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Magic Angle Spinning ^{29}Si and ^{27}Al NMR Study of Mordenite Dealumination

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Abstract. Magic angle spinning ^{29}Si NMR presents a rapid qualitative method of assessing the degree of dealumination of sodium mordenite modified by acid leaching and heat treatment. A quantitative determination of the ^{29}Si coordination sphere is hampered by the overlap of chemical shift ranges for Si–O–Al and Si–O–H species. MAS ^{27}Al NMR indicates the presence of octahedrally coordinated Al in interstitial sites in all treated samples. On treating mordenite samples at high temperatures ($\sim 700^\circ\text{C}$) much of the Al becomes invisible to the NMR experiment because of its location in sites of low symmetry and large quadrupole coupling constant.

Key words: Magic angle spinning ^{29}Si NMR, magic angle spinning ^{27}Al NMR, sodium mordenite, zeolites.

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1. Introduction

The catalytic and sorptive properties of zeolites are known to depend strongly on the silicon to aluminum ratio and the nature of the exchangeable cations in the structure. For mordenites, particularly active catalysts may be produced by acid-leaching decationation, or by calcining the ammonium-exchanged mordenites [1–3].

The nature of the active sites and the distribution of aluminum in the lattice are problems of continuing interest [1–7], as aluminosilicates may be difficult to study by conventional techniques such as X-ray diffraction.

Recent work has shown the great utility of solid state NMR techniques in the study of aluminosilicates. ^{29}Si NMR has been used [8–11] to study the type of Al–Si ordering whereas ^{27}Al NMR was utilized [12] to distinguish tetrahedrally- from octahedrally-coordinated aluminum.

In this study we use solid state ^{29}Si , ^{27}Al and ^{23}Na NMR to see if such techniques can be used to follow acid leaching and heat treatment modification of sodium mordenite.

2. Experimental

Sodium mordenite obtained from Strem Chemical Co., was leached with 1N HCl, for ~ 15 min, then washed with water several times and dried at 70°C for ~ 12 h. Before obtaining NMR spectra, samples were left to rehydrate under ambient conditions for at least a day. In some cases the time dependence of the NMR spectrum after heating was checked as well.

A second sodium mordenite sample was leached with hot 8N HCl for 12 h and washed with water until the sample was free of chloride. As for the previous sample, portions of the acid

leached sample were calcined at 500 and 750 °C. The partial rehydration of the samples heated to 750 °C was very slow and required heating of the sample in presence of water vapour.

A third sodium mordenite sample was exchanged three times with excess 1N NH₄Cl solution, washed, then calcined in air at 500 °C for ~ 12 h.

²⁹Si, ²⁷Al and ²³Na NMR spectra were obtained at 35.8, 46.9 and 47.6 MHz on a Bruker CXP-180 NMR spectrometer. Samples were spun at the magic angle ($\theta = 54.7^\circ$) in Delrin rotors of the Andrew type. Spinning speeds up to 6 kHz were used. The number of free induction decays accumulated were 400–2000 for Al or Na, 2000–4000 for Si at repetition rates of 1 to 10 s. In some instances high power ¹H decoupling was applied as well. ²⁹Si chemical shifts were measured with respect to solid hexamethylcyclotrisiloxane and converted to the TMS scale. ²⁷Al chemical shifts were measured with respect to solid Al (H₂O)₆³⁺.

3. Results and Discussion

To aid in assignment of the ²⁹Si NMR spectra, some of the ²⁹Si spectral assignments made recently [10, 11] for different kinds of Si structural types in aluminosilicates and silica gel are shown in Table I.

Table I. ²⁹Si chemical shift assignments

Structural Type	²⁹ Si chemical shift (ppm from TMS)
Si(0Si, 4Al)	– 80 to – 87 ^a
Si(1Si, 3Al)	– 88 to – 95 ^a
Si(2Si, 2Al)	– 93 to – 100 ^a
Si(3Si, 1Al)	– 97 to – 106 ^a
Si(4Si, 0Al)	– 102 to – 115 ^a
Si(2Si, 2H)	– 90.6 ^b
Si(3Si, 1H)	– 99.8 ^b

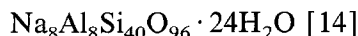
^a Chemical shifts for aluminosilicates, ref. [10].

^b Chemical shifts for silica gel, ref. [11].

The ²⁹Si NMR spectrum (Figures 1(a), 2(a)) of sodium mordenite shows three peaks at – 98.5, – 105 and – 112 ppm that can be assigned to Si(2Si, 2Al), Si(3Si, 1Al) and Si(4Si). The ²⁷Al spectrum (Figures 1(b), 2(b)) shows a single line at 52 ppm, which indicates that all of the aluminum atoms are in tetrahedral lattice sites. The Si/Al ratio for the sample can be found from the relative intensity of the three lines in the ²⁹Si NMR spectrum from [9]

$$\text{Si/Al} = \frac{\sum_{n=0}^4 I(\text{Si}(n\text{Al}))}{\sum_{n=0}^4 0.25nI(\text{Si}(n\text{Al}))} \quad (1)$$

where $I(\text{Si}(n\text{Al}))$ is the intensity of the line for Si with n Al units attached, yielding a value of 4.7, close to that expected from the ideal formula



Comparison of the ²³Na NMR spectrum of the unaltered mordenite and the sample leached with 1N HCl for 15 min shows that at least 90% of the sodium was removed. The ²⁷Al NMR spectrum shows that there is a significant quantity of octahedrally-coordinated aluminium

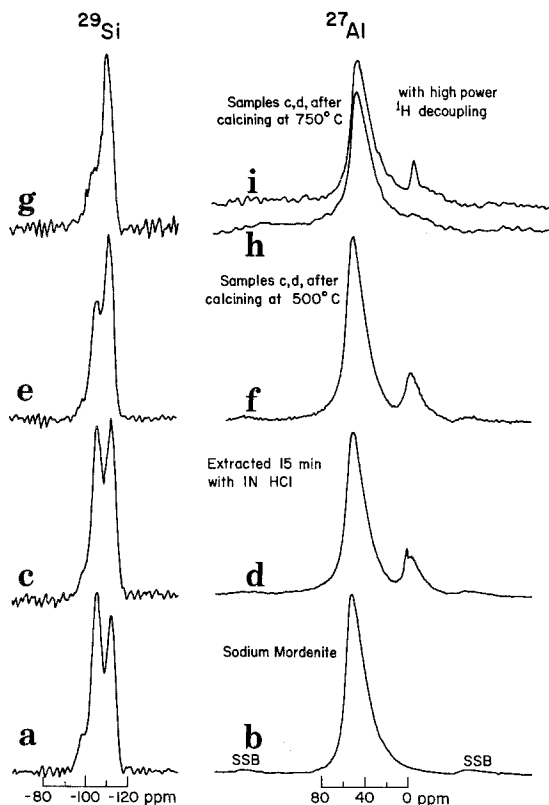


Fig. 1. MAS ^{29}Si and ^{27}Al NMR spectra of (a), (b) sodium mordenite; (c), (d) mildly extracted sodium mordenite; (e), (f) sodium mordenite mildly extracted and heated to 500 °C; (g) (h) sodium mordenite mildly extracted and heated to 750 °C and (i) with high power proton decoupling. SSB marks spinning side-bands.

located in interstitial sites, so that all of the aluminum released from tetrahedral sites is not removed from the mordenite crystal. The intensity of the low field lines in the ^{29}Si NMR spectrum reflects the decrease in the number of Si–O–Al bonds. An estimate of the Si/Al ratio can be made using Equation (1) and the relative intensities shown in Figure 1(c), giving a value of ~ 4.3 . ^1H NMR studies [13] have been used to establish the presence of OH groups in acid-leached sodium mordenite. Both Al–OH and Si–OH site types were proposed, the total number of hydroxyls being estimated to be $\sim 7/\text{unit cell}$ for a sample dehydrated at 300 or 400 °C. On consulting Table I, ^{29}Si NMR contributions from Si(3Si, Al) and Si(3Si, H) can be expected to overlap, so that the Si/Al ratio obtained from the relative line intensities must be considered as an upper limit.

Calcining the acid leached sample at 500 °C in air causes a further reduction in the low field line intensities of the ^{29}Si spectrum, whereas the ^{27}Al spectrum is virtually unchanged. The simplest explanation is that heating serves to reduce the number of Si–OH bonds, water being generated and causing a conversion of Si(3Si, H) to Si(4Si) units. The conversion of Si(3Si, Al) to Si(4Si) by heating cannot be ruled out completely, although the heating step

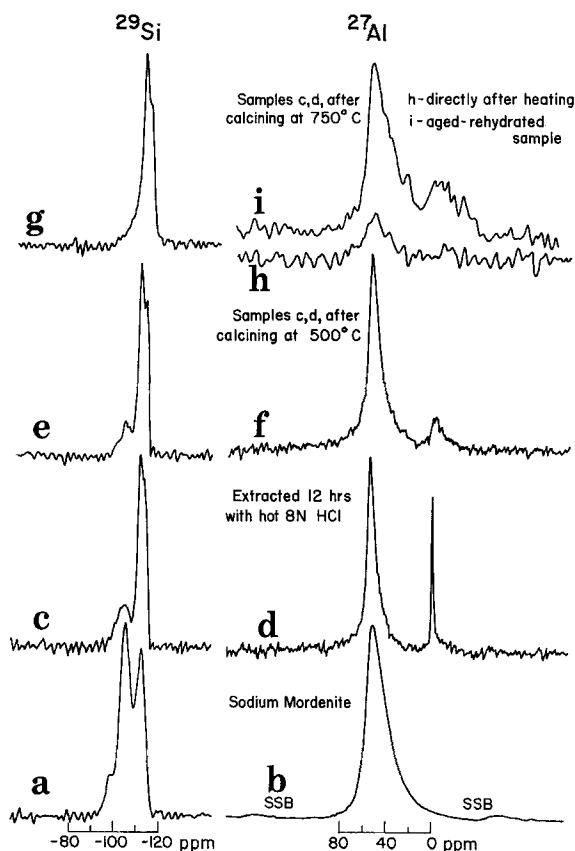


Fig. 2. MAS ^{29}Si and ^{27}Al NMR spectra of (a), (b) sodium mordenite; (c) (d) severely extracted sodium mordenite; (e) (f) sodium mordenite severely extracted and heated to 500°C ; (g) (h) sodium mordenite severely extracted and heated to 750°C and (i) same as for (h) but sample rehydrated at 80°C for several days. SSB marks spinning side-bands.

apparently has no effect on the Al line intensities (Figures 1(d), 1(f)). In general, the NMR experiments seem to bear out that heating to 500°C causes no irreversible effects on the ^{27}Al NMR spectrum (see also the results for the calcined NH_4^+ mordenite further on).

The mechanism whereby $\text{Si}(3\text{Si}, \text{Al})$ sites are converted to $\text{Si}(4\text{Si})$ is still not well understood. Some authors suggest that in each case a 'hydroxyl nest' (4 neighbouring $\text{Si}(3\text{Si}, \text{H})$ groups) is produced as an intermediate, although there is no infrared evidence for such species [4, 5]. The conversion of $\text{Si}(3\text{Si}, \text{H})$ to $\text{Si}(4\text{Si})$ with loss of water would then require the migration of Si, or distortion of the lattice to allow condensation of neighbouring $\text{Si}-\text{OH}$ units.

Heating of the leached samples to higher temperatures affects both ^{29}Si and ^{27}Al spectra markedly (Figures 1(g), (h), (i)). The ^{27}Al lines, especially the one for octahedrally coordinated Al, have broadened considerably. This means that the octahedral Al now especially resides in a less symmetric environment, probably because of dehydration accompanied by condensation of interstitial $[\text{Al}(\text{OH})_m(\text{H}_2\text{O})_{6-m}]^{(3-m)+}$ units, which on a timescale of several weeks, at least, is irreversible. Some of the octahedral Al does still reside in a symmetric environment, the main broadening mechanism being dipolar in origin, and giving a sharp line on the

application of high-power proton decoupling (Figure 1(i)). From the ^{29}Si spectrum (Figure 1(g)), the apparent number of $\text{Si}(\text{3Si}, \text{Al})$ units has declined by $\sim 70\%$. Possible contributions from $\text{Si}(\text{3Si}, \text{H})$ to the line at -105 ppm are probably extremely small in the sample after heat treatment at 750°C .

More severe acid treatment of the Na mordenite removes most of the Al from the lattice (Figure 2(c)). The corresponding ^{27}Al NMR spectrum (Figure 2(d)) shows that both tetrahedral and octahedral Al are still present in the sample, the octahedral Al apparently in a highly mobile form. On heating to 500°C , both lines, but especially the octahedral Al line, broaden significantly, although the relative areas appear to remain intact. The ^{29}Si spectrum shows an additional interesting feature: a shoulder is now visible at ~ 115 ppm which is better resolved for the sample heated to 500°C (Figure 2(e)). This line may be due to Si units which have no Al in the first or second coordination spheres. The change on heating in the line at -105 ppm may again reflect the disappearance of $\text{Si}(\text{3Si}, \text{H})$ units, as the Al spectrum, except for line broadening, changes little.

On calcining this acid leached sample at 750°C , there is a further reduction in the -106 ppm line intensity. The Al spectrum (Figure 2(h)), taken two days after heating shows only a weak tetrahedral Al line. After storing the sample over water at 80°C for several days, the spectrum shown in Figure 2(i) results, showing a marked improvement in S/N ratio, and also the presence of a significant quantity of octahedral Al. As for the previous sample, (Figure 1(i)), heating to 750°C apparently causes dehydration and condensation of complex Al species which causes the Al to reside in sites of relatively low symmetry. The very slow, partial rehydration again restores the Al to more symmetric sites. It is to be noted that both lattice and interstitial Al are affected this way, suggesting that in the absence of water the lattice must

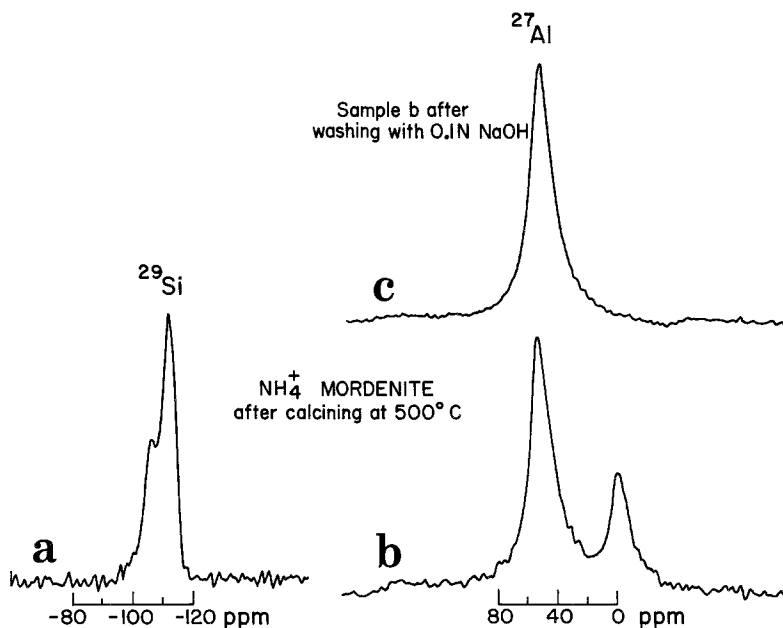


Fig. 3. (a), (b) MAS ^{29}Si and ^{27}Al NMR spectra of ammonium exchanged sodium mordenite, calcined at 500°C ; (c) same as (b) but after washing with 0.1 N NaOH solution.

be distorted. Figures 2(f), (h), (i) also illustrate how Al, by changing the symmetry of the Al sites, can become essentially invisible to the NMR experiment.

A particularly active catalyst can be made by calcining an ammonium-exchanged mordenite at 500 °C to form a hydrogen mordenite [2, 3]. Exchanging the cation does not alter the lattice structure of the mordenite and, hence, does not affect the ^{29}Si or ^{27}Al NMR spectrum. On calcining the sample at 500 °C, the spectra shown in Figures 3(a), (b) are obtained. Both ^{29}Si and ^{27}Al NMR spectra bear some resemblance to those for the mildly acid leached sample after calcining at 500 °C (Figures 1(e), (f)), although apparently the calcined ammonium mordenite has fewer Si(3Si, Al) units and more interstitial Al.

In actual fact, it may be better to regard the hydrogen mordenite as an aluminum mordenite. For purposes of charge neutrality, each ammonium ion can be replaced by a 'hydrogen ion' or $1/3 \text{ Al}^{3+}$. Figure 3(b) shows that tetrahedral and octahedral Al exists in a ratio of $\sim 3 : 1$, exactly correct if all interstitial Al exists as Al^{3+} species.

Figure 3(c) shows that the octahedral Al is quite mobile, as it can be completely exchanged from the mordenite interstices by Na^+ in dilute sodium hydroxide solution.

4. Conclusions

The dealumination of mordenites or other zeolites by acid leaching and heat treatment may be followed in a general way by ^{29}Si NMR, although a quantitative interpretation of the ^{29}Si NMR spectrum in terms of the Si coordination sphere is hampered by an overlap of the Si(3Si, Al) and Si(3Si, H) and also the Si(2Si, 2Al) and Si(2Si, 2H) chemical shift ranges. For quantitative work, ^{29}Si MAS NMR experiments may have to be combined with ^1H or ^{29}Si CP/MAS NMR experiments.

Although ^{27}Al NMR appears to reflect the Al content of samples which have not been heated to high temperatures, serious problems arise when an apparently irreversible dehydration takes place. Much of the Al then appears to occupy sites of low symmetry, and becomes 'invisible' to the NMR experiment.

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