

Preparation and Acidic Properties of Aluminated ZSM-5 Zeolites

KOUJI YAMAGISHI, SEITARO NAMBA,¹ TATSUAKI YASHIMA*Department of Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152 Japan*

Received September 20, 1988; revised June 28, 1989

A reaction mechanism for the alumination of highly siliceous HZSM-5-type zeolites with AlCl_3 was proposed. The amount of aluminum introduced into the framework at 923 K leveled off at a reaction time of 1 h and a partial pressure of AlCl_3 of 11 kPa, and was independent of the number of terminal silanol groups and of the amount of silicon released from the zeolitic framework. From these results, it is concluded that the alumination proceeds not through the substitution of silicon by aluminum, but through the insertion of aluminum into the defect sites. The acidic properties of the aluminated HZSM-5 were examined by pyridine-IR spectroscopy. Strong acid sites including both Brønsted and Lewis acid sites were generated by the alumination. Aluminated HZSM-5 zeolites exhibit a higher activity per framework aluminum for octane cracking than do HZSM-5 zeolites. © 1990 Academic Press, Inc.

INTRODUCTION

It has been reported that aluminum atoms are introduced into the framework of highly siliceous ZSM-5-type zeolites by treatment with AlCl_3 vapor at elevated temperatures (1-5), and that not only Brønsted acid sites but also Lewis acid sites are generated by such aluminations (3-5). For the introduction of aluminum into the framework, two kinds of reaction mechanisms for the aluminations have been proposed. One is the reaction of hydroxyl groups, so called "hydroxyl nests," with AlCl_3 (1), and the other is the substitution of silicon in the framework by aluminum in AlCl_3 (3). We have discussed the mechanism for aluminations in a previous paper (5). The number of hydroxyl groups in the highly siliceous HZSM-5 decreased after dehydration at 1233 K for 6 h. When the HZSM-5 dehydrated at 1233 K for 6 h was treated with AlCl_3 at 623 K, aluminum atoms were not introduced into the framework sites. However, by aluminations at 923 K, aluminum atoms were introduced into the framework sites. On the other hand,

when the HZSM-5 dehydrated at 773 K for 4 h was treated with AlCl_3 at 623 K and 923 K, aluminum atoms were introduced into the framework sites. From these results, we concluded that at the lower temperatures, such as 623 K, aluminations proceed through the reaction of hydroxyl nests with AlCl_3 , whereas at the higher temperatures, such as 923 K, the aluminations proceed mainly through the substitution of silicon in the framework by aluminum from AlCl_3 .

Chang *et al.* have reported that the maximum rate of NH_3 evolution from the aluminated $\text{NH}_4\text{ZSM-5}$ in temperature-programmed desorption occurs at a temperature near that observed for $\text{NH}_4\text{ZSM-5}$ zeolites prepared in the conventional manner (1). Namely, the strength of acid sites on the aluminated HZSM-5 is comparable to that of the HZSM-5. However, we have reported that the very strong acid sites on the aluminated HZSM-5 are generated probably by the enhancement of the Brønsted acid sites with Lewis acid sites (4, 5).

In this study, we carried out the aluminations of the HZSM-5 under various reaction conditions. The aluminated HZSM-5 was examined by means of ^{27}Al -MAS NMR and IR measurements. From these obser-

¹ To whom correspondence should be addressed.

vations, we expect to discuss the reaction mechanism for the introduction of aluminum into the framework sites. We also discuss the acidic properties of the aluminated HZSM-5 in detail, and clarify differences in catalytic performance between the aluminated HZSM-5 and the HZSM-5 zeolites.

EXPERIMENTAL

Zeolite Samples

The protonic form of ZSM-5 type zeolites (Si/Al = 41–1260) was prepared by a conventional synthesis method (16). The ion exchange was a stringent treatment with 1 M HCl at 343 K for 48 h. Proton-exchanged samples were filtered and dried in air at 383 K for 16 h. In each aluminations, two kinds of parent HZSM-5 (Si/Al = 1260, 1060) were used.

Alumination of HZSM-5 with AlCl₃

In a standard aluminations, 4 g of the parent HZSM-5 powder was placed in a vertical quartz tube reactor and dehydrated for 4 h at 773 K in a stream of dry helium. The reaction temperature was then increased to the desired value (623–923 K) and the helium passed through a AlCl₃ container. The AlCl₃ container was heated to achieve the desired vapor pressure of AlCl₃. The gas line between the container and the reactor was maintained at 473 K to prevent vapor condensation. Treatment with AlCl₃ was maintained for the prescribed time (1–6 h) and was followed by purging of the sample with dry helium for a further 1 h to remove residual AlCl₃. The sample was then cooled to 298 K in the dry helium. The sample was rinsed twice in 500 dm³ of 0.05 M HCl, washed with a large amount of water, and then dried in air at 383 K for 16 h.

Elemental Analyses of Zeolites

The amount of bulk aluminum before and after the aluminations was determined by atomic absorption spectrophotometry. The

amounts of the framework aluminum of the aluminated HZSM-5 and HZSM-5 zeolites were determined from the ²⁷Al-MAS NMR (pulse length, 4.5 μs) spectra in a manner similar to that described by Derouane *et al.* (7). ²⁷Al-MAS NMR measurements were carried out at 70.3 MHz using a JEOL GX-270 Fourier transform spectrometer equipped with a magic-angle probe. Silicon released from the zeolitic framework was recovered by passing the effluent gas through 200 dm³ of 1 M NaOH. The amount of silicon was determined by atomic absorption spectrophotometry.

Infrared Studies

Infrared spectra were measured at 2 cm⁻¹ resolution on a IR-810 (JASCO) spectrometer. The infrared cell used was fitted with KBr windows and connected to a high-vacuum system. A 30-mg sample of the zeolite powder was accurately weighed and then pressed into a 15-mm-diameter, self-supported wafer. This wafer was placed in the IR cell and evacuated at 773 K for 1.5 h before the measurements. In the observation of pyridine adsorbed on zeolites, the wafer pre-evacuated at 773 K for 1.5 h was exposed to pyridine vapor (1.3 kPa) at 423 K for 0.5 h. The IR cell was evacuated at 423 K for 1 h, followed by desorption successively at 523, 623, 673, 723, and 773 K for 1 h in each case. All IR spectra were recorded at room temperature.

Catalytic Studies

Cracking of cumene and octane was carried out in a fixed-bed-type apparatus with a continuous-flow system at atmospheric pressure. The catalyst placed in a quartz reactor was dehydrated at 773 K for 1 h in a helium stream. The temperature was then brought to a reaction temperature (cumene: 573 K, octane: 673 K). To start the reaction, the reactant was fed into the catalyst bed with a microfeeder. Helium was used as a carrier gas. The reaction products were collected periodically with a cold trap and analyzed by gas chromatography.

TABLE 1

Bulk and Framework Aluminum Content and Specific Surface Area of the Parent HZSM-5 Zeolite and Aluminated HZSM-5 Zeolites

Sample	Alumination temperature (K)	Al concn ($10^{-4}/\text{mol g}^{-1}$)		Surface area ($\text{m}^2 \text{g}^{-1}$)
		Bulk ^a	Framework ^b	
1	(Parent)	0.1	0.1	524
2	623	3.4	0.3	498
3	723	3.1	0.5	491
4	823	3.2	0.8	480
5	923	5.7	2.0	463

^a Determined by atomic absorption spectrophotometry.

^b Determined by ²⁷Al-MAS NMR spectroscopy.

RESULTS AND DISCUSSION

Effect of Reaction Temperature on Aluminations

The effect of reaction temperature on the aluminations of HZSM-5 (Si/Al = 1260) at a partial pressure of AlCl₃ of 11 kPa and 2 h is shown in Table 1. The amount of aluminum introduced into the zeolitic framework increased with an increase in temperature. The bulk aluminum content was always much higher than the framework aluminum content. In the ²⁷Al-MAS NMR spectra, the parent HZSM-5 showed only an extremely weak peak at 53 ppm due to trace amounts of 4-coordinate aluminum in the framework sites (8). On the other hand, the aluminated HZSM-5 exhibited not only a strong peak at 53 ppm but also a broad peak at 0 ppm due to 6-coordinate aluminum in nonframework sites (8). These results indicate that aluminum is introduced not only into the framework sites but also into the non-framework sites by aluminations. This non-framework aluminum is present in a nonexchangeable form, because all aluminated samples were ion-exchanged with aqueous HCl. Each of these aluminated HZSM-5 was checked by powder X-ray diffraction for crystallinity. The crystallinity was uniformly good. Moreover, the change in surface area of these zeolites from that of the parent HZSM-5 by aluminations was slight. From these results, it was concluded that aluminated HZSM-5 samples having high

crystallinity were prepared by aluminations with AlCl₃.

Effect of Partial Pressure of AlCl₃ on Aluminations

The effect of partial pressure of AlCl₃ on aluminations of HZSM-5 (Si/Al = 1060) at 923 K and 1 h is shown in Fig. 1. At low partial pressures of AlCl₃, the amounts of bulk and the framework aluminum increased with increasing partial pressure of AlCl₃. However, they reached a constant value at partial pressures higher than 11 kPa. These facts indicate that the amount of aluminum introduced into the framework sites at 923 K for 1 h levels off at least for partial pressures of AlCl₃ of 11 kPa. The amount of silicon released from the zeolitic framework from the aluminations was measured. A blank test indicated that silicon did not come from the quartz reactor. The amount of silicon released from the framework increased with increasing partial pressure of AlCl₃. These results show that the amount of silicon released from the framework is independent of the amount of aluminum introduced into the framework.

Effect of Reaction Time on Aluminations

The effect of reaction time on the aluminations of HZSM-5 (Si/Al = 1060) at 923 K

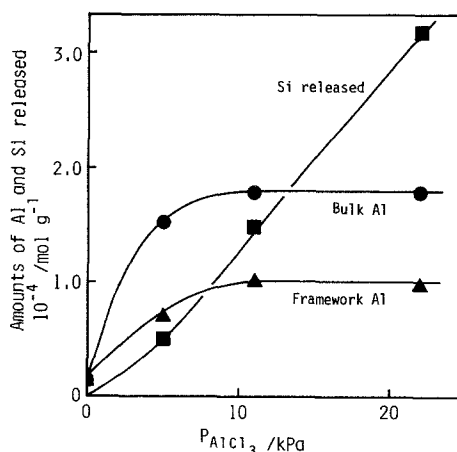


FIG. 1. Effect of partial pressure of AlCl₃ on aluminations: parent, HZSM-5 (Si/Al = 1060); reaction temperature, 923 K; reaction time, 1 h.

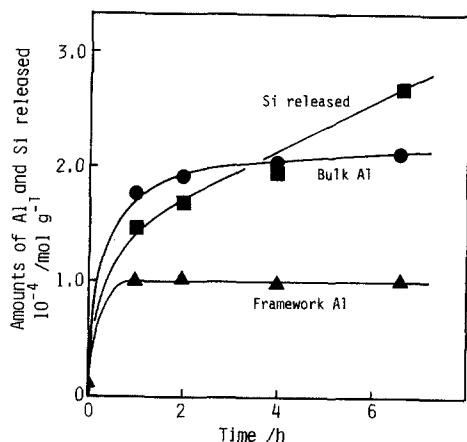


FIG. 2. Effect of reaction time on aluminations: parent, HZSM-5 (Si/Al = 1060); reaction temperature, 923 K; partial pressure of AlCl_3 , 11 kPa.

and a partial pressure of AlCl_3 of 11 kPa is shown in Fig. 2. The amount of bulk aluminum was always higher than that of framework aluminum, and slightly increased with increasing reaction time. However, the amount of framework aluminum leveled off within 1 h. Hence, the reaction, with respect to framework aluminum insertion, is complete at 923 K and a partial pressure of AlCl_3 of 11 kPa within 1 h. The amount of silicon released from the framework increased with increasing reaction time. These results show that the amount of silicon released from the framework is independent of the amount of aluminum introduced into the framework.

Mechanism of the Aluminations

If the mechanism of the aluminations is the substitution of silicon in the framework with aluminum from AlCl_3 , the following process is likely:

- i. The amount of silicon released from the zeolitic framework corresponds to the amount of aluminum introduced into the framework.
- ii. The amount of framework aluminum increases with increasing partial pressure of AlCl_3 and reaction time, because a large

number of silicon atoms are available for substitution into the framework.

As shown in Figs. 1 and 2, the amount of silicon released from the framework considerably increased with increasing partial pressure of AlCl_3 and reaction time. However, the amount of aluminum introduced into the framework sites at 923 K leveled off at a partial pressure of AlCl_3 of 11 kPa within 1 h. These results suggest that aluminum atoms could not be introduced as 4-coordinate species into the zeolitic framework sites where silicon was released. If the aluminations proceeded through the substitution of silicon in the framework with aluminum from AlCl_3 , a large number of silicon atoms would remain available for the substitution in the framework. However, the limiting amount of aluminum introduced into the framework is very small compared with the amount of silicon in the framework, i.e., Si/Al = 155. Consequently, it is suggested that the mechanism of the aluminations could not be substitution of silicon in the framework with aluminum from AlCl_3 .

The IR spectra for the parent HZSM-5 (Si/Al = 1260) and aluminated HZSM-5 zeolites in the hydroxyl stretching region are shown in Fig. 3. The highly siliceous parent HZSM-5 (Fig. 3a) showed only one band at 3740 cm^{-1} due to nonacidic hydroxyl groups (9). On the other hand, the aluminated HZSM-5 (Fig. 3b) exhibited a new band at 3610 cm^{-1} attributed to the framework $\text{Al}(\text{OH})\text{Si}$ groups responsible for Brønsted acid sites (9). These results show that aluminum atoms are introduced into the framework of highly siliceous HZSM-5 by aluminations. The IR spectrum for the aluminated sample which has not been rinsed with aqueous HCl is shown in Fig. 3c. The band at 3610 cm^{-1} responsible for Brønsted acid sites is not observed. The introduction of aluminum atoms into the zeolitic framework as 4-coordinate species results in negative framework charges. These are balanced by aluminum cations,

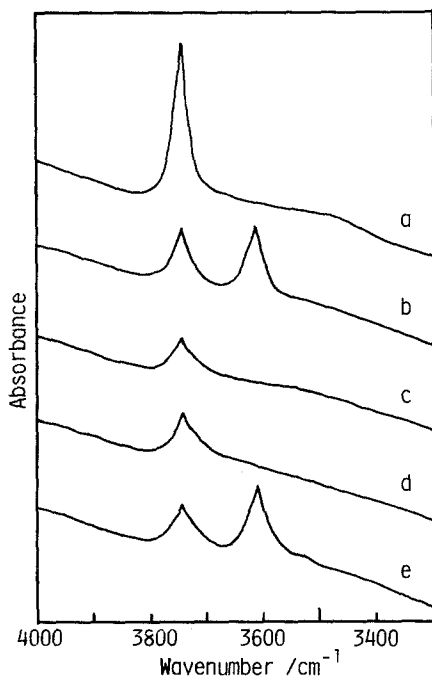


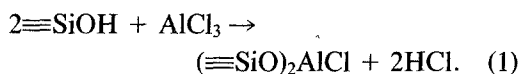
FIG. 3. Infrared spectra of parent and aluminated zeolites in the OH stretching region: (a) parent HZSM-5 (Si/Al = 1260), (b) HZSM-5 aluminated at 923 K for 2 h, (c) sample b which had not been rinsed with aqueous HCl, (d) parent HZSM-5 calcined at 1233 K for 6 h, (e) sample d aluminated at 923 K for 2 h.

perhaps as AlCl_2^+ , when the aluminated ZSM-5 has not been rinsed with aqueous HCl. When the aluminated ZSM-5 was rinsed with aqueous HCl, the band at 3610 cm^{-1} responsible for Brønsted acid sites appeared (Fig. 3b). These results suggest that Brønsted acid sites are formed by exchange of aluminum cations for protons.

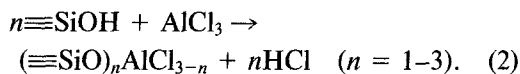
Because of the dehydration of the parent HZSM-5 at 1233 K for 6 h, the band at 3740 cm^{-1} , probably due to the terminal SiOH groups on the external surface, decreased markedly (Fig. 3d). As the number of the SiOH groups on the external surface is decreased by the dehydration at 1233 K for 6 h, the number in the hydroxyl nests is expected to decrease as well. When the HZSM-5 dehydrated at 1233 K for 6 h was treated with AlCl_3 , the intensity of the band at 3610 cm^{-1} for the aluminated sample was comparable to that in the case of the

aluminum of the parent HZSM-5 (Fig. 3e). Namely, in spite of the decrease in the number of hydroxyl nests, the results of the aluminated HZSM-5 dehydrated at 1233 K for 6 h were similar to those for the parent HZSM-5. It has been reported that the calcination changes SiOH groups in the HZSM-5 into lattice imperfections in the form of non-intact Si–O–Si bonds (10). Consequently, the SiOH groups in the hydroxyl nests could also be converted into lattice imperfections. From these results, we conclude that aluminum atoms can be introduced into the lattice imperfections as well as into the hydroxyl nests.

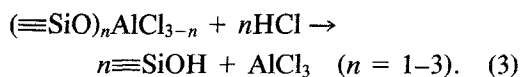
The present study provides a mechanism of the introduction of aluminum into non-framework sites as 6-coordinate species. By the aluminated at 923 K and 2 h, the amount of nonframework aluminum was 0.9–1.7 times as much as that of framework aluminum. A reaction of AlCl_3 with silica gel has been studied and shown to involve the surface hydroxyl groups according to (11)



As depicted in Fig. 3c, the band at 3740 cm^{-1} dramatically decreased by the aluminated. This observation is consistent with reaction of AlCl_3 with SiOH on the external surface, as shown in



When the aluminated sample has been rinsed with aqueous HCl, the amplitude of the band at 3740 cm^{-1} for the aluminated HZSM-5 (Fig. 3b) is larger than that of the aluminated sample which has not been rinsed with aqueous HCl (Fig. 3c). These observations indicate that a portion of the nonframework aluminum atoms has been removed by hydrolysis with aqueous HCl, as shown in



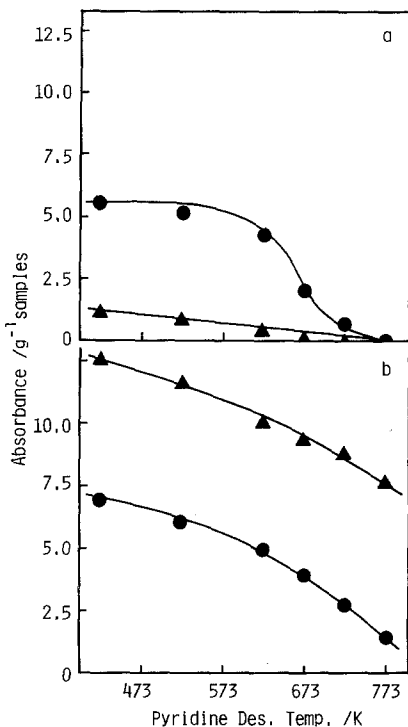
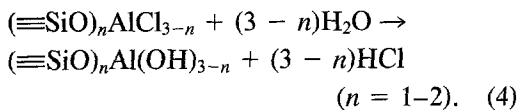


FIG. 4. Absorbance per gram of HZSM-5 (a) and aluminated HZSM-5 (b) on Lewis sites (LPy, band at 1455 cm^{-1} ; ●) and Brønsted sites (PyH^+ , band at 1545 cm^{-1} ; ▲) after desorption at 423, 523, 623, 673, 723, and 773 K.

The aluminum trichloride formed may be further hydrolyzed in aqueous HCl. We tried to determine the amount of residual chloride in the aluminated HZSM-5 which had been rinsed with aqueous HCl by Volhard's titration method (12). The residual chloride in the aluminated HZSM-5 was not detected. That is, the Cl/Al ratio was less than 0.01. This fact shows that non-framework aluminum species are hydrolyzed during the rinse with aqueous HCl, as depicted in



When the HZSM-5 dehydrated at 1233 K for 6 h was treated with AlCl_3 , the amounts of bulk and the framework aluminum were

comparable to those in the case of the aluminated parent HZSM-5. Namely, in spite of the considerable decrease in the SiOH on the external surface, the results of the aluminated HZSM-5 dehydrated at 1233 K for 6 h were similar to the results for the parent HZSM-5. Consequently, it is suggested that the introduction of aluminum atoms into the non-framework sites as 6-coordinate species proceeds not only through the reaction of the SiOH groups on the external surface but also through the reaction of the non-intact Si-O-Si bonds formed from the SiOH groups on the external surface.

In the mechanism of the aluminated, we conclude that the introduction of aluminum into the framework sites as 4-coordinate species proceeds through the reaction of the lattice imperfections (including the hydroxyl nests) with AlCl_3 , and that the introduction of aluminum into the non-framework sites as 6-coordinate species proceeds through the reaction of the SiOH groups on the external surface and/or the non-intact Si-O-Si bonds formed from the SiOH groups on the external surface.

Acidic Properties

The acidic properties of zeolites were characterized from infrared spectra of adsorbed pyridine. From IR spectra of pyridine adsorbed on zeolites, we can observe the absorption bands of pyridinium ion (PyH^+) at 1545 cm^{-1} and of the pyridine coordinated with Lewis acid sites (PyL) at 1455 cm^{-1} (13). The distribution of the acid strength of Brønsted and Lewis acid sites can be measured from the thermodesorption of pyridine. As the desorption temperature increases, only pyridine molecules adsorbed on stronger sites remain. Figure 4 shows the absorbances of the PyH^+ and PyL bands for HZSM-5 (having $1.7 \times 10^{-4}\text{ mol g}^{-1}$ framework aluminum) and for aluminated HZSM-5 (having $2.0 \times 10^{-4}\text{ mol g}^{-1}$ framework aluminum) after pyridine was desorbed at progressively

higher temperatures. The aluminated HZSM-5 has a large amount of Lewis acid sites. This is consistent with IR results of Anderson *et al.* (3). As shown in Fig. 4a, it is suggested that the strength of all Brønsted acid sites of the HZSM-5 is almost the same. On the other hand, as shown in Fig. 4b, it is apparent that both the weaker Brønsted and Lewis acid sites and the stronger Brønsted and Lewis acid sites exist in the aluminated HZSM-5, compared with those in the HZSM-5. Therefore, the strength distributions of Brønsted and Lewis acid sites of the aluminated HZSM-5 are wide. In particular, this study shows that very strong acid sites, not only Lewis acid sites but also Brønsted acid sites, can be generated by alumination.

It has been reported that the acid strength of Brønsted acid sites is enhanced by Lewis acid sites, when Lewis acid sites such as polymeric oxoaluminum species (AlO_p^+) are adjacent to Brønsted acid sites (14, 15). As depicted in Fig. 4, part of the aluminum introduced into the non-framework sites is responsible for Lewis acid sites. From these considerations, we conclude that the very strong Brønsted acid sites on the aluminated HZSM-5 are produced via the enhancement of Brønsted acid sites with the Lewis acid sites.

Moreover, the weaker Brønsted acid sites, compared with the HZSM-5, are generated by alumination at the same time. It has been conjectured that the acid strength of Brønsted acid sites in Y-type zeolite is weaker than that in a highly siliceous HZSM-5-type zeolite, because of the existence of next-nearest-neighbor aluminum (16). Therefore, we suggest that such next-nearest-neighbor aluminum in non-framework sites is generated by alumination.

These considerations show that both the weaker and the stronger Brønsted acid sites (compared with those in HZSM-5) are generated by alumination, because of the existence of Lewis acid sites as the non-framework aluminum species.

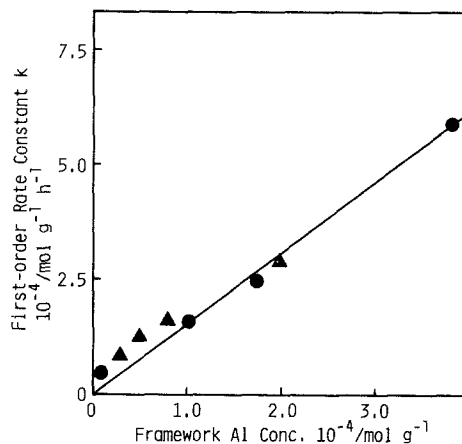


FIG. 5. Dependence of cumene cracking activity on framework aluminum content at 573 K: (●) HZSM-5, (▲) aluminated HZSM-5.

Catalytic Performance

Cumene cracking. Cumene cracking on HZSM-5 and aluminated HZSM-5 zeolites was examined. This reaction is generally believed to require Brønsted sites whose strength is at least medium. As shown in Fig. 5, if rate constant k is plotted versus framework aluminum content for the HZSM-5 series, a good linear relationship is revealed. This is in general agreement with the results of Chu *et al.* (17), who found alkylbenzene cracking activity to be proportional to framework aluminum content in HZSM-5. Data for the aluminated HZSM-5 series, as well as the HZSM-5, are almost fit by a common straight line. These facts indicate that the total activity of the aluminated HZSM-5, which has Brønsted acid sites with a wide distribution of strength for this reaction, is comparable with that of the HZSM-5.

Octane cracking. Octane cracking on the HZSM-5 and the aluminated HZSM-5 was examined. A linear relationship between the activity for cracking and the framework aluminum content in the case of the HZSM-5 series has been reported by Lago *et al.* for hexane cracking at 811 K (18) and by Namba *et al.* for octane cracking at 673 K

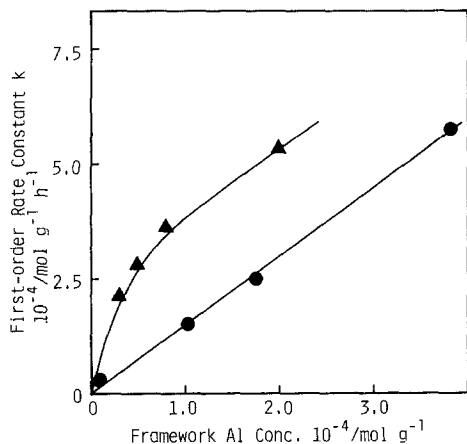


FIG. 6. Dependence of octane cracking activity on framework aluminum content at 673 K: (●) HZSM-5, (▲) aluminated HZSM-5.

(19). In the HZSM-5 zeolite series, there was a linear relationship between the activity for octane cracking and the framework aluminum content, as depicted in Fig. 6. On the other hand, the activity for octane cracking per one framework aluminum of the aluminated HZSM-5 was remarkably enhanced, compared with that for HZSM-5. The relationship found for aluminated HZSM-5 zeolites suggests the presence of enhanced or high-activity sites of the kind reported by Ashton *et al.* (20) and Lago *et al.* (18). They have explained that the reason for the activity enhancement is the existence of the strong Brønsted acid sites.

In conclusion, it is apparent that the total activity of the aluminated HZSM-5 for octane cracking is higher than that of the HZSM-5, while the total activity of the aluminated HZSM-5 for cumene is comparable to that of the HZSM-5. We cannot determine why the activity of the aluminated HZSM-5 for cumene is enhanced so slightly, while that for octane is substantially enhanced. However, these experimental data are shown in this paper, because the results are interesting in terms of the comparison between the catalytic ac-

tivities of the aluminated HZSM-5 and those of the HZSM-5.

ACKNOWLEDGMENTS

We thank Dr. Shinichi Nakata and Dr. Sachio Asaoka, R&D Center, Chiyoda Chemical Engineering & Construction Company Ltd., for ^{27}Al -MAS NMR measurements and for stimulating discussions. This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

REFERENCES

1. Chang, C. D., Chu, C. T.-W., Miale, J. N., Bridger, R. F., and Calvert, R. B., *J. Amer. Chem. Soc.* **106**, 8143 (1984).
2. Dessau, R. M., and Kerr, G. T., *Zeolites* **4**, 315 (1984).
3. Anderson, M. W., Kilinowski, J., and Xinsheng, L., *J. Chem. Soc. Chem. Commun.*, 1596 (1984).
4. Namba, S., Yamagishi, K., and Yashima, T., *Chem. Lett.*, 1109 (1987).
5. Yashima, T., Yamagishi, K., Namba, S., Nakata, S., and Asaoka, S., in "Innovation in Zeolite Materials Science" (P. J. Grobet *et al.*, Eds.), p. 175. Elsevier, Amsterdam, 1987.
6. Yashima, T., Sakaguchi, Y., and Namba, S., in "Proceedings, 7th International Congress on Catalysis" (T. Seiyama and K. Tanabe, Eds.), p. 739. Kodansha, Tokyo, 1981.
7. Derouane, E. G., Baltusis, L., Dessau, R. M., and Schmitt, K. D., in "Catalysis by Acids and Bases" (B. Imelik *et al.*, Eds.), p. 135. Elsevier, Amsterdam, 1985.
8. Thomas, J. M., and Klinowski, J., *Adv. Catal.* **33**, 200 (1985).
9. Jacobs, P. A., and von Ballmoos, R., *J. Phys. Chem.* **86**, 3050 (1982).
10. Hunger, M., Karger, J., Pfeifer, H., Caro, J., Zibrowius, B., Bulow, M., and Mostowicz, R., *J. Chem. Soc. Faraday Trans. 1* **83**, 3459 (1987).
11. Kopylov, B. V., Kol'tsov, S. I., Volkova, A. N., Smirnov, V. N., and Aleskovskii, V. D., *Izv. Vyssh. Ucheb. Zaved. Khim. Khim. Tekhnol.* **15**, 957 (1972).
12. Ayres, G. H., in "Quantitative Chemical Analysis," p. 388. John Weatherhill, Tokyo, 1964.
13. Parry, E. P., *J. Catal.* **2**, 371 (1963).
14. Olah, G. A., in "Friedel Crafts and Related Reactions," p. 879. Interscience, New York, 1963.
15. Mirodatos, C., and Barthomeuf, D., *J. Chem. Soc. Chem. Commun.*, 39 (1981).
16. Mikovsky, R. J., and Marshall, J. F., *J. Catal.* **44**, 170 (1976).
17. Chu, C. T.-W., Kuehl, G. H., Lago, R. M., and Chang, C. D., *J. Catal.* **93**, 451 (1985).

18. Lago, R. M., Haag, W. O., Mikovsky, R. J., Olson, D. H., Hellring, S. D., Schmitt, K. D., and Kerr, G. T., in "Proceedings, 7th International Zeolite Conference" (Y. Murakami *et al.*, Eds.), p. 677. Kodansha, Tokyo, 1986.
19. Namba, S., Sato, K., Fujita, K., Kim, J. H., and Yashima, T., in "Proceedings, 7th International Zeolite Conference" (Y. Murakami *et al.*, Eds.), p. 661. Kodansha, Tokyo, 1986.
20. Ashton, A. G., Batamanian, S., Clark, D. M., Dwyer, J., Fitch, F. R., Hincheliffe, A., and Machado, R. J., in "Catalysis by Acids and Bases" (B. Imelik *et al.*, Eds.), p. 101. Elsevier, Amsterdam, 1985.