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Acidic Properties of HZSM-5 Zeolite Aluminated with $AlCl_3$

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The alumination of highly siliceous HZSM-5 with $AlCl_3$ vapor was carried out for 2 h at 923 K. ^{29}Si- and ^{27}Al-MAS NMR and IR spectroscopies show that introduction of 4- and 6-coordinated aluminium atoms occurs during the alumination. Moreover, NH_3-TPD spectroscopy exhibits that a considerable amount of the acid sites, whose intensity is stronger than that observed for a common HZSM-5, is generated by the alumination.

It has been reported that aluminium atoms can be introduced into the framework of highly siliceous ZSM-5 zeolite by the treatment with $AlCl_3$ vapor at elevated temperatures[1-3] and not only Brønsted acid sites but also Lewis acid sites are generated by the treatment.[3] It has been also reported that the maximum rate of NH_3 evolution from the aluminated NH_4ZSM-5 in NH_3-TPD occurs around a temperature similar to that observed for NH_4ZSM-5 zeolites prepared in the conventional manner. This fact might suggest that the acid strength of the aluminated HZSM-5 was almost the same as that of a common HZSM-5. However, in this letter, we expect to emphasize that by the alumination of highly siliceous HZSM-5 a considerable amount of acid sites, whose intensity is stronger than that observed for a common HZSM-5 prepared in the conventional manner, is generated.

The parent zeolite was highly siliceous HZSM-5 with a Si/Al atomic ratio of 1260. The parent HZSM-5 and a reference HZSM-5 with a Si/Al ratio of 91 were prepared according to the method described in Ref. 4. The parent zeolite (4 g) was placed in powder form in a vertical quartz tube reactor and dehydrated for 4 h at 773 K in a dry helium stream, and the temperature was brought to an alumination temperature of 923 K. Then the helium stream was saturated at 423 K with $AlCl_3$. The treatment with $AlCl_3$ vapor was carried out for 2 h. The alumination product was purged with dry helium for 1 h at 923 K to remove $AlCl_3$ unreacted, cooled to room temperature, rinsed out twice in a 500 ml of 0.05 mol dm^{-3} aq. HCl with stirring for 1 h, washed with a large amount of water and dried at 383 K.

The bulk and framework Si/Al atomic ratios of the aluminated HZSM-5 were determined by atomic absorption photometry and by ^{27}Al- and ^{29}Si-MAS NMR spectroscopy, respectively. Acidic properties of the aluminated HZSM-5 and the reference HZSM-5 zeolites were examined by IR and NH_3-TPD spectroscopies. ^{27}Al- and ^{29}Si-MAS NMR measurements were carried out at 70.3 and 53.5 MHz, respectively, using a JEOL GX-270 Fourier Transform Spectrometer equipped with a magic-angle

probe. NH_3-TPD experiments were performed using a conventional static adsorption system connected to a quadrupole mass spectrometer through a high-vacuum line. Samples dehydrated for 1 h at 773 K were in contact with NH_3 gas of 21 kPa for 1/2 h at 423 K, evacuated for 1 h at 423 or 573 K, and then cooled to room temperature. Spectra were obtained at a heating rate of 10 K/min.

The IR spectra for the parent, aluminated, and common (reference) HZSM-5 zeolites in the hydroxyl stretching region are shown in Fig. 1. Whereas the highly siliceous parent zeolite showed only a single band at 3740 cm^{-1} due to non-acidic silanol groups, the aluminated zeolite clearly exhibited a new band at 3610 cm^{-1}. This band has been associated with framework Al(OH)Si groups responsible for Brønsted acidity.[5] The intensity of the 3610 cm^{-1} band for the aluminated HZSM-5, whose bulk Si/Al ratio was 27, was almost the same as that of the common HZSM-5 with a Si/Al ratio of 91, suggesting that the number of Brønsted acid sites on the aluminated HZSM-5 was similar to that on the common one with a Si/Al ratio of 91. Therefore, the framework Si/Al ratio of the aluminated HZSM-5 may be around 91.

^{29}Si-MAS NMR spectra for the parent and aluminated HZSM-5 zeolites are shown in Fig. 2. In the spectrum for the parent zeolite, considerable fine structure responsible for Si(0Al) sites in highly siliceous ZSM-5 zeolites[6] was observed around -113 ppm together with a weak signal at -103 ppm due to Q^3 sites ($\equiv$Si-OH).[6] In the spectrum for the aluminated zeolite, not only the Si(0Al) signal but also a new weak signal at -106 ppm due to Si(1Al) sites[6] was observed and the fine structure and the Q^3 signal were not found. These facts indicate that 4-coordinated aluminium atoms can be introduced into the framework of the parent HZSM-5 by the alumination with $AlCl_3$.

The spectrum for the aluminated HZSM-5 was computer-simulated using Gaussian peak shapes, and the areas of the individual deconvoluted signals were measured. From these values it must be possible to calculate the framework Si/Al ratio.[6] The framework Si/Al ratio thus obtained was 90.

The introduction of 4-coordinated aluminium atoms into the framework was also supported by ^{27}Al-MAS NMR studies. ^{27}Al-MAS NMR spectra for the parent and aluminated HZSM-5 zeolites were measured. The parent zeolite showed only an extremely weak peak at 53 ppm due to trace

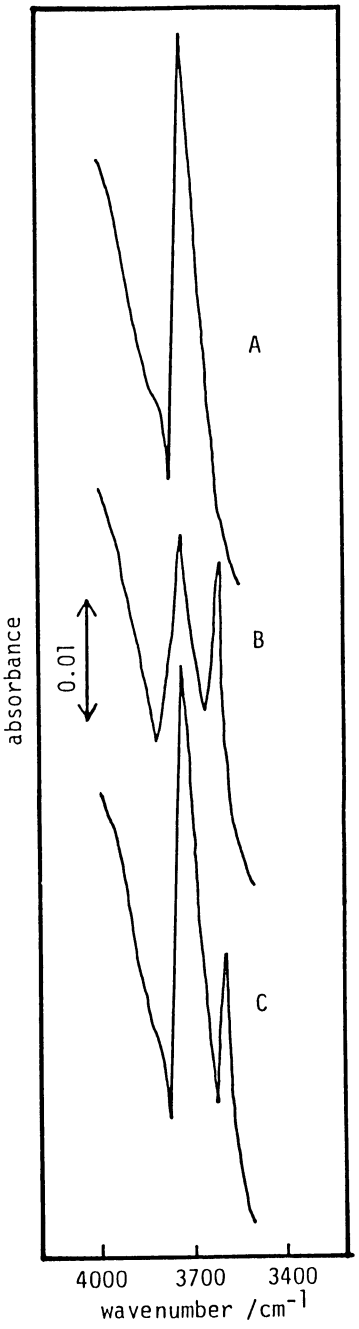

Fig. 1. IR spectra for the parent (A), aluminated (B), and common (C) HZSM-5 zeolites in the hydroxyl streching region.

amounts of 4-coordinated aluminium. On the other hand, the aluminated zeolite exhibited a strong peak at 53 ppm and a broad peak around 0 ppm due to 6-coordinated aluminium. These results are similar to those reported by Dessau and Kerr.[2] The peak due to 4-coordinated aluminium appeared at 53 ppm. Such a low chemical shift indicates that Al-O-Al linkages are absent and the peak is due to Al(4Si) sites.[6] Therefore, every 4-coordinated aluminium atom in the aluminated HZSM-5 exists in the framework. The broadness of the peak at 0 ppm indicates the mobility of 6-coordinated aluminium is very low. Therefore, Al^{3+} on ion exchange sites is replaced by H^{+} during the rinse of the alumination product with aq. HCl (0.05 mol dm^{-3}).

From the ^{27}Al-MAS NMR spectra for the aluminated and common HZSM-5 zeolites with a certain amount of aluminium sulfate as an internal standard, the framework Si/Al ratios can be calculated. The calculated framework Si/Al ratios of the aluminated and common zeolites were 80 and 91, respectively. The bulk Si/Al ratio of the common HZSM-5 coincides with the framework one, while in the case of the aluminated HZSM-5, the framework Si/Al of 80, which is in fair agreement with that obtained from ^{29}Si-MAS NMR studies, 90, is much higher than the bulk Si/Al ratio of 27. This fact indicates that the introduction of 4- and 6-coordinated aluminium atoms occurs during the alumination.

NH_3-TPD spectra provide significant information regarding acid strength. Figure 3 shows NH_3-TPD spectra for the common and aluminated HZSM-5 zeolites. The spectra obtained after evacuation at 423 K indicate only a single peak at 543 K for the common zeolite and not only a main peak at the same temperature but also a shoulder peak at 643 K for the aluminated one. These facts suggest that the intensity of a considerable part of acid sites on the aluminated HZSM-5 is much stronger than that observed for the common HZSM-5. More-

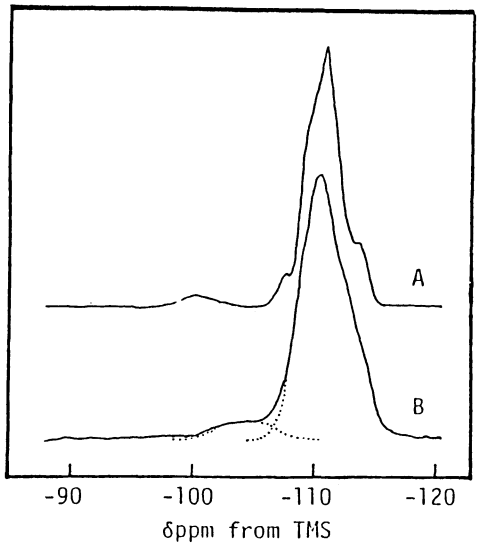

Fig. 2. ^{29}Si-MAS NMR spectra for the parent (A) and aluminated (B) HZSM-5 zeolites. Dotted spectra are computer-simulated.

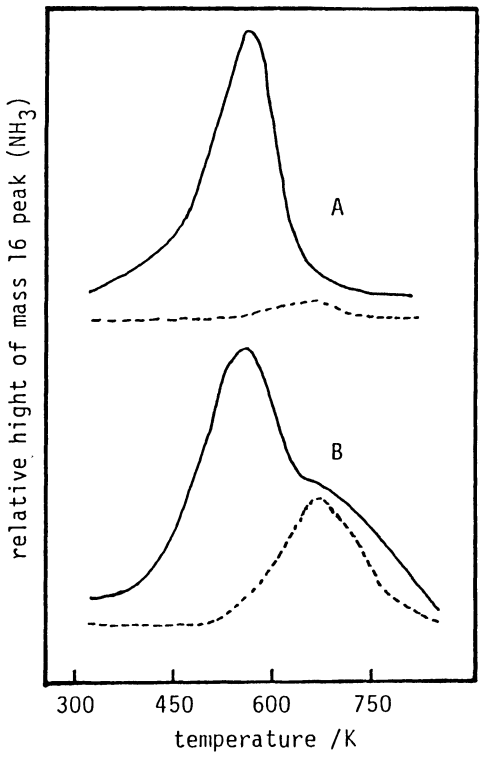

Fig. 3. NH_3-TPD spectra obtained after evacuation at 423 K (——) or 573 K (---) for the common (A) and aluminated (B) HZSM-5 zeolites.

Table 1. Bulk and Framework Aluminium Concentrations and Amounts of NH_3 Desorbed

HZSM-5	Aluminium concentration 10^4/mol g^{-1}		Amount of NH_3 desorbed[c] 10^4/mol g^{-1}
	Bulk[a]	Framework[a,b]	
Common	1.74 (91)	1.74 (91)	1.85
Aluminated	5.70 (27)	1.99 (80)	3.33

a) Numbers in parenthesis indicate Si/Al atomic ratios.
b) Determined by ^{27}Al-MAS NMR.
c) Evaluated from TPD spectra obtained after evacuation at 423 K.

over, the spectra obtained after evacuation at 573 K strongly support such a suggestion. Whereas the common zeolite scarcely exhibited a peak around 643 K, the aluminated one exhibited a considerably strong peak at 643 K. Therefore, the strong acid sites, which are not observed for common HZSM-5 zeolites, together with normal acid sites are generated by the alumination of highly siliceous HZSM-5 with $AlCl_3$.

The amount of acid sites can be evaluated from the amount of NH_3 desorbed during the TPD measurements. The evaluated amounts of acid sites on the common and aluminated HZSM-5 zeolites are tabulated together with the bulk and framework aluminium concentrations in Table 1. In the case of the common zeolite, the aluminium comcentration of the framework coincided with that of the bulk, and was compatible with the amount of acid sites. In the case of the aluminated zeolite, however, the amount of acid sites was more than the framework aluminium concentration, and was less than the bulk aluminium concentration. These facts suggest that not only the framework aluminium but also a part of the non-framework aluminium is responsible for the acid sites on the aluminated HZSM-5.

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