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Dealumination of ZSM-5 Zeolites with Water

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Dealumination of a framework of H-ZSM-5 zeolites with water was investigated by ^{27}Al MASNMR. It was found that the rate of dealumination is apparently second-order dependent on the concentration of framework aluminium.

Dealumination of a framework of high aluminium zeolites such as Y-zeolite, A-zeolite and mordenite has been extensively investigated.[1-5] It has been observed that a degree of dealumination depends upon a SiO_2/Al_2O_3 mole ratio in a zeolite framework and dealumination is lessened by the introduction of various metal cations. However, an exact reason for the dependence of dealumination on the SiO_2/Al_2O_3 mole ratio and the metal cations introduced is still not elucidated, although the effect of dealumination by hydrothermal treatment and chemical treatment with acids, chelating agents, or volatile compounds such as $SiCl_4$ and $COCl_2$ on the stability and catalytic properties of zeolites has been considerably studied. From this standpoint, in this paper, we report the dealumination of a framework of highly siliceous ZSM-5 zeolites which have the unique catalytic properties.

The H-ZSM-5 zeolites were synthesized following the procedure previously described.[6] The zeolite crystal size was controlled by varying an amount of alkali added. X-Ray diffraction patterns showed that the zeolites obtained were well crystallized without any detectable phase. Some analytical data of the zeolites are listed 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 500 - 600 °C in stream of 100% steam. High resolution ^{27}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 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 $Al(H_2O)_6^{3+}$ as an external reference.

As has already been reported, the ^{27}Al MASNMR spectrum of H-ZSM-5 zeolite has one peak at about 53 ppm assigned to the framework (tetrahedrally coordinated) aluminium.[7] In order to examine the dependence of dealumination on the concentration of framework aluminium, H-ZSM-5 zeolites with various SiO_2/Al_2O_3 mole ratios were steamed at 600 °C for 13.5 h and the degrees of dealumination for them were measured by means of ^{27}Al MASNMR. The plots in Fig. 1 show the relationship between the concentration of framework aluminium before steaming and the intensity ratio (x100) of the 53 ppm peak of the steamed zeolite to the corresponding unsteamed zeolite. The intensity ratios of the peak decreased with an increase in the aluminium concentration, indicating that the rate of dealumination predominantly depends upon not the crystal size but the concentration of framework aluminium. This aluminium concentration dependence of the dealumination of ZSM-5 zeolites is similar to that of Y-zeolite or mordenite.

Then, in order to obtain the rate equation of dealumination, the H-ZSM-5 zeolites with SiO_2/Al_2O_3 mole ratios of 66 and 174 were steamed at 600 °C varying the steaming time and the degrees of dealumination for them were determined by

Table 1. Characteristics of Various H-ZSM-5 Zeolites

Sample No.	SiO_2/Al_2O_3 mole ratio[a] before steaming	BET surface area[b] $m^2\ g^{-1}$	Crystal size[c] μm
1	66	379	0.5 - 2
2	91	390	1 - 2
3	174	381	2 - 3
4	446	373	0.3 - 0.5
5	680	372	4 - 6

a) Determined by X-ray fluorescence spectrometry.
b) Measured by a method of single point N_2 adsorption at -196 °C.
c) Measured by scanning electron micrography.

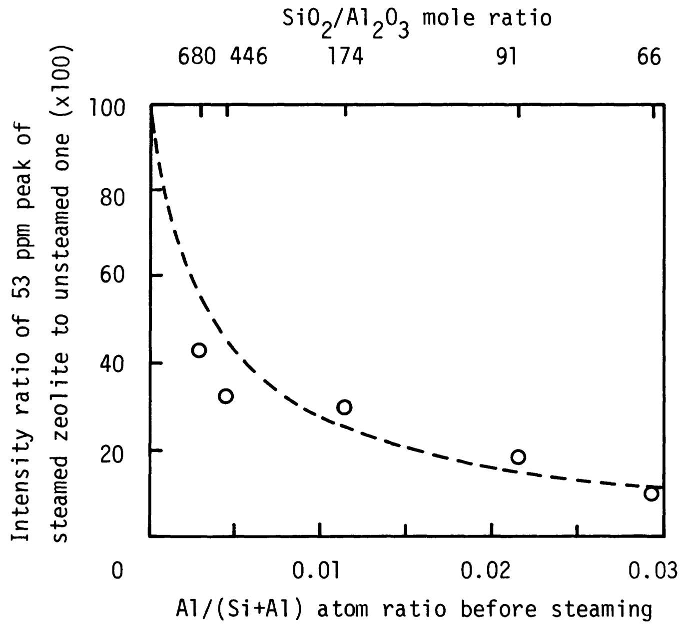

Fig. 1. Effect of aluminium concentration on dealumination of H-ZSM-5 zeolites. Steaming was carried out at 600 °C for 13.5 h.

means of ^{27}Al MASNMR. As shown in Fig. 2, it was found that the rate of steam dealumination is apparently second-order dependent on the concentration of framework aluminium, as is expressed by the following equation.

$$-dA/dt=k\cdot A^2 \qquad (1)$$

where A is a concentration of framework aluminium, t is a steaming time, and k is a rate constant. In tegrating Eq. 1, we have

$$(1/A - 1/A_0)=k\cdot t \qquad (2)$$

where A_0 is the initial concentration of framework aluminium in the zeolite. The rate constants calculated from the straight lines, k (day^{-1}), were 6.1×10^2 and 3.5×10^2 for H-ZSM-5 (SiO_2/Al_2O_3=66) and H-ZSM-5 (SiO_2/Al_2O_3=174), respectively. In calculation, A_0 is the value of Al/(Si+Al) atom ratio of the zeolite before steaming and A is the value of A_0 multiplied by the intensity ratio of 53 ppm peak from ^{27}Al MASNMR. The data calculated from Eq. 2 by using the avarage value of k are represented as the dotted curve in Fig. 1. It may be noted that the experimental data are considerably content with the dotted curve. From the Arrhenius plots of k obtained for the two steamed zeolites at 500, 550, and 600 °C, an apparent activation energy for dealumination of the ZSM-5 zeolite was about 88 kJ mol^{-1} (Fig. 3).

As the framework aluminium atoms are isolated from each other in the case of highly siliceous zeolites, it seems that the rate of dealumination is first-order dependent on the concentration of framework aluminium and is expressed by the following equation.

$$-dA/dt=k_1\cdot A \qquad (3)$$

However, our dealumination data were not expressed by the equation. We have now considered the reason of the disagreement with our present results of the second-order dependence of dealumination on the concentration of framework aluminium. The

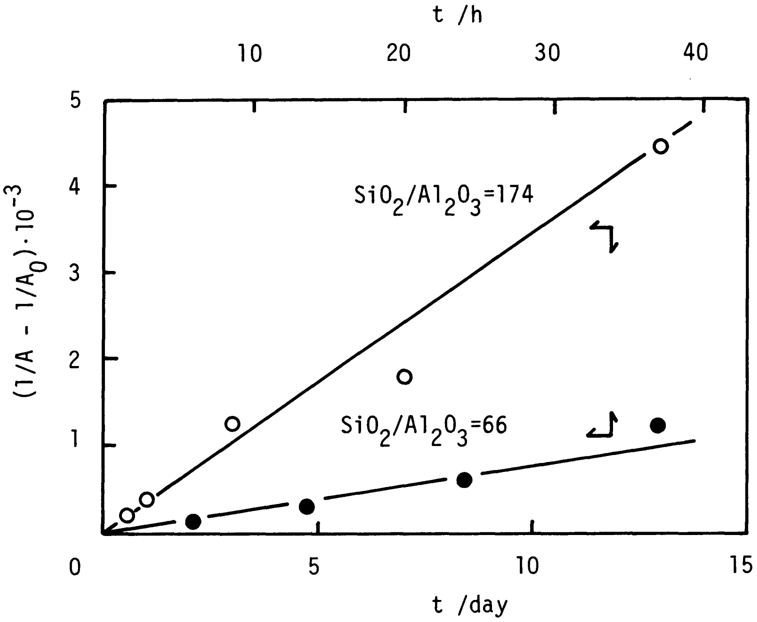

Fig. 2. Relationship between $(1/A - 1/A_0)$ and t.

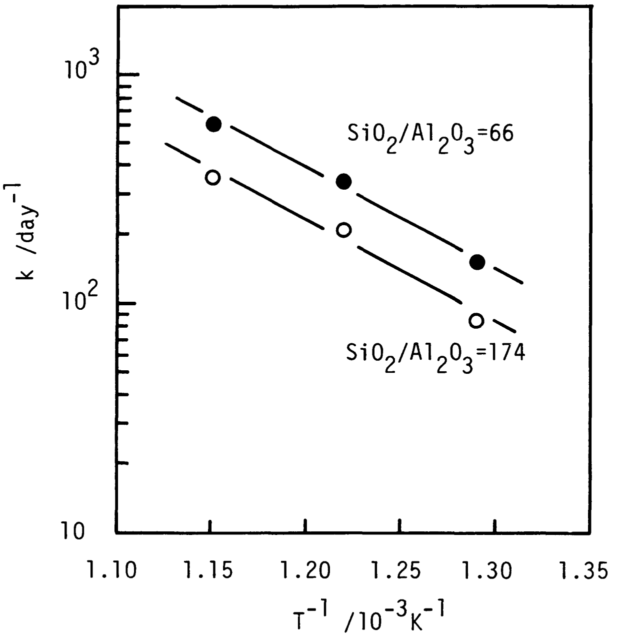

Fig. 3. Arrhenius plot of k.

dealumination is the cleavage of a Si-O-Al bond with water and the hydrolysis reaction may be catalyzed by acid (H^+), whose concentration is equivalent to that of framework aluminium. The hydrolysis catalyzed by H^+ is supported by the thought that H^+ freely moves in the pore of zeolite which plays a role of a solvent for H^+. Then, k_1 in Eq. 3 is given as follows.

$$k_1 = k \cdot H^+ = k \cdot A \qquad (4)$$

From the substitution of Eq. 4 for Eq. 3, we have Eq. 1 and this corresponds to our results of the second-order dependence of dealumination on the concentration of framework aluminium.

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