JOURNAL OF CATALYSIS **85**, 521–526 (1984)

Role of Acid Property of Various Zeolites in the Methanol Conversion to Hydrocarbons

INTRODUCTION

Methanol conversion to hydrocarbons has received much attention since the announcement of the Mobil process (*1*) which offers new hopes to overcome the energy shortage. Various studies on the mechanism have proposed reaction pathways via intermediates such as carbene (*2*), carbenium ion (*3*), and oxonium ion (*4*). Much of the studies have been concerned with the unique pore structure of ZSM-5, since the high performance of ZSM-5 for the conversion of methanol is believed to be attributable to shape selectivity owing to its pore structure (*5, 6*). In fact, little formation of coke deposit (*7*) and a different trend of product distribution on ZSM-5 (*8*), compared with mordenite, offretite, or H-L, etc., may be explained by the unique property of the structure of this zeolite. It is certain that the activity not only in the methanol conversion but also in other acid-catalyzed reactions can be modified by controlling the transport restriction of reactant or product (*9, 10*).

On the other hand, the role of the acid property of zeolites in the methanol conversion is relatively disregarded, although the acidity of ZSM-5 has been investigated using current techniques (*7, 11–13*). The authors have studied, however, H-mordenite and a series of cation-exchanged mordenite and observed the dependence of the activity and the product distribution on the acidic property (*14*). The acidity of zeolite, i.e., amount and strength of Brønsted acid sites, have been measured satisfactorily by the TPD of ammonia, as reported in the previous paper (*15*). Therefore, the purpose of the present study is to show in detail the correlation between the catalytic performance in the methanol conversion and the acidity of zeolites. It is of significance to know what extent of the activity of zeolite is controlled by the acidity.

EXPERIMENTAL

Materials. Zeolites used are the same as in the former study (*15*). H-mordenite, 100-H supplied by Norton Company, was modified by cation exchange and/or dealumination using the method previously described (*15*). Degree of cation exchange and SiO_2 to Al_2O_3 ratio are denoted by numbers in parenthesis next to alkali and zeolite species, respectively. A series of ZSM-5 was prepared according to the Mobil patent (*20*). Y-Type zeolites were obtained from Union Carbide, Linde division: NaY (SK-40) was ion-exchanged to HY as precisely described in (*15*), and NH_4NaY (SK-41) was used without further treatment.

Pulse method. Pulse method was used to examine the activity of zeolites for methanol conversion (*14*). Proceeding the measurement, the catalyst packed in a 4-mm-i.d. glass tube was heated up to 773 K and dehydrated for 3 h with helium flowing. Two microliters of methanol was then injected into the catalyst bed at 698 K. Products eluted from the reactor were once collected in the trap cooled at 77 K, and then flushed into GC through valves. Silicon OV 101 glass capillary column operating at temperatures ranging from room temperature to 180°C was used for separating products higher than C_4 hydrocarbons, while squalane on Al_2O_3 maintained at 60°C was used for products lower than C_5 hydrocarbons.

0021-9517/84 $3.00

RESULTS AND DISCUSSION

General Scope of Methanol Conversion

Typical results of methanol conversion on different types of zeolites are listed in Table 1, including that on HM which has been previously reported (*14*). Under this condition, methanol was completely converted into hydrocarbons. Recovery of hydrocarbons was more than 90% on all the cases. Product distribution, however, was dependent on the kind of zeolite. In the selectivities of C_4^- hydrocarbons (hydrocarbons with four or less carbons) which included paraffins as well as olefins, the former was found to be predominant on HM and DM (dealuminated HM), while on HZSM-5 and HY it was the latter. Selectivity to C_5^+ aliphatics (hydrocarbons with five or more carbons) on HZSM-5 was higher than those on other zeolites. It is remarkable, therefore, that the sum of C_5^+ hydrocarbons and aromatics, corresponding to gasoline fraction is highest on HZSM-5. The importance of HZSM-5 for gasoline production is thus confirmed.

TABLE 1

Activity and Product Distribution on Various Zeolites[a]

	Recovery of hydrocarbons (μmol)			
	HM	HY	HZSM-5(56)	DM(27)
	40.3	45.9	44.5	42.8
Distribution in hydrocarbon products (C%)[b]				
Paraffins	46.0	39.2	16.6	42.1
C_4^- Olefins	38.0	48.7	50.9	36.3
C_5^+ Aliphatics	1.5	7.0	19.7	6.2
Aromatics	14.5	5.1	12.7	15.4
Distribution in aromatics (C%)[b]				
A_6	1.4	3.0	5.6	2.6
A_7	7.6	11.1	15.8	7.8
A_8	17.3	24.4	52.0	13.0
A_9	23.4	33.1	22.8	16.2
A_{10}	28.3	20.2	3.4	21.4
A_{11}	21.4	7.3	0.4	31.2
A_{12}	0.7	1.0	0.0	7.8

[a] Experimental condition of the pulse experiment: catalyst weight, 20 mg; reaction temperature, 698 K; He gas flow rate, 40 cm^3/min; pulse size, 2 μl.

[b] Contained carbon as a percentage of that in the hydrocarbon products.

The selectivities to aromatics on HM, HZSM-5, and DM were similar, but much higher than on HY. Distribution in aromatics was, on the other hand, so much dependent on the type of zeolite. As pointed out previously (*1*), little formation of aromatics with more than 10 carbons was observed on HZSM-5, and about three-quarters of aromatics were fractions of A_8 (aromatics with 8 carbons) and A_9. On the other zeolites, however, aromatics distribution ranged up to large compounds such as A_{12}.

Dependence of the Activity on the Acidity

The conversion of methanol was 100% on the catalysts shown above, although it was lowered greatly by cation exchange. Product distribution was also changed greatly by the cation exchange as well as dealumination, as described below. In addition, it was found that not only the activity but also the product distribution of HZSM-5 zeolites was influenced by the ratio of SiO_2/Al_2O_3. In order to elucidate these reaction profiles, the activity was, at first, correlated with the acidity.

As described in the former study (*15*), acidity can be characterized by the TPD of ammonia. The spectra consisted of two peaks named *l* and *h* whose maximum temperatures (T_M) were located at about 430 and 680 K, respectively. It was verified that ammonia was adsorbed on and desorbed from the Brønsted acid sites of zeolites, although the TPD peaks were not identified in detail. The *l*-peak acid site was found to be of little importance to the reaction, because the KM and K(63)HZSM-5(56) with only *l*-peak sites possessed no activity in the methanol conversion. One can therefore regard the relatively strong acid sites as the active sites. The acidity of zeolites as characterized by the TPD of NH_3 was then used, since it effectively gave a quantitative evaluation of acid sites, and it is a practical method of acid measurement. One method would be to regard the whole of *h*-peak as active sites. However, it was rather difficult to resolve the spectrum particularly on HY zeolite because of overlapping of peaks. As has been previously reported (*15*), T_M of *h*-peak on HM shifted to lower temperatures with increasing degree of cation exchange. It shifted to about 300°C with the disappearance of the *h*-peak and simultaneously a complete loss of catalytic activity was observed. Thus, 300°C was set as the minimum desorbing temperature of NH_3 from active sites. In other words, the strong acid sites which were found active for methanol conversion are defined as the amount of NH_3 desorbed above 573 K.

The yield of hydrocarbon from methanol on various zeolites is plotted against the amount of strong acid sites as defined above (Fig. 1). The hydrocarbon yield increased linearly with increasing acid amount and attained 100% conversion at about 2.5 μmol of acid amount. However, further increase in the acid amount resulted in the decrease in hydrocarbon recovery. The decrease in the hydrocarbon yield seemed to be due to the coke deposit on the catalyst. Results on very small amount of catalyst such as HZSM-5(38) and HM maintained the relationship. One can therefore conclude that the activity of methanol conversion is well related with the amount of strong acid sites. Catalytic activity, irrespective of different structures, depends on a simple parameter such as the amount of strong acid.

Dependence of Product Distribution on Acid Amount

It has been reported in a previous paper that the product distribution on a series of partially ion-exchanged mordenites depends on the amount of Brønsted acid sites which was measured by ir spectroscopy (*14*). As in the former study, the products can be conveniently classified into the following groups: C_4^- paraffins, C_4^- olefins, C_5^+ hydrocarbons, and aromatic compounds. In the C_4^- olefins, however, ethylene was less reactive than propylene and butene as reactant (*14*). It has been already reported that the reactivity of ethylene is very small on HZSM-5, although acid bleaching can modify it greatly (*17*). Current study indicates that ethylene is produced from methanol not as a primary C_1 coupling product, but rather as a secondary

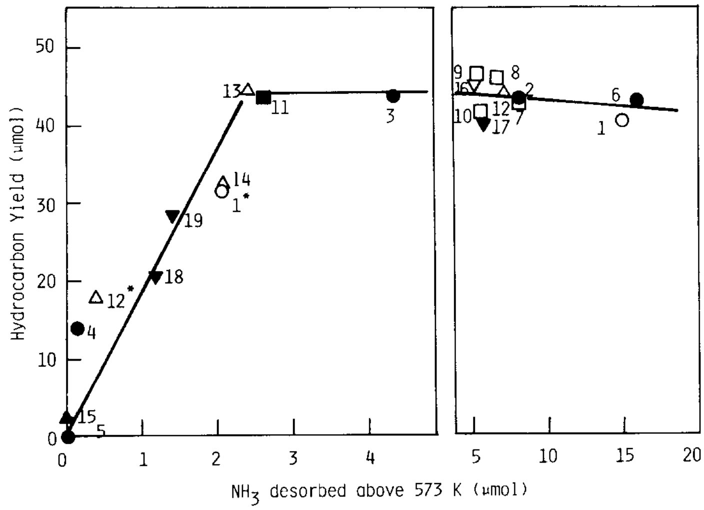

FIG. 1. Hydrocarbon yield against the amount of strong acid sites on mordenite (○), ZSM-5 (△), Y-zeolite (▽), dealuminated mordenite (□), and those cation-exchanged ones (shown as their corresponding closed symbols). Catalyst weight was 20 mg except for cases on HM (2.7 mg) and HZSM-5(38) (3.3 mg) marked by asterisk. Symbols are referred to in Fig. 2.

product derived from methyl attack on C_3^+ olefins (*18*). On the other hand, interconversion of propylene and butene has been confirmed (*14*), since using either olefin as starting material gave almost the same product distribution. These facts indicate the unique activity of ethylene in comparison with butene or propylene. Therefore, in the C_4^- olefins, propylene and butene selectivities were considered separately from that of ethylene.

Yield of hydrocarbons classified above is then plotted against the strong acid amount. Contrary trends were observed in C_5^+ aliphatics and C_4^- paraffins, as shown in Figs. 2 and 3, respectively. As the acid amount increased, the yield of C_5^+ decreased, while that of C_4^- increased. Furthermore, the relationship of C_5^+ hydrocarbons on cation-exchanged zeolites was slightly different from that of pure acid type zeolites except for NaHY.

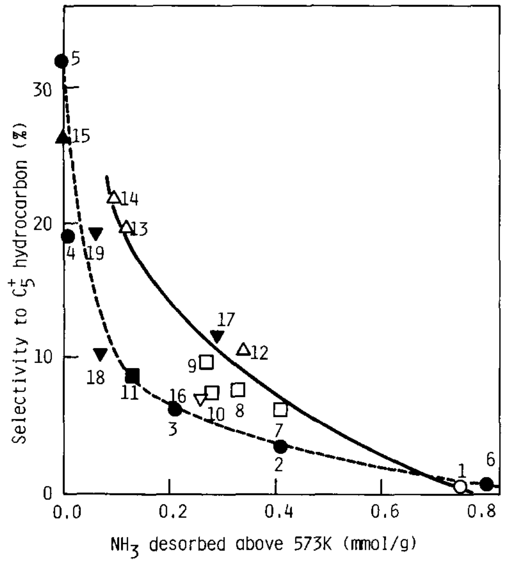

FIG. 2. Relationship of selectivity to C_5^+ hydrocarbons with the amount of strong acid sites on mordenite (○), ZSM-5 (△), Y-zeolite (▽), dealuminated mordenite (□), and those cation-exchanged ones (shown by their corresponding closed symbols and dashed line): (1) HM; (2) K(37)HM; (3) K(53)HM; (4) K(78)HM; (5) KM; (6) Ca(24)HM; (7) DM(27); (8) DM(36); (9) DM(66); (10) DM(71); (11) K(68)DM(27); (12) HZSM-5(38); (13) HZSM-5(56); (14) HZSM-5(103); (15) K(63)HZSM-5(56); (16) HY; (17) Na(17)HY; (18) K(25)HY; (19) Rb(25)HY.

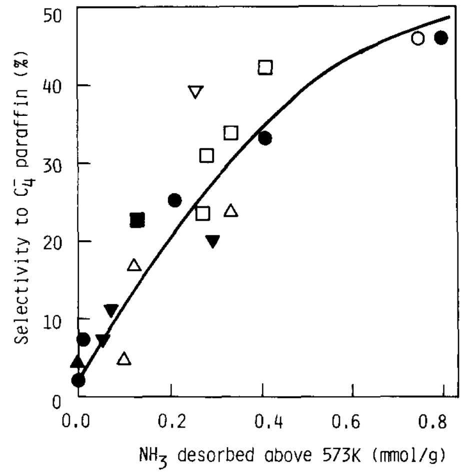

FIG. 3. Relationship of selectivity to C_4^- paraffins with the amount of strong acid sites. Symbols are referred to in Fig. 2.

Change of product distribution with acidity was observed also in the C_4^- olefins. Increase in the acid amount resulted in the increase of C_2' (ethylene), and inversely in the decrease of $C_3' + C_4'$ (propylene and butene), as shown in Fig. 4. It seems that results on various kinds of zeolites were well correlated with the amount of strong

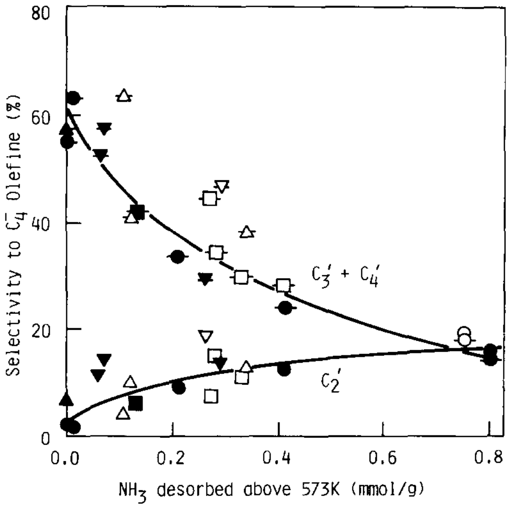

FIG. 4. Relationship of selectivity of ethylene (C_2') and to propylene and butene ($C_3' + C_4'$) with the amount of strong acid sites. Symbols are referred to in Fig. 2.

acid sites, although plots of ethylene selectivities on Y-zeolites deviated to some degree.

The relationship of aromatics yield with the amount of strong acid is shown in Fig. 5. The yield of cation-exchanged zeolites was much higher than on pure acid type zeolites. However, on either hydrogen or cation-exchanged zeolites, aromatics yield increased with increasing acid amount.

The aromatics yield was suppressed when the amount of strong acid sites was large. As mentioned above, formation of coke deposit resulted in the decrease in hydrocarbon yield at high acid amount. Therefore, such a decrease in aromatics yield can be attributed to coke formation. This is supported by the concept previously described that polymethylbenzenes are the intermediate compound in the formation of coke on the catalyst (*17*).

As shown above, product distribution on various kinds of zeolites was summarized as a function of the amount of strong acid. One can conclude that the product distribution is not dependent on the kind of zeolites, but rather on the amount of strong acid. It is of significance that the activities of various zeolites for the conversion of methanol are explained mainly by the acidity, although the structure and pore size of the zeolites used varied widely. In addition, the effect of cations such as K, Na, Ca, and Rb on the activity was found on the formations of C_5^+ hydrocarbons and aromatics. It appears that the decrease in the C_5^+ aliphatics yield due to the cation incorporation results in a corresponding increase in the aromatics yield. It has been reported that cation exchange such as zinc increased the aromatics fraction (*20*). It is, however, difficult at present to indicate the activity of such cations on this reaction.

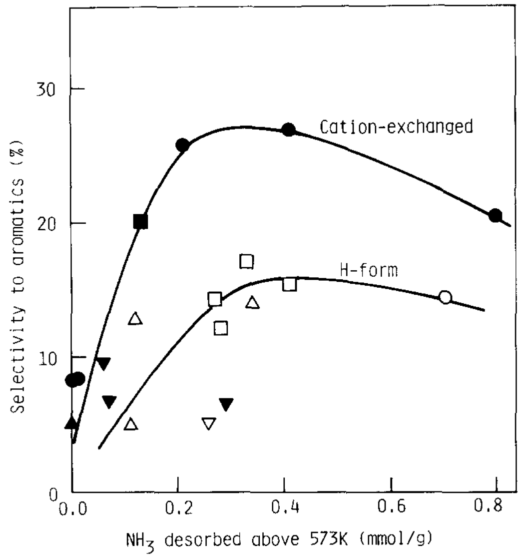

FIG. 5. Relationship of selectivity to aromatics with the amount of strong acid sites on H-form (open symbols) and ion-exchanged ones (closed symbols). Symbols are referred to in Fig. 2.

High performance of ZSM-5 type zeolite in MTG reaction has been understood by the shape selective property owing to the unique pore structure, which is effective in inhibiting the formation of coke and producing the gasoline-like product. As far as the present study is concerned, however, the major trend in the product distribution of zeolites, including ZSM-5, is not regulated by the pore dimension. The characteristics of Brønsted acid may have to be taken into consideration.

As mentioned above, one of the characteristics of ZSM-5 is its little formation of polyalkylbenzene. The portion of A_{10} to A_{12} in the aromatics was then plotted against the amount of strong acid, as shown in Fig. 6. Unlike the cases shown above, relationships were observed in each species of zeolite material. In the relationship the dealuminated mordenite was included in the mordenite. It was therefore confirmed that the formation of polyalkylbenzenes on ZSM-5 was much smaller than on HY and HM zeolites. Such a small formation of large molecules may be understood easily by the restriction of product elution due to pore dimension or steric restrictions of the transition states leading to such products. Because aromatics with 10 to 12 carbons are regarded to be intermediates of coke deposit, this also suggests the high resis-

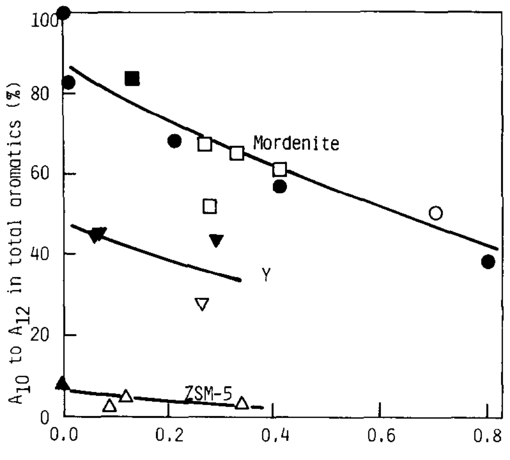

FIG. 6. Relationship of selectivity to A_{10} to A_{12} (aromatics with 10 to 12 carbons) in total aromatics with the amount of strong acid sites on mordenites, Y-zeolites, and ZSM-5. Symbols are referred to in Fig. 2.

tance of ZSM-5 to the loss of activity. After all, one can indicate that the ZSM-5 possesses the unique property incomparable to others only in the formation of large molecules such as polyalkylbenzenes.

CONCLUSION

The catalytic performance of various zeolites in methanol conversion was discussed in the light of acid property measured by the temperature-programmed desorption (TPD) of NH_3. The catalytic activity was found to be proportional to the amount of strong acid sites defined as the amount of NH_3 desorbed above 573 K. The product distribution also was well correlated with the amount of the strong acid sites. As the strong acid sites decreased, C_4^- paraffin, ethylene, and aromatics increased, while C_5^+ aliphatics and propylene and butene decreased. Alkaline ion-exchange resulted in the increase of C_5^+ aliphatics and aromatics. The peculiarity of ZSM-5 was observed only in lower selectivity to polyalkylbenzene due to shape selectivity.

REFERENCES

1. Meisel, S. L., McCullough, J. P., Lechthaler, C. H., and Weisz, P. B., *Chem. Tech.* **6**, 86 (1976).
2. Chang, C. D., and Silvestri, A. J., *J. Catal.* **47**, 249 (1977).
3. Dejaifve, P., Vedrine, J. C., Bolis, V., and Derouane, E. G., *J. Catal.* **63**, 331 (1980).
4. van den Berg, J. P., Wolthuizen, J. P., and van Hooff, J. H. C., *in* "Proceedings, 5th International Conference on Zeolites" (L. V. Rees, Ed.), p. 649. Heyden, London, 1980.
5. Weisz, P. B., *in* "Proceedings, 7th International Congress on Catalysis" (T. Seiyama and K. Tanabe, Eds.), p. 3. Kodasha, Tokyo, 1981.
6. Derouane, E. G., "Catalysis by Zeolites" (B. Imelik *et al.* Eds.), p. 5. Elsevier, Amsterdam, 1980.
7. Dejaifve, P., Auroux, A., Gravelle, C., Vedrine, J. C., Gabelica, Z., and Derouane, E. G., *J. Catal.* **70**, 123 (1981).
8. Langner, G., *Appl. Catal.* **2**, 289 (1982).
9. Chen, N. Y., Gorring, R. L., Ireland, H. R., and Stein, T. R., *Oil Gas J.* 165 (1977).
10. Kaeding, W. W., Chu, C., Young, L. B., and Butter, S. A., *J. Catal.* **69**, 392 (1981).
11. Vedrine, J. C., Auroux, A., Bolis, V., Dejaifve, P., Naccache, C., Wierzchowski, P., Derouane, E. G., Nagy, B., Gilson, J-P., van Hoof, J. H. C., van den Berg, J. P., Wolthuizen, J., *J. Catal.* **59**, 248 (1979).
12. Anderson, J. R., Foger, K., Mole, T., Rajadhyaksha, R. A., Sanders, J. V., *J. Catal.* **58**, 114 (1979).
13. Topsøe, N.-Y., Pedersen, K., and Derouane, E. G., *J. Catal.* **70**, 41 (1981).
14. Itoh, H., Hattori, T., and Murakami, Y., *Appl. Catal.* **2**, 19 (1982).
15. Hidalgo, C. V., Itoh, H., Hattori, T., Niwa, M., and Murakami, Y., *J. Catal.* **85**, 362 (1984).
16. Morrison, R. A., U.S. Patent, 3,953,366 (1976).
17. Rajadhyaksha, R. A., and Anderson, J. R., *J. Catal.* **63**, 510 (1980).
18. Dessau, R. M., LaPierre, P. B., *J. Catal.* **78**, 136 (1982).
19. Walsh, D. E., and Rollmanm, L. D., *J. Catal.* **56**, 195 (1979).
20. Plank, C. J., Rosinski, E. J., and Schwartz, A. B., U.S. Patent 1,402,981 (1975).

HIROFUMI ITOH
CARMELA V. HIDALGO
TADASHI HATTORI[1]
MIKI NIWA
YUICHI MURAKAMI

Department of Synthetic Chemistry
Faculty of Engineering
Nagoya University
Furo-cho, Chikusa-ku
Nagoya 464, Japan

Received March 4, 1983

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[1] To whom queries concerning this paper should be sent.