

## Inhibition of Dealumination of ZSM-5 Zeolites by Alkali Metals

Kunio SUZUKI, Tsuneji SANNO,\* Hiroshi SHOJI,<sup>+</sup> Tohru MURAKAMI,<sup>++</sup>  
Shigeru IKAI,<sup>+++</sup> Shigemitsu SHIN, Hiroyuki HAGIWARA, and Haruo TAKAYA  
National Chemical Laboratory for Industry, Yatabe, Ibaraki 305

<sup>+</sup> Maruzen Petrochemical Co. Ltd., Hatchobori, Chuo-ku, Tokyo 104

<sup>++</sup> Nippon Petrochemical Co. Ltd., Uchisaiwai-cho, Chiyoda-ku, Tokyo 100

<sup>+++</sup> Ube Industries Co. Ltd., Kasumigaseki, Chiyoda-ku, Tokyo 100

Effect of alkali metal cations on dealumination of a framework of ZSM-5 zeolite with water was investigated by using <sup>27</sup>Al MASNMR and FT-IR. It was found that under the steaming conditions of 600 °C for 13.5 h, dealumination of the zeolite is quantitatively controlled by alkali metal cations introduced by an ion-exchange method, leaving framework aluminium in the concentrations nearly equal to those of the metal cations.

Dealumination is one of the most important practical problems in zeolite catalysts. There are many patents and literatures concerning dealumination of high aluminium zeolites such as Y-zeolite, A-zeolite and mordenite.<sup>1-3)</sup> It has been observed that the degree of dealumination of the zeolites is considerably lowered by an introduction of alkali and alkaline earth metal cations. Recently, we have found that highly siliceous ZSM-5 type zeolites containing alkaline earth metals have a high resistance against steaming.<sup>4)</sup> However, in these patents and literatures a relationship between the degree of dealumination and the concentrations of metal cations was stated in a qualitative way. Therefore, we have studied the effect of the concentration of alkali and alkaline earth metals introduced by an ion-exchange method on dealumination of ZSM-5 zeolites in more detail.

The H-ZSM-5 zeolite (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=66) was synthesized according to the procedure previously described.<sup>4)</sup> The zeolite obtained was confirmed to be highly crystalline and free of extraneous matter. Cation-exchanged forms were prepared by multitreating of the hydrogen forms with 0.01 - 1 M (1M= mol dm<sup>-3</sup>) aqueous solutions of the corresponding metal chlorides at 80 °C, followed by washing to remove the chloride ions. The degrees of ion-exchange were determined by atomic absorption spectrometry and X-Ray fluorescence spectrometry. The analytical data of the zeolites are summarized in Table 1. Steaming was carried out on 1.8 g of the charged zeolite (14 - 28 mesh) using an atmospheric pressure flow system at 600 °C for 13.5 h in stream of 100% steam. High resolution <sup>27</sup>Al NMR was measured at 51.9 MHz using a JEOL FX-200 Spectrometer equipped with a probe for magic angle spinning (MAS). The spectra were obtained for 0.33 g of the various zeolites in Delrin bullets spinning at about 3.5 kHz, using 4.6 μs pulses. The chemical shifts in ppm were obtained with respect to Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> as an external reference. The diffuse reflectance infrared spectra of the zeolites were measured at room temperature

using a Digilab FTS-60 Spectrometer equipped with an evacuable, heatable chamber. The powdered zeolites were placed in thin-walled ampules with a diameter of 8 mm and then evacuated to about  $10^{-6}$  Torr at 500 °C for 2 h. The spectra were taken at a  $2\text{ cm}^{-1}$  resolution for 1000 scans.

It is well known that the  $^{27}\text{Al}$  MASNMR spectrum of H-ZSM-5 zeolite has one peak at about 53 ppm assigned to framework (tetrahedrally coordinated) aluminium.<sup>5)</sup> In order to examine the effect of alkali and alkaline earth metal cations on dealumination, a variety of metal cation-exchanged ZSM-5 zeolites with various ion-exchange degrees were steamed at 600 °C for 13.5 h. Figure 1 shows the relationship between the degree of ion-exchange and the intensity ratio (x100) of the 53 ppm peak of the steamed zeolite to the corresponding unsteamed zeolite. Under the present steaming conditions, about 90% of the framework aluminium in the hydrogen form was dealuminated. In the case of alkali metal ion-exchanged forms as represented by a symbol O, there was a good correlation of the ion-exchange degree with the intensity ratio. It may be noted that the concentrations of framework aluminium in the zeolites after steaming do not depend upon the kind of the alkali metal cations but depend upon the degree of ion-exchange. That is to say, the concentrations of framework aluminium after steaming are nearly equal to those of alkali metal cations. We have previously found that a rate of dealumination of the hydrogen form is expressed as follows.<sup>6)</sup>

$$-dA/dt = k \cdot A^2 = k \cdot A \cdot H^+ \quad (1)$$

Table 1. Characteristics of Various Metal Cation-Exchanged ZSM-5 Zeolites

Sample No.	Metal cation	Metal/Al atom ratio	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> mole ratio
1 <sup>a)</sup>	(H <sup>+</sup> )		66
2	Li <sup>+</sup>	0.77	66
3	Na <sup>+</sup>	0.79	66
4	K <sup>+</sup>	0.20	66
5	K <sup>+</sup>	0.34	67
6	K <sup>+</sup>	0.90	67
7	Rb <sup>+</sup>	0.20	66
8	Rb <sup>+</sup>	0.37	66
9	Rb <sup>+</sup>	0.89	65
10	Cs <sup>+</sup>	0.37	67
11	Cs <sup>+</sup>	0.70	66
12	Cs <sup>+</sup>	0.94	66
13	Mg <sup>2+</sup>	0.15	66
14	Ca <sup>2+</sup>	0.22	66
15	Sr <sup>2+</sup>	0.37	67
16	Ba <sup>2+</sup>	0.37	66

a) BET surface area measured by using a method of single point N<sub>2</sub> adsorption at -196 °C is 379 m<sup>2</sup> g<sup>-1</sup>.

where A is a concentration of framework aluminium, t is a steaming time, k is a rate constant, and  $H^+$  is a concentration of acid. Therefore, the result that dealumination is quantitatively inhibited by the introduction of alkali metal cations can be understood from the decrease in the concentration of acid ( $H^+$ ) regardless of the location of alkali metal cations in the zeolite framework. Of course, it is quite plausible that under the present steaming conditions, the dealumination of framework aluminium, being bound by an alkali metal cation via an oxygen atom, is inhibited, while the dealumination of framework aluminium as expressed in the form  $Si(OH)Al$  takes place; however, the detailed study concerning the dealumination of ion-exchanged zeolites is now in progress. In the case of alkaline earth metal ion-exchanged forms as represented by a symbol  $\square$  in Fig. 1, the relationship between  $Mg^{2+}$  or  $Ca^{2+}/Al_2$  ratio and the intensity ratio of the 53 ppm peak is in accord with that in the case of alkali metal ion-exchanged forms.

Figure 2 shows the diffuse reflectance FT-IR spectra of hydroxyl groups of the hydrogen forms and the alkali metal ion-exchanged forms before and after steaming. The spectra of the steamed zeolites followed by treating with 0.6 M HCl at room temperature are also shown in Fig. 2. As has already been reported,<sup>7)</sup> the spectrum of H-ZSM-5 zeolite was characterized by two well-defined peaks at 3605 and 3730-3740  $cm^{-1}$ . The low-frequency hydroxyl has been assigned to an acidic bridged OH of  $Si(OH)Al$ , while the high-frequency hydroxyl to terminal SiOH or extraframework silica gel. The broad peak at near 3500  $cm^{-1}$  is attributed to hydrogen bonding adjacent hydroxyl groups. The peak intensity at 3605  $cm^{-1}$  in the spectrum of the hydrogen form after steaming remarkably decreased and hardly changed even by HCl treatment. On the other hand, in the spectrum of  $K^+$  (or  $Cs^+$ ) ion-exchanged form after steaming, the peak at 3605  $cm^{-1}$  was hardly observed. However, it was observed by HCl treatment. These FT-IR data definitely indicate that the dealumination of the framework aluminium only as expressed in  $Si(OH)Al$  proceeds under the present steaming conditions and the dealumination of the framework aluminium in  $Si(OM)Al$  (M:alkali metal) is inhibited. As it is considered that four SiOH are created by a removal of one framework aluminium atom, an increase in the peak intensity at 3740  $cm^{-1}$  would be presumed. However, the peak intensities before and after steaming for both the hydrogen form and the ion-exchanged forms were not different. These results indicate that the steaming causes not only the

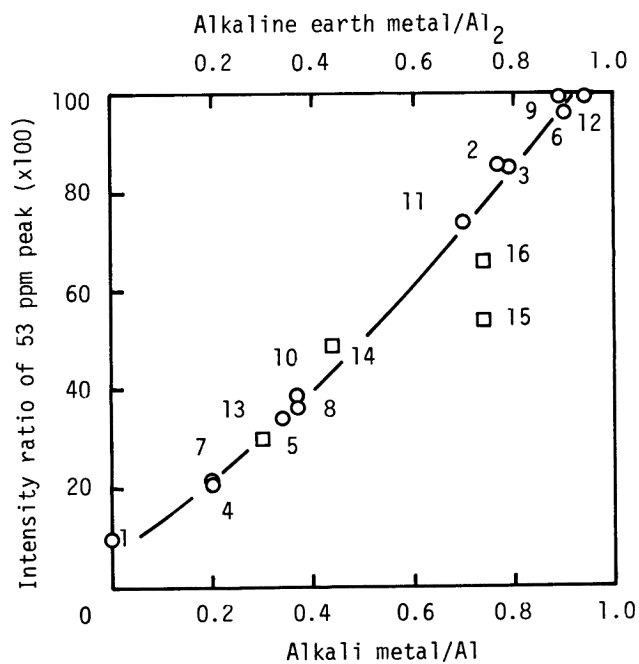


Fig. 1. Effect of various metal cations on dealumination of ZSM-5 zeolites. Arabic numbers in Fig. denote sample No. in Table 1.

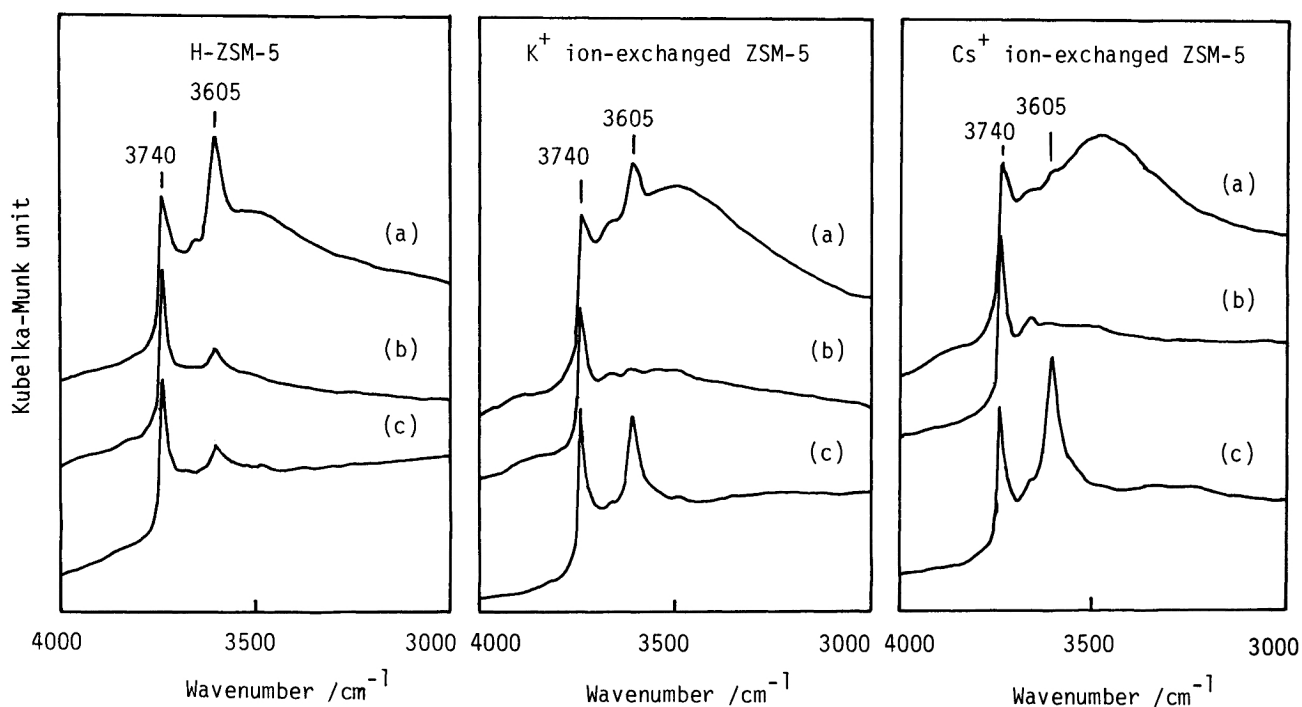


Fig. 2. Diffuse reflectance FT-IR spectra of various zeolites.  
 (a) H-ZSM-5 and the partially ion-exchanged ZSM-5 zeolites before steaming (Sample Nos. 1, 5, and 11 in Table 1).  
 (b) the zeolites steamed at 600 °C for 13.5 h.  
 (c) the steamed zeolites followed by treating with 0.6 M HCl.

dealumination of framework aluminium, but also a structural rearrangement in the zeolite framework with a transformation of SiOH to Si-O-Si.<sup>3)</sup>

This work is a part of the "C<sub>1</sub> Chemistry Project," a National Research and Development Program of the Agency of Industrial Science and Technology, Ministry of International Trade and Industry (M.I.T.I.), Japan.

#### References

- 1) D. W. Breck, "Zeolite Molecular Sieve," Wiley, New York (1974), p.493.
- 2) H. K. Beyer and I. Belenykaja, "Catalysis by Zeolite," ed by B. Imelik, C. Naccache, Y. Ben Taarit, J. C. Vadrine, G. Coudurier, and H. Pralia, Elsevier, Amsterdam (1980), p.203.
- 3) J. Scherzer, "Catalytic Materials," in "ACS Symposium Series," ed by T. E. Whyte, R. A. Dalla Betta, E. G. Derouane, and R. T. Baker, 248, (1984), p.157.
- 4) K. Fujisawa, T. Sano, K. Suzuki, H. Okado, K. Kawamura, Y. Kohtoku, S. Shin, H. Hagiwara, and H. Takaya, Bull. Chem. Soc. Jpn., 60, 791 (1987).
- 5) C. A. Fife, J. M. Thomas, J. Klinowski, and G. C. Gobbi, Angew. Chem., Int. Ed. Engl., 22, 259 (1983).
- 6) T. Sano, K. Suzuki, H. Shoji, S. Ikai, K. Okabe, T. Murakami, S. Shin, H. Hagiwara, and H. Takaya, submitted to Chem. Lett.
- 7) N. Y. Topose, K. Pedersen, and E. G. Derouane, J. Catal., 70, 41 (1981).

(Received April 30, 1987)