Dealumination of Zeolites using an Aqueous Solution of Ammonium Tetrafluoroborate

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A new dealumination method using an aqueous solution of NH_4BF_4 has been developed; characterization of the product clearly shows that substitution of Si for Al occurs during the treatment and that boron atoms do not insert into the framework of the product.

Framework dealumination of zeolites has been known for several years. Many methods based on gas–solid[1—3] and liquid–solid[4—6] reactions for dealumination were developed. Research on dealumination is of great importance, both fundamentally and practically, due to the significance of changing the siting of Al and Si atoms in the zeolitic frameworks and, as a consequence, to the improvement of acidities and catalytic properties of the dealuminated products.

We report here a new method of framework dealumination

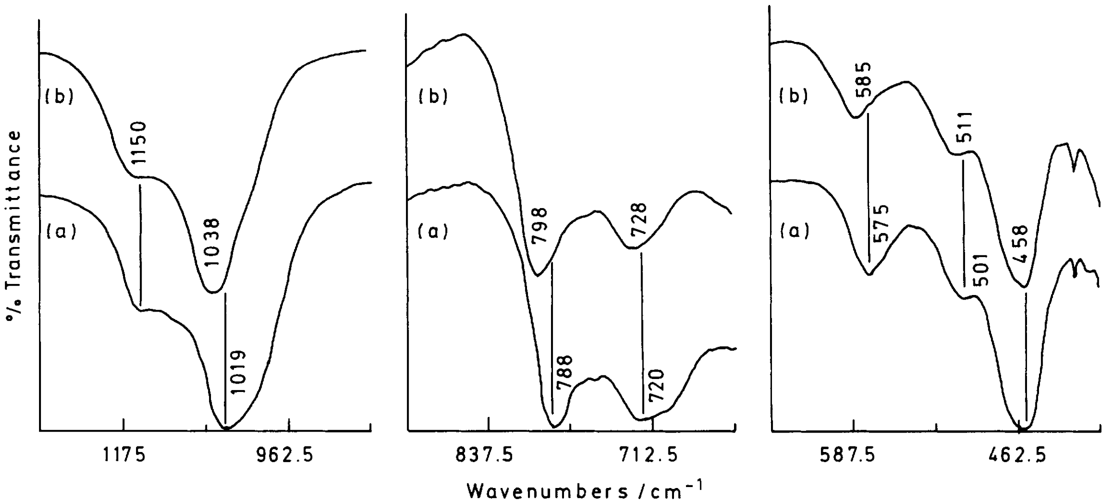

Figure 1. IR spectra of NH_4Y before and after treatment with aqueous NH_4BF_4 solution (a) NH_4Y; (b) treated NH_4Y.

Table 1. Chemical compositions of the starting NH_4Y and the product.

Sample	Si/Al_{XRF}	Si/Al_{NMR}
NH_4Y	2.55	2.50
$B\text{-}NH_4Y$[a]	3.41	3.43

[a] NH_4Y treated with an aqueous NH_4BF_4 solution (0.095 M).

of zeolites using an aqueous solution of ammonium tetrafluoroborate, NH_4BF_4, and characteristics of the method demonstrated by characterization of the dealuminated products.

Zeolite Y used in this study was synthesized as described by Breck.[7] NH_4Y was obtained by ion-exchanging the zeolite Y with an aqueous solution of NH_4Cl (2 M). Dealumination was performed typically as follows. Dried NH_4Y (2 g) was added to an aqueous solution of NH_4BF_4 (100 ml, 0.095 M). The suspension was then heated to 60 °C in an oil bath and maintained at this temperature for 24 h. The product was filtered, washed with distilled water, and dried in air. Characterization of the product was carried out by using *X*-ray diffraction (XRD), IR spectroscopy, differential thermal analysis (DTA), *X*-ray fluorescence (XRF), *X*-ray photoelectron spectroscopy (XPS), and magic-angle-spinning NMR (MAS NMR) techniques. The XRD identification was done on a Rikagu D MAX-IIIA *X*-ray diffractometer operated at 30 kV and 20 mA with Cu-K_α radiation. The IR spectra were recorded on a Nicolet 5DX Fourier transform instrument. DTA measurement was performed on a Rigaku TGA-DTA instrument and XPS was done on a VG Mark-II electron spectrometer. XRF analysis was carried out on a VF-300 *X*-ray fluorescence spectrometer and ^{29}Si and ^{27}Al MAS NMR measurements were performed on a Varian XL-200 spectrometer. The spinning rate was 2.5 kHz, and tetramethylsilane (TMS) and an aqueous solution of Al $(NO_3)_3$ were taken as standards for ^{29}Si and ^{27}Al respectively.

In Table 1 chemical compositions of the starting NH_4Y and the product analysed both by XRF and by ^{29}Si MAS NMR are given. An increase of the Si/Al ratio of the product compared to the starting NH_4Y and the similarity of the Si/Al ratios obtained from XRF and from ^{29}Si MAS NMR analysis indicate that during treatment of the zeolite NH_4Y with an aqueous solution of NH_4BF_4, dealumination followed by Si insertion takes place and that boron atoms do not insert into the framework of the product. Wet chemical analysis shows that boron atoms are undetectable in the product. Characterization of the product using the techniques mentioned above supports the mechanism of boron-exclusion and dealumination followed by Si insertion. XPS measurements do not provide any evidence for the presence of B atoms on the surface (the most possible substitution position) of the product. IR spectroscopic measurements of the product also do not show the bands at about 3720 and 1380 cm^{-1} (see Figure 2), characteristic of the acidic B–OH group and the framework BO_4 vibrations respectively, observed for boron-

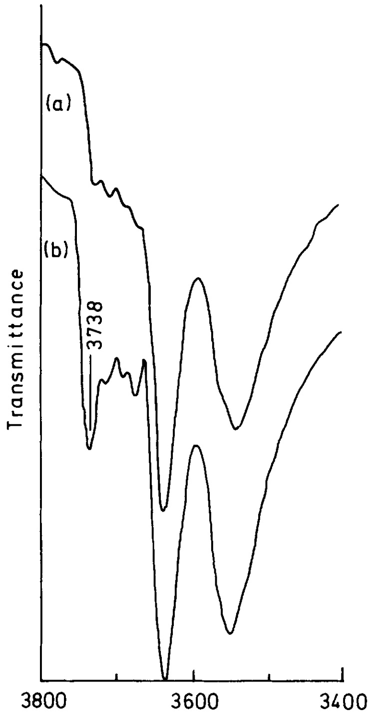

Figure 2. IR spectra of OH vibrations of NH_4Y before and after treatment with aqueous NH_4BF_4 solution. (a) NH_4Y; (b) treated NH_4Y.

containing ZSM-5.[9] Dealumination followed by Si insertion of the NH_4Y during the treatment is suggested by the following results. The IR spectrum of the product, given in Figure 1, shows shifts of the bands towards higher frequency in the regions of asymmetric, symmetric, double-six-membered ring and T–O bending vibrations.[8] The asymmetric vibration at 1019 cm^{-1} of the starting NH_4Y is shifted about 19 cm^{-1} to 1038 cm^{-1} after treatment. The symmetric vibration at 788 and 720 cm^{-1}, as well as the double-six-membered ring vibration at 575 cm^{-1} and a T–O bending vibration at 501 cm^{-1}, show similar shifts to 798, 728, 585, and 511 cm^{-1}, respectively. The T–O bending vibration at 458 cm^{-1} and the external asymmetric stretching vibration at 1150 cm^{-1} do not show the shift. ^{29}Si MAS NMR spectroscopic measurements show that the peaks which are assigned to SiAl(0) and SiAl(1) in the spectrum significantly increase their relative intensities, indicating that substitution of Si for Al occurs during the treatment. ^{27}Al MAS NMR shows one peak with a chemical shift of δ 57.3 p.p.m. relative to the $Al(H_2O)_6^{3+}$ solution. No octahedral Al species are observed in the product. DTA study shows increase of the thermal stability of the product. The collapse temperature increases from 882 °C for the starting NH_4Y to 970 °C for the product.

However, the Si insertion into the product after removal of Al is incomplete due to the lack of Si in the liquid phase of the system studied. The Si species for occupation of the Al vacancies can only be obtained from dissolution of the Si atoms located on the external surface of the zeolite and the SiO_2 amorphous materials (if any). This is in contrast to what has been observed in the cases of dealumination with either $(NH_4)_2SiF_6$ solution or $SiCl_4$ vapour[2] where additional Si species are present. A new band at about 3738 cm^{-1} for the product in the OH vibration region of the IR spectrum (see Figure 2) demonstrates that surface silanols, or Si–OH nests,[10] are present in the product.

In comparison of the method with the $(NH_4)_2SiF_6$ method and with an approach of dealumination with hydrofluoric acid, which is a possible intermediate species after hydrolysis of NH_4BF_4, the characteristics of the method are clearly seen. Dealumination of the NH_4Y with an aqueous solution of $(NH_4)_2SiF_6$ under the same conditions gives a product with a large amount of amorphous material. The crystallinity of the sample is dramatically decreased. Treatment of the sample using a solution of hydrofluoric acid under the same conditions also decreases the crystallinity significantly. These results indicate that dealumination of the sample with these solutions is so vigorous that the structure of the NH_4Y cannot be entirely maintained. The difference between dealumination with NH_4BF_4 and with $(NH_4)_2SiF_6$ and HF clearly demonstrates that the slow hydrolysis of NH_4BF_4 is the key factor for controlling the crystallinity of the product. The pH measurement of the solution before and after dealumination is about 6. For dealumination of other zeolites such as NH_4-ZSM-5, the pH of the solution before and after dealumination changes slightly from 6 to 3.

The framework composition of the zeolite by the dealumination method is controlled by adjusting the concentration of NH_4BF_4 used. The higher the concentration of NH_4BF_4, the more the aluminium is removed, and therefore the higher the Si/Al ratio of the product.

The method can be extended to dealuminate zeolites such as β, ZSM-5, and many others. Dealumination of these zeolites is efficient.

In conclusion, a new dealumination method using an aqueous solution of NH_4BF_4 has been developed. Characterization of the product clearly shows that substitution of Si for Al occurs during the treatment, and that boron atoms do not insert into the framework of the product during the process.

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