Realumination of dealuminated HZSM-5 zeolites by acid treatment

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^{27}Al MAS NMR and FTIR spectroscopy shows that part of non-framework aluminiums in dealuminated HZSM-5 zeolites are reinserted into the framework upon treatment with aqueous hydrochloric acid.

Physicochemical properties of zeolites such as catalytic, sorptive and ion-exchange abilities are strongly dependent on their framework (tetrahedrally coordinated) aluminiums in the zeolite structure. Dealumination from zeolite framework has been widely studied to alter the SiO_2/Al_2O_3 ratio of the framework. We have kinetically investigated the dealumination behavior of ZSM-5 zeolite and metallosilicate by thermal and hydrothermal treatments, and already reported that the dealumination rate by hydrothermal treatment has an apparent third-order dependence on the number of framework aluminiums.[1–3] As the framework aluminium atoms are isolated from each other in the case of highly siliceous zeolites such as ZSM-5, this indicates that the dealumination *via* hydrolysis of Si–O–Al bonds in the zeolite framework is catalyzed by acid (protons) which move freely in the zeolite pores. Realumination, the reverse reaction of hydrolysis of the Si–O–Al bond, as well as dealumination of zeolites has received considerable attention from the standpoint of regeneration of zeolite catalysts. There are several papers concerning the realumination of dealuminated zeolite by treatment with aqueous alkali solution, suggesting the reinsertion of non-framework aluminium into the framework (a decrease in the framework SiO_2/Al_2O_3 ratio).[4–10] However, no study of realumination by acid treatment has been reported in the literature. Here, the realumination of dealuminated HZSM-5 zeolites by treatment with aqueous HCl was investigated.

HZSM-5 zeolite was prepared following the procedure previously described.[1] A SiO_2/Al_2O_3 ratio of 71 was determined by X-ray fluorescence (XRF, Philips PW-2400) while a framework SiO_2/Al_2O_3 ratio of 78 was determined by ^{27}Al MAS NMR spectroscopy (Varian VXP-400) using a calibration curve, which was produced by measuring ^{27}Al MAS NMR spectra of HZSM-5 zeolites with various SiO_2/Al_2O_3 ratios.[2,3] Dealumination of the HZSM-5 zeolite was carried out by thermal and hydrothermal treatments at 600 °C using a muffle furnace and a quartz reactor tube. The water vapor pressure in the hydrothermal treatment was 10 kPa, generated using nitrogen as the diluent gas. HCl treatment (realumination) was carried out as follows: 1 g of dealuminated HZSM-5 zeolite was treated with 100 ml of aqueous 2 M HCl at 100 °C, stirring for a given time. The product was filtered off, washed thoroughly with deionized water, dried at 100 °C and calcined at 380 °C for 8 h. Characterization of dealuminated and realuminated HZSM-5 zeolites was achieved by ^{27}Al MAS NMR spectroscopy, diffuse reflectance FTIR (JEOL JIR-7000), and nitrogen adsorption (Bel Japan Belsorp 28SA).

X-Ray diffraction diagrams of realuminated HZSM-5 zeolites after HCl solution treatment show no peaks other than those corresponding to ZSM-5 zeolite. The intensities of the peaks observed were almost the same as those of the dealuminated zeolite, indicating no structural degradation. This was also confirmed by the fact that no difference in the micropore volume $W_0(N_2)$ of 0.18 cm^3 (liquid) g^{-1} obtained by the Dubinin–Raushkevich (DR) plot of the nitrogen adsorption isotherm was observed between dealuminated and realuminated zeolites. Fig. 1 shows FTIR spectra of the parent HZSM-5 (total SiO_2/Al_2O_3 ratio 71), the dealuminated HZSM-5 prepared by thermal treatment at 600 °C for 48 h (total SiO_2/Al_2O_3 ratio 72) and the realuminated HZSM-5 after HCl treatment (total SiO_2/Al_2O_3 ratio 78). The decrease in the peak at 3605 cm^{-1} assigned to an acidic bridged OH of Si(OH)Al was observed in the spectrum of dealuminated HZSM-5 zeolite, while a clear increase in the peak intensity was observed in the spectrum of realuminated zeolite. This result suggests the reinsertion of non-framework aluminiums in the dealuminated zeolite into the framework.

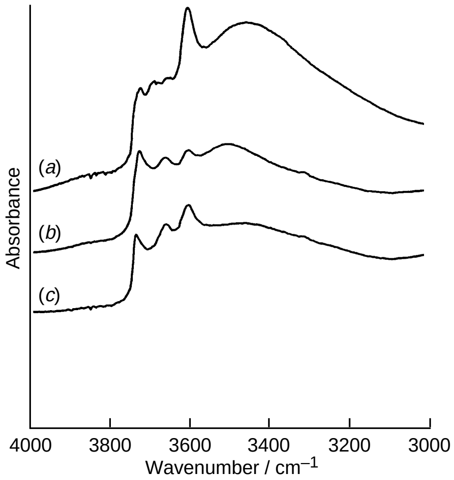

Fig. 1 FTIR spectra of HZSM-5 zeolites of (*a*) parent, (*b*) after thermal dealumination at 600 °C for 48 h and (*c*) after realumination of (*b*) with 2 M HCl at 100 °C for 120 h

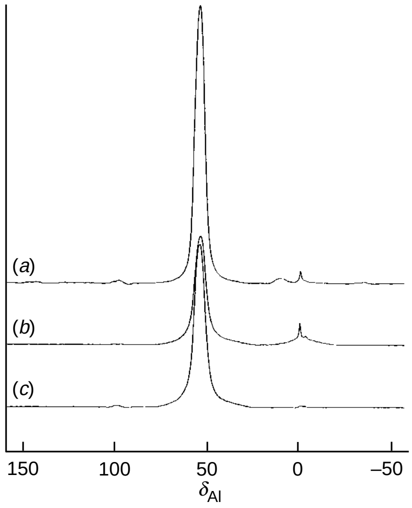

Fig. 2 ^{27}Al MAS NMR spectra of HZSM-5 zeolites of (*a*) parent, (*b*) after thermal dealumination at 600 °C for 48 h and (*c*) after realumination of (*b*) with 2 M HCl at 100 °C for 120 h

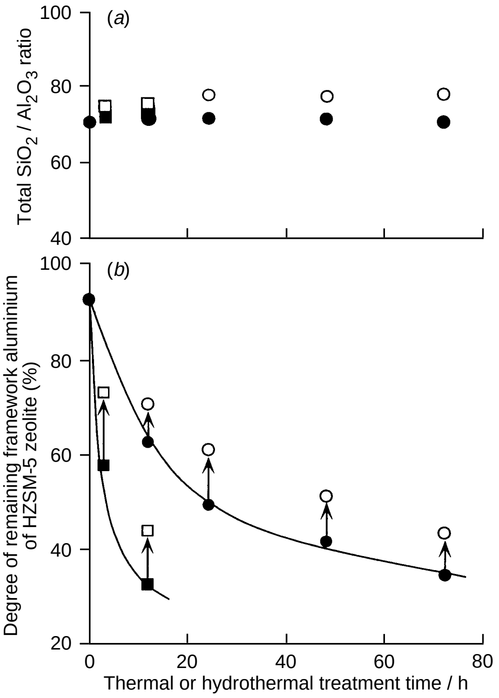

Fig. 3 Total SiO_2/Al_2O_3 ratios and degrees of remaining framework aluminium of dealuminated and realuminated HZSM-5 zeolites. (●), HZSM-5 dealuminated by thermal treatment at 600 °C; (○), after treatment with 2 M HCl at 100 °C for 120 h; (■), HZSM-5 dealuminated by hydrothermal treatment at 600 °C and P_{H_2O} of 10 kPa; (□), after treatment with 2 M HCl at 100 °C for 120 h.

To clarify this possibility of reinsertion, the ^{27}Al MAS NMR spectra of these samples were measured. The normalized intensity of the peak at δ 53 assigned to framework aluminium of HZSM-5 zeolite was based on 1 g of zeolite. As shown in Fig. 2, the peak intensity of the dealuminated HZSM-5 zeolite definitely increased upon treatment with HCl. The calculated framework SiO_2/Al_2O_3 ratios of the dealuminated and the realuminated HZSM-5 zeolite were 173 and 140, respectively. As the total SiO_2/Al_2O_3 ratio of the realuminated zeolite was 78, dissolution of non-framework aluminium occurred during treatment with HCl; this indicates that some of the non-framework aluminium in dealuminated HZSM-5 zeolite is reinserted into the framework.

However, there is another possible explanation for the increase in the peak intensities of ^{27}Al MAS NMR and FTIR spectra, namely that the increase is attributable to the removal of the framework silicon atoms.[12,13] To clarify this, therefore, silicon and aluminium concentrations in the liquid phase after HCl treatment were analyzed by inductively coupled argon emission spectroscopy (Seiko SPS7700). The degrees of elution of silicon and aluminium atoms from the dealuminated zeolite during the HCl treatment were 0.99 and 9.3%, respectively, indicating that the removal of framework silicon atoms scarcely takes place during this process. This is consistent with the result reported by Kooyman *et al.*[14] Therefore, we can conclude that realumination of dealuminated zeolite occurs during acid treatment.

To gain more information about the realumination, the realumination of several dealuminated HZSM-5 zeolites with different framework SiO_2/Al_2O_3 ratios was carried out at 100 °C for 120 h using 2 M HCl. Dealuminated HZSM-5 zeolites with different degrees of dealumination were prepared by varying the thermal treatment time. Fig. 3 shows the total SiO_2/Al_2O_3 ratios and the degree of remaining framework aluminium of dealuminated and the corresponding realuminated HZSM-5 zeolites. The total SiO_2/Al_2O_3 ratios of realuminated HZSM-5 zeolites were slightly higher than those of dealuminated zeolites. All framework aluminium ion concentrations of dealuminated HZSM-5 zeolite increased upon HCl treatment. Dealuminated HZSM-5 zeolites were also prepared by hydrothermal treatment at 600 °C under a water vapor pressure of 10 kPa and then treated with HCl and the result is also illustrated in Fig. 3 with reinsertion of non-framework aluminium into the framework also being observed.

From the above results, it is concluded that some of the non-framework aluminium in dealuminated HZSM-5 zeolite is reinserted into the framework in the presence of an aqueous solution of hydrochloric acid although the detailed mechanism of the realumination is not clear. As it is well known that non-framework aluminium is not uniform and exists in different states,[15] we primarily speculate that realumination proceeds mainly through reinsertion of non-framework aluminium species where the aluminium atom is connected to the zeolite framework by only one or two chemical bonds.

Footnote and References

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