rostrup-Nielsen, V. *U. S. Patent 4,520,216*, 1985.
12. Fujimoto, K.; Asami, K.; Shikada, T.; Tominaga, H. *Chem. Lett.* **1984**, 2051.