

ARTICLES

 ^{27}Al – ^1H REDOR NMR and ^{27}Al Spin-Echo Editing: A New Way To Characterize Brönsted and Lewis Acidity in Zeolites

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A new approach to the NMR characterization of acid zeolites is described. The approach is based on (i) the quantitative comparison of the rotational echo double-resonance (REDOR) evolution curves obtained by one-pulse excitation and by cross-polarization excitation and (ii) the spin-echo editing technique. The procedure that is described allows a “reconstruction” of ^{27}Al NMR spectra corresponding to either Lewis sites or nonframework (NF) Al. The approach is applied to the characterization of the dealuminated mordenite DHM600 with chemisorbed ammonia as a proton reservoir for polarization transfer. The second moment analysis suggests that the NF Lewis sites are constituted by a pair of Al atoms having chemisorbed NH_3 . The procedure provides a means for obtaining framework Si/Al ratios. The values obtained are more reliable than ones determined by the standard ^{29}Si MAS NMR method, since a possible coupling between NF species and the framework is taken into account.

1. Introduction

It is a common knowledge that catalytic activity of dealuminated H–zeolites in acid-catalyzed reactions is dictated by a combined effect of Brönsted and Lewis acid sites.¹ The Brönsted sites are acidic OHs bridging silicon to framework aluminum (FAI) in the zeolite structure, while the Lewis sites are assigned to coordinately unsaturated Al in the nonframework (NF) alumina-like nanoparticles. In order to understand the nature of acidity in zeolites, a reliable characterization of the two kinds of acid sites is required that would provide information on their number, relative strength, and local topology. Several techniques are available for this purpose; currently, NMR spectroscopy is the technique chosen most often.^{2,3}

Earlier, we showed that chemisorbed ammonia is well-suited for NMR characterization of acid sites in transition aluminas,⁴ and dealuminated zeolites,⁵ since NH_3 protons can serve as a polarization reservoir for nearby magnetic nuclei, either ^{27}Al ⁴ or ^{29}Si .⁵ This is achieved by the NMR technique known as cross-polarization (CP) excitation. Combined with standard magic-angle spinning (CP/MAS), it can give high-resolution NMR spectra of either ^{27}Al or ^{29}Si which are in the proximity of the acid sites.

In this presentation we describe a new way to characterize acid sites (Lewis and Brönsted) in dealuminated H–zeolites prepared under a controlled atmosphere using chemisorbed NH_3 as a surface probe. The approach is founded on (i) the quantitative comparison of the rotational echo double-resonance (REDOR) evolution curves obtained by one-pulse and CP excitation⁶ and (ii) the spin-echo editing technique.⁷ The REDOR technique allows one to reintroduce heteronuclear dipolar interaction into conventional CP/MAS NMR spectra and, thus, provides valuable structural information.^{5,8} In the case of CP excitation, all excited nuclei contribute to the REDOR

response; alternatively, in the one-pulse experiment only those nuclei that are at less than 4–5 Å from chemisorbed ammonia produce a detectable REDOR effect.

The spin-echo editing procedure for ^{27}Al NMR spectra of zeolites, aluminosilicates, and transition alumina has been described in several publications.^{7,9–11} In this paper we demonstrate the potential of this approach in the quantitative characterization of different kinds of surface acidity in dealuminated H–mordenite/ NH_3 (Si/FAI ratio ≈ 10). Several reasons dictated the choice of this zeolite. It has a relatively large number of both strong Brönsted and Lewis acid sites,¹² and its crystallinity is barely affected by the dealumination treatment.¹³ Finally, earlier studies in this laboratory yielded a rather complete characterization of the material.¹⁴

2. Experimental Section

Materials. The parent Na–mordenite was a commercial product from Union Carbide, Linde Division (LZM5), with an Si/Al ratio of 5.2. DHM600 was obtained by modifying the parent Na–mordenite as described in ref 14, where it was designated as VG600. The Si/FAI ratio (from ^{29}Si MAS NMR) was ~ 10 .

DHM600 was reactivated under vacuum (10^{-4} Torr) at 450 °C for 3 h before it was exposed to gaseous ammonia (Aldrich, 98% ^{15}N enrichment). $^{15}\text{NH}_3$ adsorption was performed at 115 °C for 20 min, following which the sample (DHM600/ NH_3) was outgassed at the same temperature for 30 min and sealed in glass vials. The vials were broken in a glovebox under N_2 atmosphere, and their content was transferred directly into the MAS spinner. It is important to point out that in this spinner the proton NMR spectrum of the sample remained unchanged during the entire experiment (for about 3 days). Hence, rehydration, if it ever occurred, did not produce any observable modification.

Instrumentation. All NMR experiments were performed under MAS conditions in a 11.7 T static field with a GN500

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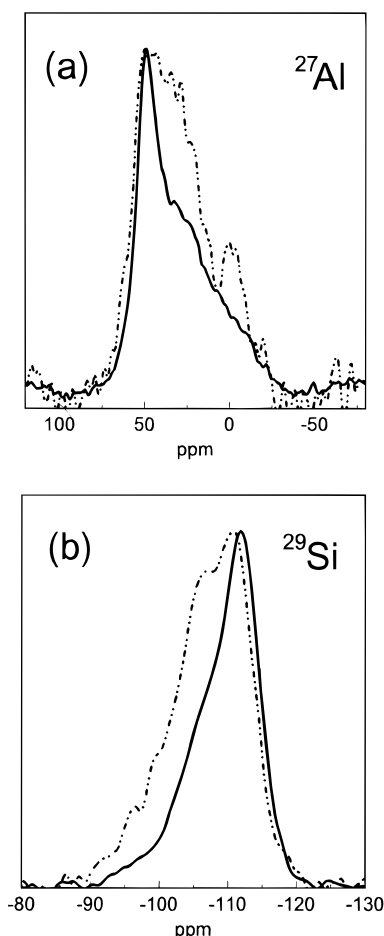


Figure 1. One-pulse and CP MAS NMR spectra of DHM600/ NH_3 : (a) ^{27}Al , (b) ^{29}Si . Solid lines are one-pulse spectra, and dashed lines are CP spectra.

spectrometer equipped with a Doty 5 mm MAS probe. The spinning rates were 7 kHz for ^{29}Si and 12 kHz for ^{27}Al . The contact times for cross-polarization were 10 ms for ^{29}Si and 1 ms for ^{27}Al . The Hartmann–Hahn condition was adjusted prior to each experiment with a fixed power level in the proton channel (≈ 50 kHz for cross-polarization and ≈ 60 kHz for 180° pulses). We used a standard REDOR pulse sequence with two symmetric 180° pulses per rotor cycle⁸ and proceeded either by one-pulse or by a ^1H - ^{29}Si (^{27}Al) CP excitation.⁶ The Hahn spin-echo ^{27}Al spectra were obtained as part of the REDOR experiment by switching off the proton amplifier. The setup and fitting procedures for the REDOR experiments have been detailed in earlier publications.^{6,7}

3. Results

One-Pulse and CP MAS ^{27}Al and ^{29}Si NMR Spectra.

Examples of such spectra are shown in Figure 1. The CP spectra should exhibit a noticeable enhancement of the signal intensities of the nuclei that are in the vicinity of chemisorbed ammonia. However, there are several reasons that make the quantitative analysis of CP spectra quite ambiguous.

In the case of ^1H - ^{27}Al CP experiments the very low efficiency of the magnetization transfer from protons to quadrupolar nuclei¹⁵ causes problems of sensitivity.

On the other hand, while the efficiency of the ^1H - ^{29}Si CP experiment is rather high, it suffers from very low selectivity. The latter is due to the wide variety of ^{29}Si sites in the zeolite framework; the discrimination of the sites with respect to their dipolar interaction with chemisorbed ammonia does not neces-

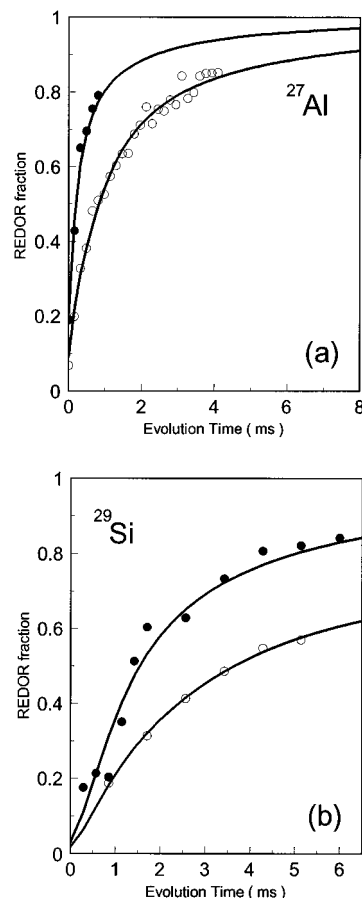


Figure 2. Total REDOR response curves: (a) ^{27}Al , (b) ^{29}Si ; (○) One-pulse REDOR experimental points, (●) CP REDOR experimental points. Solid lines are calculated best-fitting curves.

sarily mean the establishment of bonding connectivities. Due to specific features of the three-dimensional zeolite structure, different silicon atoms belonging to either the $^4\text{Q}(0\text{Al})$ or $^4\text{Q}(1\text{Al})$ type may experience a comparable dipolar coupling with ammonia. Also, poor resolution of the spectra presented in Figure 1, which is typical for disordered dealuminated and dehydrated zeolite materials, hampers reliable deconvolution and assignments of discrete Si or Al sites.

REDOR. Four total REDOR response curves (^1H - ^{27}Al CP, ^1H - ^{27}Al one pulse, ^1H - ^{29}Si CP, and ^1H - ^{29}Si one pulse) for the sample DHM600/ NH_3 are shown in Figure 2. These data provide the basis for the subsequent treatment and discussion.

From these plots it is evident that there is a pronounced difference between one-pulse and CP REDOR behavior of ^{27}Al and ^{29}Si . Closer inspection will show that the REDOR responses differ inherently.

In ^1H - ^{27}Al experiments both curves eventually approach the level at which $\Delta S/S_0 = 1$ (complete REDOR dephasing), but in the case of CP excitation the evolution proceeds on an apparently faster time scale. This means that almost every Al atom (either FAI or NFAI) has some protons within a 4–5 Å distance, but the efficiency of the CP procedure is not enough to excite all Al sites.

In contrast, the limiting values of the ^1H - ^{29}Si REDOR curves are 1.0 for the CP excitation and about 0.7 for one-pulse excitation, the time scale of both evolutions being approximately the same. The asymptotic behavior of the one-pulse ^1H - ^{29}Si REDOR curve suggests that a certain portion (about 30%) of Si atoms has no proton neighbors within a 4–5 Å distance. Thus, these Si atoms are isolated from protons or from the Brönsted or Lewis sites.

TABLE 1: Calculated Heteronuclear Second Moment for Various Structural Fragments in Zeolites (kHz²)^a

²⁷ Al– ¹ H		²⁹ Si– ¹ H	
L: Al:NH ₃	2–4 ^b	B: Si–O–(NH ₄) ⁺ –Al	0.4–0.8 ^c
L: Al:NH ₃ ···Al	8–9 ^c	NB: Si–	1–2
L: Al–O–Al:NH ₃	0.5–1.0	O(H···NH ₃)–Al	
B: Al–O–(NH ₄) ⁺ –Si	0.8–1.5 ^d		

^a L = Lewis; B = Brönsted; NB = non-Brönsted. ^b Assuming Al–N distance 1.95 Å, depending on the rotational state of NH₃. ^c See text for structural parameters. ^d Geometry of the fragment was taken from ref 16. ^e See ref 5.

The fitting procedure described in ref 5 allows one to fit REDOR evolution curves with a sum of several components, each corresponding to the contribution from nuclei with a specified value of the heteronuclear second moment. For the ¹H–²⁷Al CP REDOR evolution curve, only one component with very strong ¹H–²⁷Al coupling (²⁷Al–¹H heteronuclear second moment $M_2 \approx 9$ kHz²) was found. On the contrary, the fitting of ¹H–²⁷Al one-pulse REDOR evolution curve required at least two components. One component (42%) was the same as that found for the CP REDOR curve, and the other one (57%) was a component with a much smaller second moment of about 0.4 kHz².

The theoretical ²⁷Al–¹H heteronuclear second moments in the order of magnitude of the experimental ones may be easily calculated for various structural fragments.² In these calculations we used the well-known structure of the NH₃ molecule with the N–H bond length of 1 Å. The most difficult problem was to suggest the structure that would correspond to the strong REDOR component with $M_2^{\text{Al–H}} \approx 9$ kHz². If one considers the simplest fragment Al:NH₃ as a candidate for the NH₃ chemisorbed adduct, the required value of the second moment is achieved with the Al–N distance of ~ 1.6 Å. This value is far too small; typical Al–N distances lie in the range 1.85–2.05 Å. Quantum-mechanical calculations for various structures of NH₃ chemisorption on Lewis sites gave the Al–N distances in the range 1.90–2.05 Å in all cases.¹⁶

An alternative structural model could be the one in which the chemisorbed NH₃ molecule is shared by two Al atoms: Al···(NH₃):Al. In this case the tilt of Al–N vector with respect to the Al–Al one shortens the effective Al–H distances. The calculations showed that the large value of $M_2^{\text{Al–H}} \approx 9$ kHz² can be achieved with the following structural parameters: $r_{\text{Al–N}} = 2 \pm 0.05$ Å, $\angle \text{N–Al–Al} = 38 \pm 3^\circ$. The Al–N–Al angle is, thus, close to the tetrahedral value.

The calculated values of the second moments for various structural fragments are given in Table 1.

From the second moment analysis it follows that the strong component with $M_2 \approx 9$ kHz² cannot be assigned to a structural fragment other than a Lewis acid site with chemisorbed ammonia shared by two aluminums.

The weaker component with $M_2 \approx 0.4$ kHz² corresponds to the remaining Al atoms. These atoms are constituents of either an Al–O(NH₄⁺)–Si unit within a framework Brönsted center or to an Al–O–Al–NH₃ fragment, which is a nonacidic NFAI neighboring a Lewis center. The latter two structures have close values of ²⁷Al–¹H second moments and are not distinguishable by a fitting procedure.

These data lead us to an important and rather unexpected conclusion that a typical ¹H–²⁷Al CP experiment with chemisorbed NH₃ as a proton reservoir can excite only Lewis acidic nonframework Al sites. The reason for this is, of course, the low efficiency of the magnetization transfer from chemisorbed ammonia to the adjacent aluminum. The contact time used in

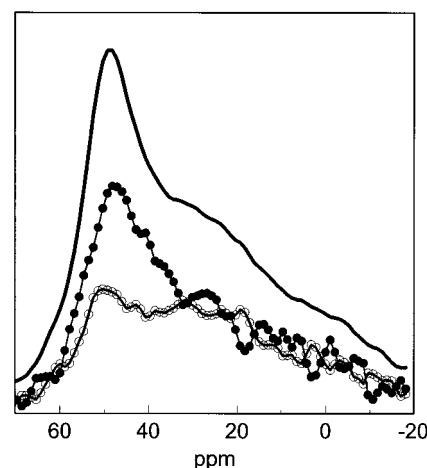


Figure 3. Deconvolution of ²⁷Al one-pulse spectrum by two REDOR components: (O) “strong” REDOR component; (●) “weak” REDOR component. The one-pulse ²⁷Al MAS NMR spectrum is also shown (solid line).

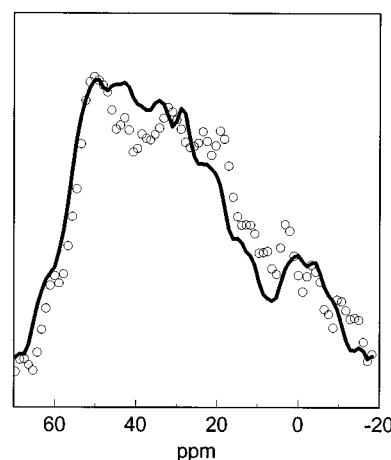


Figure 4. Similarity of REDOR strong component and CP MAS spectrum: (O) REDOR strong component, (solid line) CP MAS ²⁷Al spectrum.

the ¹H–²⁷Al CP experiment was less than 1 ms as compared to 10 ms for the ¹H–²⁹Si CP experiments.

In order to get a spectral distribution of the two REDOR components in a ¹H–²⁷Al one-pulse REDOR experiment, every spectrum was cut into narrow slices, and every slice was fitted with two components (the “strong” component with $M_2 = 9$ kHz² and the “weak” one with $M_2 = 0.4$ kHz²) in order to get the relative weights of the two components for each slice. We did not fix the sum of the two components to be 1, but for every slice the sum fell into the region 0.9–1.1. The relative weights of the two components were then multiplied by the experimental one-pulse spectrum, and the distribution of the two components was obtained (Figure 3).

One can see that the line shape of the strong component is very similar to the CP spectrum (Figure 4), which confirmed our former statement that CP from chemisorbed NH₃ can excite only Lewis acidic nonframework Al sites.

²⁷Al Spin–Spin Relaxation. Figure 5 displays the integrated intensity of the one-pulse ²⁷Al spin-echo NMR spectrum as a function of the evolution time. This is a typical Hahn echo two-pulse experiment under MAS conditions, each point being collected at a time synchronized with the rotor period. The relaxation decay is apparently biexponential; it has a “fast” component with a short T_2 (1.2 ms) and a “slow” one with a longer T_2 (5.8 ms). Following the procedure described above, we obtained the spectral distribution of the two components by

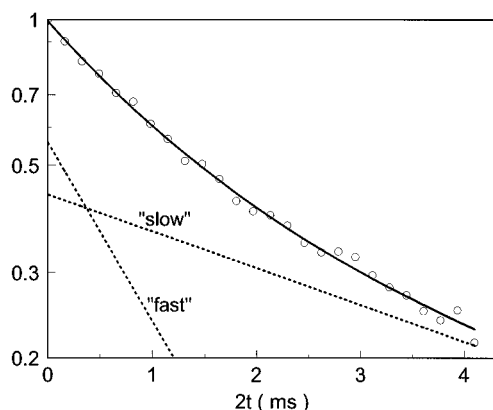


Figure 5. Integrated intensity of one-pulse ^{27}Al spectrum vs evolution time: fitting curve (solid line), components (dotted lines). Note that the vertical scale is logarithmic.

cutting the spectra into narrow slices. For each slice, the decay of the relative intensity of the slice was fitted with the above two T_2 values. The resulting distribution of the two T_2 components is shown in Figure 6a.

^1H - ^{29}Si REDOR. As mentioned above, about 30% of all Si atoms are isolated from protons. Obviously, the distribution of the isolated sites is not uniform throughout the zeolite structure. One can expect more Si(0Al) sites to be isolated than Si(1Al) sites or Si(2Al) sites. In order to get a distribution of the isolated sites, the asymptotic value of the ^1H - ^{29}Si one-pulse REDOR response was compared with the asymptotic value of the CP REDOR counterpart for each spectrum slice. (We used our experimental points with the longest evolution period as the approximation of the asymptotic value.) The resulting curve, which is the ratio of two asymptotic values ($S_{1\text{pulse}}/S_{\text{CP}}$) vs ppm, is shown in Figure 7 together with the ^{29}Si one-pulse and CP spectra.

Three plateaus can be clearly seen in Figure 7. At the Si-(2Al) region, there is a plateau with value close to 1, which means that 100% of the Si(2Al) atoms have protons close by (4–5 Å), and none of them is isolated. At the Si(1Al) region, the value is about 0.8, which means that about 20% of Si(1Al) atoms are isolated, and at the Si(0Al) region, the percentage of isolated Si atoms is about 35%.

4. Discussion

It follows from the previous section that the dipolar coupling between magnetic nuclei plays an important role in this study as a source of structural information. The approach generally used is to study spinning sidebands pattern in ^1H MAS NMR spectra, when it is due to the ^1H - ^{27}Al heteronuclear dipolar coupling.^{17–19} Using this method, the ^1H - ^{27}Al distance in H-zeolites may be obtained in appropriate cases. $^1\text{H}\{^{27}\text{Al}\}$ double-resonance experiments²⁰ may also provide information on connectivities in zeolite framework.

The theory and practice of spin-editing by a spin-echo technique has been developed by Oldfield et al.^{9–11} They have shown that the main contribution to the ^{27}Al spin-spin relaxation in zeolites and transition alumina comes mainly from ^{27}Al quadrupolar interaction and from the ^{27}Al - ^{27}Al homonuclear interaction. A clear distinction between the spin-spin relaxation rate of framework zeolitic aluminum and that of nonframework or “nonzeolitic” aluminum has been observed.⁹

^1H - ^{27}Al REDOR Analysis and Spin-Spin Relaxation. Depending upon the technique, three different distributions of Al species along the chemical shift (ppm) axis were obtained. The first one is the distribution of Al atoms with different

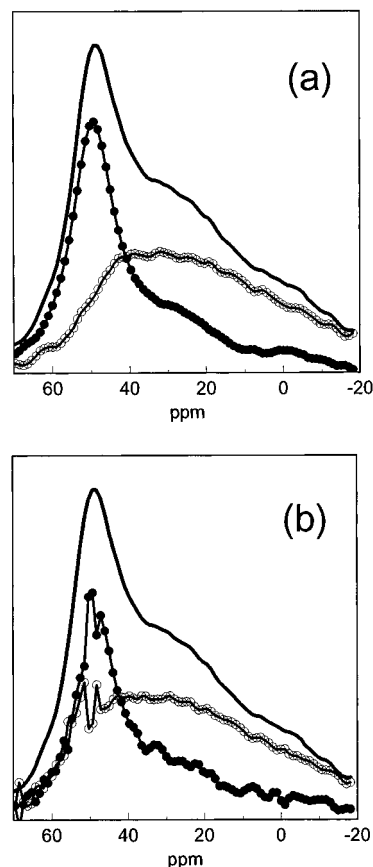


Figure 6. Deconvolution of ^{27}Al one-pulse spectrum by spin-editing technique. (a) Both time constants are fixed: (O) “fast” component, (●) “slow” component. (b) Only the time constant for the “slow” component is fixed: (O) “fast” component, (●) “slow” component.

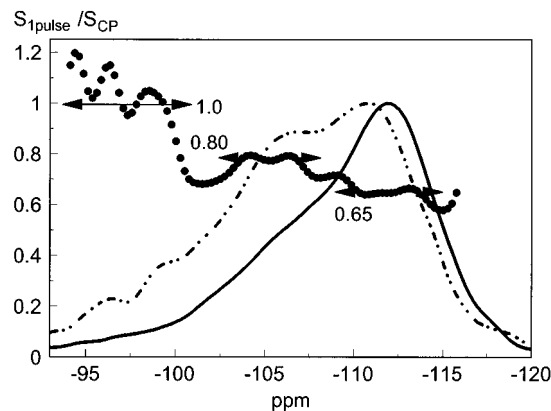


Figure 7. Ratio of two ^{29}Si REDOR asymptotic values ($S_{1\text{pulse}}/S_{\text{CP}}$) vs ^{29}Si chemical shift (●). The one-pulse (—) and CP MAS (---) ^{29}Si NMR spectra are also shown.

coordination numbers, which is simply the one-pulse spectrum of the sample. The second one is the distribution of the Al species with different ^1H - ^{27}Al dipolar coupling with chemisorbed NH_3 (Figure 3). The third one is the distribution of Al species with different spin-spin relaxation time T_2 (Figure 6).

Oldfield et al.⁹ have shown that T_2 for framework Al and nonframework Al are quite different, with T_2 being about 5 ms for framework Al and about 1 ms for nonframework Al. On this basis, the line with $T_2 = 5.8$ ms is assigned to the framework Al while that with $T_2 = 1.2$ ms is coming from the nonframework species. One can see that the framework Al is mostly composed of tetrahedral Al^{IV} , while nonframework Al span all possible aluminum coordinations, Al^{IV} , Al^{V} , and Al^{VI} .

Different ^1H - ^{27}Al dipolar couplings provide another criterion

for spectra editing. The line with strong coupling ($M_2 = 9 \text{ kHz}^2$) is assigned to Al atoms bonded to NH_3 directly ($\text{Al}:\text{NH}_3\cdots\text{Al}$), which is a Lewis acid center. The line with weak coupling ($M_2 = 0.4 \text{ kHz}^2$) is assigned either to Al at a Brönsted center or to a nonacidic nonframework Al neighboring a Lewis center.

It should be outlined here that these models are evidently oversimplified. Actually, both T_2 values and ^1H – ^{27}Al dipolar coupling should exhibit distributions rather than take two discrete values as assumed. If the distribution is taken into account, the shape of lines may change. But, since the discrete values representing the distribution were reasonably chosen, the line shape should not change significantly.

Since T_2 is mostly affected by Al quadrupolar interaction and Al–Al dipolar coupling, T_2 distribution in the framework should be narrow. On the other hand, the distribution of T_2 in the nonframework Al is, perhaps, broader, and using a single value for it may be oversimplification. In order to take into account a T_2 distribution, we fixed the T_2 value for the framework Al at 5.8 ms and let T_2 for the nonframework Al change while fitting the slices. The result is a slightly different distribution, as observed when comparing parts a and b of Figure 6.

From these assignments it follows that the distributions presented in Figures 3 and 6b may be considered as “reconstructed ^{27}Al NMR spectra” of the NF Lewis sites and NF species, respectively.

The quantification of the acid sites in the DHM600 proceeds now in a straightforward way. The “as-synthesized” mordenite has Si/Al = 5.2 by chemical analysis; DHM600 has Si/Al = 10 in framework determined by ^{29}Si MAS NMR. The estimated ratio NFAl/FAI ≈ 0.5 from these data is not very reliable. First, there might already be some nonframework Al in the original mordenite, which was introduced during the synthesis process. Second, the determination of the Si/FAI ratio from poorly resolved ^{29}Si MAS NMR spectrum (Figure 1) could be also ambiguous. The reason for this is that the defect ^3Q Si sites (with no Al atoms in the first coordination sphere) contribute to approximately the same spectral region as the ^4Q Si(1Al) sites.^{2,21,22} Moreover, the possible coupling between nonframework Al and the framework sites will also change the distribution of ^{29}Si chemical shifts.

The integration of the two components in Figure 6b yields relative amounts of nonframework and framework aluminum, 62% and 38%, respectively. Taking into account the data of chemical analysis, these numbers correspond to the framework Si/Al ratio of 13.5. This value is probably more reliable than the one obtained the standard way from ^{29}Si MAS NMR.

The strong REDOR component, which contributes 44% to the total Al content, is assigned to Lewis acid sites associated to the nonframework Al. Since the strong REDOR component represents the Lewis acid centers and the short T_2 component represents NFAl, the ratio between them is the Lewis site dispersion ($\text{L}:\text{NH}_3/\text{NFAl}$). The total dispersion is $44\%/62\% = 0.71$, and it is not uniform along the ^{27}Al MAS NMR spectrum (Figure 8). It decreases when going downfield from 1–0.9 (Al^{IV}) through 0.8 (Al^{V}) to 0.6–0.7 (Al^{VI}). The dispersion of Lewis sites with respect to the number of surface aluminum increases with decreasing coordination numbers, as expected.

The distribution of Al atoms in the zeolite DHM600 is given in Table 2. The calculated quantities were obtained by the procedure described elsewhere.²³ The experimental amounts of Brönsted and Lewis sites per gram were obtained earlier¹² from IR studies of NH_3 chemisorption on the same sample. The two values of Si/FAI ratios, 10 and 13.5, correspond to those obtained from ^{29}Si MAS NMR and T_2 spectra editing, respectively.

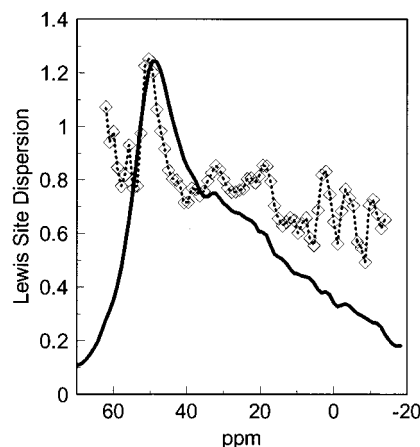


Figure 8. Lewis sites dispersion ($\text{L}:\text{NH}_3/\text{NFAl}$) vs ^{27}Al chemical shift (\diamond). The one-pulse ^{27}Al MAS NMR spectrum is also shown (solid line).

TABLE 2: Distribution of Al Atoms in DHM600/ NH_3

	Si/FAI = 10	Si/FAI = 13.5
NFAl (calculated, $\times 10^{-20}/\text{g}$)	7.9	10.1
FAI (calculated, $\times 10^{-20}/\text{g}$)	8.5	6.3
Q_1 (calculated, $\times 10^{-20}/\text{g}$)	6.2	5.1
FAI ₁ (calculated, $\times 10^{-20}/\text{g}$)	3.0	2.9
Lewis sites (exp, $\times 10^{-20}/\text{g}$)	5.0 ^a	5.0 ^a
Brönsted sites (exp, $\times 10^{-20}/\text{g}$)	5.4 ^a	5.4 ^a
L/NFAl	0.62	0.50
L/NFAl from this work	0.71	0.71

^a From ref 12.

According to concepts developed in our previous publications,^{7,23} the Q_1 quantity is the number of framework OH groups that bridge Al atoms with Si(1Al) atoms, e.g., the total number of Brönsted sites. The quantity FAI₁ is the number of isolated framework Al atoms, e.g., the number of strong Brönsted sites.

As stated above, the standard ^{29}Si MAS NMR method underestimates the Si/FAI ratio. While the experimental number of Brönsted sites agrees with the calculated one within 10% (Q_1 for Si/FAI is 13.5), the Lewis sites dispersion value found in this work (0.71) exceeds the discrepancy expected for the IR technique. This discrepancy could be attributable to the fact that with one-pulse/CP REDOR experiments one counts the number of Al atoms bonded to chemisorbed ammonia, while IR studies yield the number of chemisorbed NH_3 species. The apparent overestimate of the number of Lewis sites measured by the REDOR technique could mean that NH_3 molecules are bonded by two Al atoms. The second moment analysis discussed in the previous section supports this assumption.

The intensity distribution in the ^{27}Al CP spectrum gives information on the identity of the partners in the pair of Al nuclei involved in the Lewis site. It is obvious that the intensity in the spectral domains of the resonance frequencies of tetrahedral and pentahedral aluminum are similar in Figure 4, that is, at about 55 or at 40 ppm. This suggests that the most probable pair in a Lewis site is $\text{Al}^{\text{IV}}-\text{Al}^{\text{V}}$. The pair $\text{Al}^{\text{IV}}-\text{Al}^{\text{IV}}$ should have a lower probability because of the lattice strain generated by tetrahedral aluminum in a spinel. Meanwhile, the pair $\text{Al}^{\text{IV}}-\text{Al}^{\text{VI}}$ should also be improbable because Al^{VI} has a fully developed coordination shell.

It has been shown elsewhere²⁴ that the initial heats of NH_3 or of water chemisorption on transition aluminas are almost identical, but water ultimately reconstructs the surface. From the discussion above, it can be predicted that the pair $\text{Al}^{\text{IV}}-\text{Al}^{\text{V}}$ should be the first affected by the reconstruction or that Al^{V} will become $\text{Al}^{\text{VI}}-\text{OH}$. In fact, this is what was observed.

^1H – ^{29}Si REDOR Analysis. Similar analysis applied to the ^1H – ^{29}Si REDOR experiments did not reach the same high level of selectivity as in the case of ^1H – ^{27}Al experiments. However, our data indicate that about 20% of Si atoms with one aluminum neighbor in the first coordination sphere do not experience dipolar coupling with chemisorbed ammonia. Further experimental verification is needed to determine whether this is an evidence for the “poisoning” of Brønsted sites by nonframework species.

5. Conclusions

A new approach to quantitative NMR characterization of surface acidity in zeolites is proposed that will bring into consideration several nuclear interactions such as chemical shift and dipolar and quadrupolar interactions. The experimental strategy is based on the high level of selectivity of double-resonance and spin-echo NMR techniques toward the local environment of magnetic nuclei in zeolites. The “reconstructed” ^{27}Al NMR spectra of nonframework aluminum and Lewis sites provide valuable information on the structure of the nanosized particles, number of acid sites, and their distribution. The obtained data testify that an interaction occurs between NFAl and zeolite framework. Additional experiments with other zeolites (such as DHM, USY, and ZSM-5) with different degrees of dealumination are in progress.

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