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STABILITY OF THE TETRAHEDRAL ALUMINIUM SITES IN ZEOLITE BETA

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Calcination of as-synthesized or ammonium-exchanged forms of zeolite BETA induces an extensive loss of framework aluminium evidenced by ^{27}Al MAS NMR, XRD and FTIR spectroscopies. Treatment of the calcined solids in ammonium nitrate restores the tetrahedral Al sites. Material balances show that the latter process is quantitative.

1. Introduction

The acidic properties of zeolites originate from the presence of protons balancing the excess of negative charge associated to aluminium in tetrahedral sites. The possibility of altering the number and strength of acidic sites by dealumination, while preserving the crystallinity of the material, is particularly convenient and extensively used for the commercial preparation of cracking catalysts. In some cases however, dealumination may be an undesired phenomenon occurring during thermal activation or in the course of the reaction. Zeolite BETA is such a system where extensive dealumination takes place when submitted to relatively mild thermal [1,2] or acidic [3] treatments.

This note describes a physico-chemical study of the activation of zeolite BETA by combined thermal and exchange treatments. The main conclusion is that the tetrahedral aluminium sites disappearing upon calcination can be readily restored by a simple treatment in ammonium nitrate.

2. Experimental

The parent sample of zeolite BETA with a Si/Al ratio of 16.9 was synthesized at 130 °C using tetraethylammonium hydroxide (TEA) as template. Thermal

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treatments were performed in flowing dry air (100 ml/min) using thin bed configuration (diameter 15 mm; height 2 mm). The samples were dehydrated first at 200 ° C for two hours, then the temperature was raised (1°/min) up to 550 ° C and maintained for four hours. Ion exchange was carried out at 80 ° C using 2 M aqueous ammonium nitrate, a liquid to solid weight ratio of 100 (pH of the suspension 4.5–5) and a reaction time of four hours. The products were characterized by X-ray diffraction (XRD, crystallinity, unit cell parameters), ^{27}Al MAS NMR and FTIR (framework and hydroxyl frequencies) spectroscopies. Details of the procedures are given elsewhere [4]. Material balances were calculated from the elemental analyses of the solids and filtrates.

3. Results and discussion

The parent zeolite exhibited the characteristic XRD pattern [5,6] and IR spectrum [7] of zeolite BETA with no extra lines. In the ^{27}Al NMR spectrum a single signal at 53 ppm, due to tetrahedral aluminium, was detected (fig. 1a). The oxidative decomposition of the template resulted in a decrease of the intensity of the XRD peaks and dealumination of the framework, as evidenced by the appearance of a ^{27}Al NMR signal of octahedral aluminium at 0 ppm (fig. 1b), a decrease of the unit cell parameters and a shift towards higher frequencies of all the framework IR vibrations (table 1). The extent of dealumination corresponded approximately to 25% as estimated from the relative intensity of the NMR signal at 53 ppm. The IR spectrum of the hydroxyl region of the calcined zeolite is shown in fig. 2. Besides the bands at 3750 cm^{-1} (isolated silanols) and 3620 cm^{-1} (bridged hydroxyls) it features signals at 3680 and 3780 cm^{-1} due to hydroxyl groups associated to extra-framework species [8] and a broad absorption band between 3750 and 3000 cm^{-1} related to $(OH)_4$ groups in framework defect sites [9].

When this material was subsequently treated with ammonium nitrate solution, washed and oven dried at 70 ° C, the signal of octahedral aluminium was no longer detected (fig. 1c) while that at 53 ppm narrowed and increased to 95% of its original value. The unit cell parameters and the crystallinity increased and the IR lattice frequencies decreased. All these changes are consistent with a reinsertion of aluminium in the framework. The amounts of silicon and aluminium present in the filtrate corresponded to 3% and 5% of the total Si and Al of the sample respectively. The Si/Al ratio of the solid was hardly modified (table 1) and the NH_4/Al ratio equaled 0.98 indicating that the dislodged aluminium had been nearly quantitatively reinserted during the exchange treatment. Evidences for framework realumination have been obtained when hydrothermally-treated Y [9,10] and ZSM-5 [11] zeolites have been treated with a concentrated solution of a strong base.

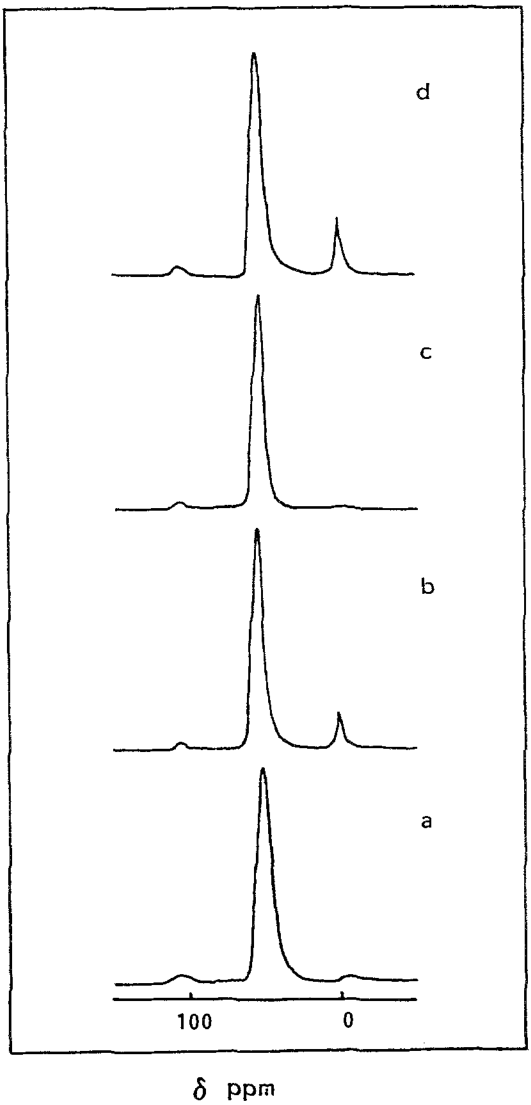

Fig. 1. ^{27}Al MAS NMR spectra at 104.27 MHz of the BETA zeolites. a: As-synthesized, b: solid a calcined at 550 °C, c: solid b treated in NH_4NO_3 and d: solid c calcined at 550 °C.

According to some reports (see ref. [12]), realumination occurs by elimination, through dissolution, of Si(4Si) sites and further incorporation of aluminate anions in the tetrahedral vacancies. The presence of a strong base is then required in order partially to dissolve the zeolite. In the present case, the reaction occurs in a slightly acidic medium. In these conditions the silicate framework is not expected to dissolve and this accounts for the absence of significant amounts of silicates in the filtrate. The ease of aluminium reinsertion in zeolite BETA is likely to be related to the high density of defect sites evidenced by IR spectroscopy. When the

Table 1
Physico-chemical characteristics of BETA zeolites as a function of the various treatments. C: calcination in air at 550 °C and E: exchange with NH_4NO_3 at reflux for 4 h

Zeolite	Si/Al	Unit cell		IR lattice frequencies (cm^{-1})		
		a (nm)	c			
BETA	16.9	1.245	2.659	1076	781	568
BETA C	16.6	1.234	2.631	1087	793	571
BETA CE	16.2	1.247	2.655	1085	788	569
BETA CEC	16.2	1.242	2.640	1088	791	571
BETA CECE	16	1.246	2.647	1085	790	569
BETA CECEC	16.1	1.245	2.638	1089	791	572

calcination-exchange procedure was repeated on the ammonium-exchanged samples, the very same phenomena described above occurred: nearly 25% of the framework aluminium was extracted at high temperature and quantitatively reinserted by ion-exchange (table 1, fig. 1d).

Since the thermal decomposition of ammonium cations is widely and efficiently used for the preparation of protonic (acidic) zeolites, experiments were designed to test whether a true H-form of zeolite BETA, i.e. not containing extra-framework species, could be obtained in this way. A sample of NH_4-BETA

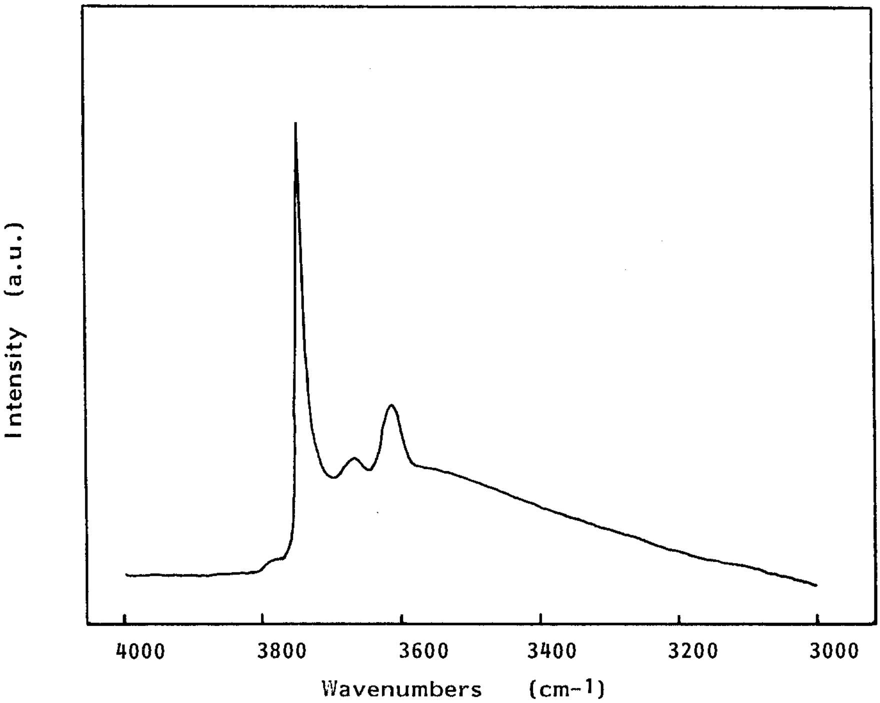

Fig. 2. FTIR spectrum of the hydroxyl region of the parent zeolite calcined at 550 °C.

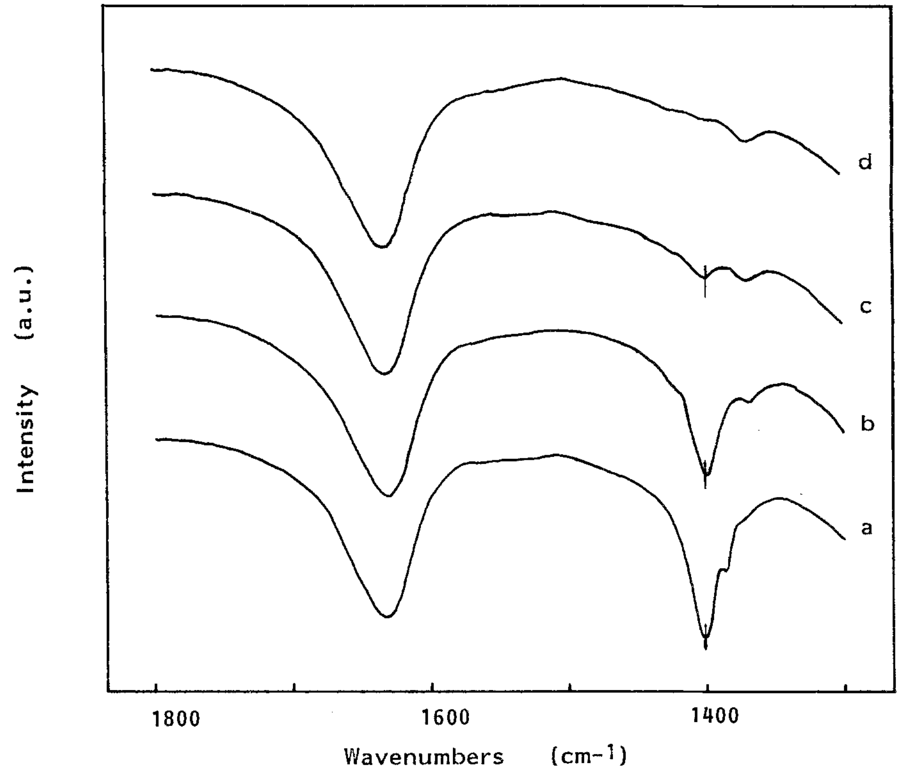

Fig. 3. FTIR spectra of the region 1800–1300 cm^{-1} of NH_4-BETA calcined at increasing temperatures. a: starting material, b: 250 ° C, c: 300 ° C and d: 450 ° C.

was calcined for two hours at increasing temperatures using dry air or nitrogen as gas purge. At each step the solid was characterized. The decomposition of the ammonium cation was monitored by IR spectroscopy, by following the disappearance of the N–H bending band at 1400 cm^{-1}, and by measuring the residual nitrogen content of the sample by elemental analysis.

Figures 3 and 4 summarize results obtained under air atmosphere The decomposition of the ammonium cations began at 250 ° C and was completed at 450 ° C, which is a relatively low temperature for deammoniation of a zeolite. In spite of this, ^{27}Al NMR gave evidence for the presence of octahedral aluminium in the solid. The signal at 0 ppm was already detected after calcination at 250 ° C (fig. 4b), its intensity increased with the level of deamoniation. The experiments performed under nitrogen led to a similar behavior.

These data demonstrate a low thermal stability of tetrahedral sites occupied by aluminium atoms in zeolite BETA. It has been suggested recently [3] that aluminium atoms in zeolite BETA were located in the center of chains of five four-rings in the form of double S. Such a location would result in highly strained environments of the aluminium sites which could account for their ready removal

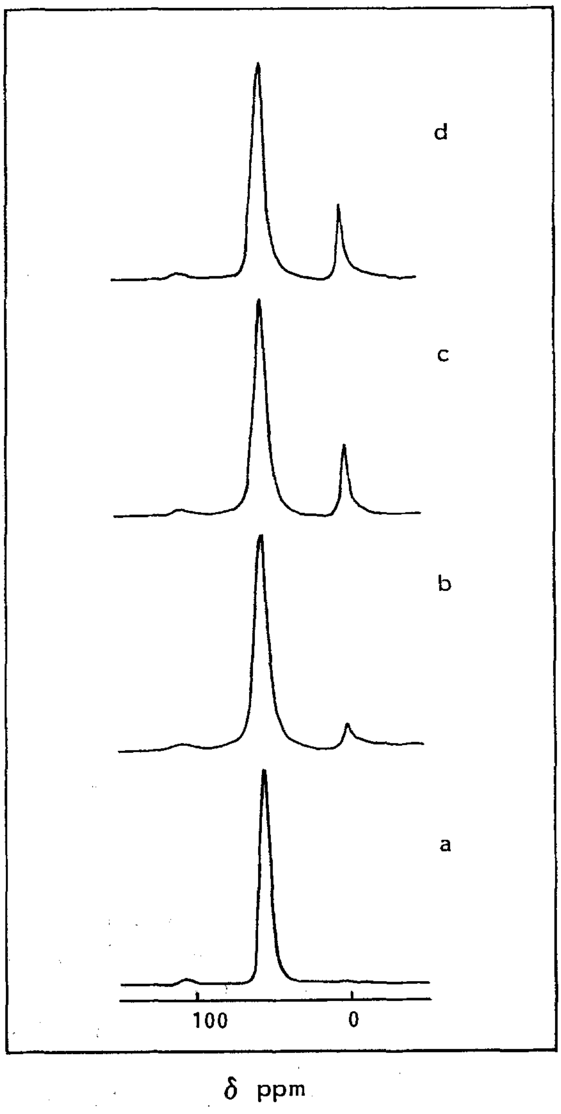

Fig. 4. ^{27}Al MAS NMR spectra of NH_4-BETA calcined at increasing temperatures. a: starting material, b: 250 °C, c: 300 °C and d: 450 °C.

upon heating. The latter assumption is however not fully consistent with the ease of reinsertion shown here. The reversibility of the dealumination-realumination process in zeolite BETA requires obviously further attention. At this stage, it can be nevertheless concluded that the conventional method of preparation of protonic zeolites by calcination of ammonium exchanged forms may not allow to obtain solids free of octahedral aluminic species in the case of zeolite BETA.

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