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Table I

catalyst	Hg present	% conversion 5 min	% conversion 1 h
$CODPtCl_2$ (CH_2Cl_2)	–	0.6	7.2
$CODPtCl_2$ (CH_2Cl_2)	+	0	0
colloid-2 (CH_2Cl_2)	–	43.7	68.7
colloid-2 (CH_2Cl_2)	+	0	0.2
H_2PtCl_6 (isopropyl alcohol)	–	10.9	34.3
H_2PtCl_6 (isopropyl alcohol)	+	0	0

Preparation of Colloid-2. Colloid-2 was prepared by dissolving $CODPtCl_2$ (0.065 g, 0.17 mmol) in 2 mL of CH_2Cl_2 and then adding $(EtO)_3SiH$ (0.2 mL, 1.06 mmol). Over the course of 2 h, the initially colorless solution changed color from yellow and then to orange. Gas evolution began after 1 h. A variant of colloid-2 was prepared by combining $CODPtCl_2$ (0.0304 g, 0.0812 mmol) in 1 mL of CH_2Cl_2 with $MeCl_2SiH$ (0.05 mL, 0.48 mmol).

Effect of Mercury. $Me_3Si(CH{=}CH_2)$ (0.5 mL, 3.45 mmol) and 100 ppm (final concentration) of a platinum solution (see below) were combined in a vial with a stir bar. The solutions were stirred for $7^1/_2$ h in air with or without Hg (large excess). $(EtO)_3SiH$ (0.65 mL, 3.45 mmol) was added, and then conversions were monitored by GC (Table I).

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Solid-State Oxygen-17 Nuclear Magnetic Resonance Spectroscopic Studies of Zeolites and Related Systems. 1[§]

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Abstract: We have obtained static, "magic-angle", and "variable-angle" sample-spinning ^{17}O NMR spectra of ^{17}O-labeled A, Y, and dealuminated Y zeolites at 67.8 and 48.8 MHz (corresponding to magnetic field strengths of 11.7 and 8.45 T). Our results indicate that the ranges of ^{17}O nuclear quadrupole coupling constants (e^2qQ/h) of the Si[^{17}O]Al and Si[^{17}O]Si fragments are 3.1–3.2 and 4.6–5.2 MHz, respectively, in general agreement with those predicted on the basis of the empirical correlation presented previously (Schramm, S.; Oldfield, E. *J. Am. Chem. Soc.* **1984**, *106*, 2502). The asymmetry parameters are 0.2 for Si[^{17}O]Al and 0.1 for Si[^{17}O]Si. The isotropic chemical shifts of the Si[^{17}O]Al fragments are in the range of 31–45 ppm relative to H_2O, while those of the Si[^{17}O]Si fragments are in the range of 44–57 ppm.

There has recently been considerable interest in the use of ^{27}Al and ^{29}Si "magic-angle" sample-spinning (MASS) nuclear magnetic resonance (NMR) spectroscopy to study the structures of zeolites and other framework aluminosilicates.[1-6] The ^{29}Si NMR spectra of these systems can exhibit up to five resonances, depending on the number of next-nearest-neighbor aluminums. As a result, ^{29}Si MASS NMR techniques can be used to determine the composition of the aluminosilicate framework,[2,3] in addition to providing information on silicon–aluminum ordering.[3,4] ^{27}Al MASS NMR has been shown to be a sensitive technique for determining the coordination of aluminum,[7] and probing the location of Al atoms in chemically treated zeolites,[5] and for the quantitative determination of Al.[6]

Oxygen, the last major framework nucleus of zeolites, has received only a cursory examination so far,[8] because its NMR active isotope has a low natural abundance. Since it is the most abundant element in the earth's crust and is the main constituent of zeolites, the possibilities of carrying out detailed ^{17}O NMR studies of zeolites are particularly attractive. In this paper, we report the first comprehensive investigation of ^{17}O NMR of A and Y zeolites by means of static, MASS, and VASS ("variable-angle" sample spinning[9]) NMR techniques. We believe that determination of the ^{17}O isotropic chemical shifts (δ_i), nuclear quadrupole coupling constants (e^2qQ/h) and electric field gradient tensor asymmetry parameters (η) should provide valuable supplementary information on zeolite structure, as we have seen recently for the ^{17}O NMR of pure SiO_2 (low cristobalite: Janes, N.; Oldfield, E. *J. Am. Chem. Soc.* **1986**, *108*, 5743). In this paper we present our findings for the two chemically distinct oxygen species (Si[^{17}O]Si and Si[^{17}O]Al) of Na-, NH_4-, and Ba-exchanged Y zeolites, and for Na–A and dealuminated Na–Y. Our results indicate that the electronic structure around oxygen in the Si–O–Si fragments is close to that in low cristobalite, while that in the Si–O–Al fragment is considerably more ionic, as predicted on the basis of the empirical electronegativity and quadrupole

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Table I. Preparation of ^{17}O-Labeled Zeolites

sample	precursor	reaction time (h)	Si/Al[a]
Na-A	direct synthesis	143	1.0
Na-Y	direct synthesis	9	2.74
NH_4-Y	SK-40	171	2.92
NH_4-Y	LZY-82	200	4.98
NH_4-Y	LZY-20	200	7.51
Ba,Na-Y	Na-Y[b]		2.74
dealuminated Na-Y	Na-Y[b]		>25

[a] Si/Al mole ratios were measured by ^{29}Si MASS NMR simulations using a Nicolet curve-fitting routine. The simulations used 50–90% Gaussian line broadening, and four lines for the faujasite-type zeolites. [b] Directly synthesized, ^{17}O-labeled Na-Y zeolite.

coupling constant correlation discussed previously.[10] Such results should form the basis for further, more detailed studies of structure and bonding in zeolites.

Experimental Section

Synthetic Aspects. ^{17}O-Labeled zeolites were prepared by two different routes: (a) direct synthesis, incorporating (13X), in the synthesis gel; and (b) exchange techniques, in which commercially available zeolites were exchanged with $H_2{}^{17}O$ under "hydrothermal" conditions. The former method ensures random distribution of ^{17}O throughout the framework, but requires relatively large quantities of $H_2{}^{17}O$. The exchange technique permits study of commercially available materials, but the potential for preferential incorporation of ^{17}O exists, as does the possibility of partial destruction of some systems under hydrothermal steaming conditions.

Direct Synthesis of [^{17}O]Na-Y.[11] Sodium hydroxide (0.287 g) was dissolved in 2.59 g of 51% ^{17}O-enriched water; then sodium aluminate (0.615 g) was added and the mixture stirred to dissolution. Next, Ludox HS-40 (3.333 g) was added dropwise, with stirring, and the resultant gel loaded into a 25-mL Parr bomb, which was autoclaved at 100 °C for 143 h. The sample of Na-Y was washed until the pH was 7.0, then dried at 100 °C for 16 h, yielding 1.16 g of crystalline material. The overall ^{17}O enrichment should be 22%, assuming random incorporation.

Direct Synthesis of [^{17}O]Na-A.[12] Sodium aluminate (1.07 g) was dissolved in 3.20 g of 51% ^{17}O-enriched water. To this solution was added 1.26 g of sodium water glass, and the mixture was stirred until homogeneous. The resultant gel was then autoclaved at 100 °C for 9 h. The sample of Na-A was washed to pH 7.0, then dried at 100 °C for 16 h, yielding 0.88 g of crystalline material. The overall ^{17}O enrichment should be 32%, assuming random incorporation.

Labeling of Commercial Zeolites. Three ^{17}O-enriched NH_4-Y zeolites having differing Si/Al ratios were prepared. The commercially available starting materials and exchange times used are given in Table I. For NH_4-Y with Si/Al = 2.92, commercially available Na-Y faujasite (SK-40, from Union Carbide) was first ion exchanged to prepare the NH_4^+ form, which exchanges ^{17}O readily.[13] The other samples indicated in Table I were prepared from commercially available "high silica" faujasites from Union Carbide (LZY-82 and LZY-20). These were already in the NH_4^+ form and were thus used without further treatment. ^{17}O-Labeling was achieved by heating the solid materials with half their weight of $H_2{}^{17}O$ in a pressure vessel for the times given in Table I; then the samples were dried for 16 h at 110 °C.

Barium Exchange of [^{17}O]Na-Y. $BaCl_2$ (0.1 M, 10 mL) was heated to 50 °C; then 0.50 g of [^{17}O]Na-Y from the direct synthesis was added. The slurry was stirred for 1 h at 50 °C, filtered on a Büchner funnel, and then washed. This procedure was then repeated four more times. The resultant Ba,Na-Y was then dried at 100 °C for 3 h, yielding 0.40 g of partially exchanged material. Atomic absorption analysis indicated that the final composition is approximately $Ba_{0.65}Na_{0.35}$ (mole ratio).

Dealumination of [^{17}O]Na-Y. This sample was prepared using Beyer's procedure,[14] in which aluminum in the framework is substituted by Si from $SiCl_4$ vapor at ~500 °C for 4 h. The $AlCl_3$ produced is flushed out in an N_2 stream. Our product was purged with dry N_2 to remove residual $SiCl_4$ and $AlCl_3$, then washed until all chloride disappeared from the wash, and dried at 120 °C for 3 h. X-ray powder diffraction indicated a crystalline faujasite-like structure remained.

Caution: We experienced a number of MASS rotor explosions when attempting to study "fresh" dealuminated samples (i.e., those that did not have the above water wash), due presumably to buildup of HCl pressure or swelling of the sample from H_2O absorption. Such studies should proceed with due caution.

Final calcination of all zeolites was performed at 350 °C for 3 h in a dry N_2 stream, in order to remove residual $H_2{}^{17}O$. All samples were characterized by X-ray powder diffraction, and ^{27}Al and ^{29}Si MASS NMR. All samples were initially run without hydration and were handled under a dry N_2 atmosphere.

Reagents used in the direct synthesis included DuPont Ludox HS-40 colloidal silica (40 wt % SiO_2), Nalco sodium aluminate 680-W (46% Al_2O_3), Fisher Purified granular sodium aluminate ($Na_2O{\cdot}Al_2O_3{\cdot}3H_2O$), MCB sodium hydroxide (reagent grade, 97.0% purity), and Diamond Shamrock Grade-42 sodium water glass (25.6 wt % SiO_2, 7.97 wt % Na_2O). Samples were ion exchanged using Fisher Certified ACS grade ammonium nitrate, or Mallinckrodt Analytical Grade barium chloride ($BaCl_2{\cdot}2H_2O$). The ^{17}O-enriched water was obtained from U.S. Services, Inc. (51 atom % enrichment) and Isotec (50 atom % enrichment). Y zeolite was dealuminated with silicon(IV) chloride purchased from Aldrich.

Nuclear Magnetic Resonance Spectroscopy. ^{17}O NMR spectra were obtained on FT NMR spectrometers operating at 67.8 and 48.8 MHz, using Oxford Instruments (Osney Mead, Oxford, U.K.) 11.7-T, 52-mm bore or 8.45-T, 89-mm bore superconducting solenoid magnets. We used Nicolet Instrument Corp. (Madison, WI) Model-1280 computer systems for data acquisition, and Amplifier Research (Souderton, PA) Model 200L and 150LA amplifiers for final rf pulse generation. ^{27}Al and ^{29}Si spectra were obtained only at 8.45 T (corresponding to resonance frequencies of 93.4 and 71.5 MHz, respectively). ^{17}O MASS NMR spectra at both fields were obtained using Doty probes (Doty Scientific, Columbia, SC) with spinning speeds of between ~4.5 and 6 kHz. Static ^{17}O spectra were obtained using a "home-built" horizontal solenoid-type sample probe. A second "home-built" MASS-VASS NMR probe equipped with an Andrew-Beams-type rotor system (spinning rate 3–4 kHz) was used for ^{27}Al and ^{29}Si MASS, and ^{17}O 75°-VASS NMR spectra. ^{17}O pulse widths used on solid samples were 3–5 μs (H_2O reference, 90° pulse width = 9~15 μs). Chemical shifts are reported in ppm from external standards of tap water (^{17}O), Me_4Si (^{29}Si), and 1 M $Al(H_2O)_6Cl_3$ (^{27}Al), where more positive values correspond to low-field, high-frequency, paramagnetic, deshielded values (δ scale). Line broadenings due to exponential multiplication for ^{17}O NMR were 400 Hz for static and 50 Hz for MASS and VASS spectra, 10 Hz for ^{29}Si MASS spectra, and 30 Hz for ^{27}Al MASS spectra. ^{17}O chemical shift accuracies are ±1 to ±3 ppm, depending on the line width. In all cases only the central ($^1/_2$, $-^1/_2$) transition was observed in the ^{17}O spectra.

Results and Discussion

First, we shall consider our NMR results on Na-A. Zeolite A has three crystallographically distinct oxygen sites,[15] but the Si/Al ratio of 1 gives only one kind of chemically distinct oxygen, Si[^{17}O]Al. Unless there are large chemical shift nonequivalences between the different crystallographic sites, we expect the Si[^{17}O]Al resonance to be a broad line whose width and shape are governed by the second-order quadrupole interaction. This assumes only defect levels of silanol groups. Using the empirical correlation described previously,[10] we can estimate from the mean ionicity of 57% a quadrupole coupling constant of 3.2 MHz.

Second, we consider *dealuminated* Na-Y, which has a faujasite-like structure containing solely Si[^{17}O]Si bonds, resulting in e^2qQ/h values similar to those observed in the SiO_2 polymorph low cristobalite,[10] of ~5.8 MHz.

Third, we consider the ^{17}O NMR spectrum of Na-Y. Na-Y zeolite has four crystallographically distinct oxygen sites.[15] Since our sample has a Si/Al ratio of 2.74, it is expected to have two chemically distinct types of oxygen: Si[^{17}O]Si and Si[^{17}O]Al. There are no Al[^{17}O]Al linkages, according to Loewenstein's rule.[16] There could thus be up to eight different signals for Na-Y, due to the presence of four crystallographic oxygen sites in the zeolite structure, and the two distinct oxygen environments (Si[^{17}O]Si and Si[^{17}O]Al). However, to a first approximation, we might

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Table II. Static Solid-State ^{17}O NMR Chemical Shifts, Apparent Quadrupole Coupling Constants and Asymmetry Parameters for Zeolites at 11.7 T

		Si[^{17}O]Si				Si[^{17}O]Al			
zeolite	Si/Al mol ratio	%^{a}	e^2qQ/h^b (MHz)	η^c	δ_i^d (ppm)	%^{a}	e^2qQ/h^b (MHz)	η^c	δ_i^d (ppm)
Na-A	1.0	0				100	4.2 (3.8)^e	0.2 (0.2)^e	33 (32)^e
Na-Y	2.74	46.5	5.7 (5.3)^e	0.1 (0.1)^e	46 (48)^e	53.5	4.2 (4.0)^e	0.2 (0.2)^e	31 (32)^e
NH_4-Y	2.92	49.0	5.7	0.1	47	51.0	4.3	0.2	31
NH_4-Y	4.98	66.6	5.5	0.1	56	33.4	4.2	0.2	33
NH_4-Y	7.51	76.5	5.5	0.1	55	23.5	4.2	0.2	33
Ba,Na-Y	2.74	46.5	5.6	0.1	57	53.5	4.0	0.2	45
dealuminated Na-Y	>25	100	5.7	0.1	47	0			
SiO_2^f	∞	100	5.8	0.0	46	0			

^{a}Calculated percentage from Si/Al mole ratio. ^{b}Quadrupole coupling constant in MHz. ^{c}Electric field gradient tensor asymmetry parameter. ^{d}Isotropic chemical shift in ppm from external tap water. ^{e}The result for a 48.8-MHz spectrum is given in parentheses. $^f SiO_2$, low cristobalite.

Table III. Magic-Angle Sample-Spinning (MASS) Solid-State ^{17}O NMR Chemical Shifts, Quadrupole Coupling Constants, and Asymmetry Parameters for Zeolites at 11.7 T

		Si[^{17}O]Si				Si[^{17}O]Al			
zeolite	Si/Al mole ratio	%^{a}	e^2qQ/h^b (MHz)	η^c	δ_i^d (ppm)	%^{a}	e^2qQ/h^b (MHz)	η^c	δ_i^d (ppm)
Na-A	1.0	0				100	3.2	0.2	32
Na-Y	2.74	46.5	4.6	0.1	44	53.5	3.1	0.2	31
NH_4-Y	2.92	49.0	5.0	0.1	48	51.0	3.2	0.2	31
NH_4-Y	4.98	66.6	5.0	0.1	51	33.4	3.2	0.2	31
NH_4-Y	7.51	76.5	5.0	0.1	50	23.5	3.2	0.2	34
Ba,Na-Y	2.74	46.5	5.1	0.15	52	53.5	3.4	0.4	40
dealuminated Na-Y	>25	100	5.2	0.2	45	0			
SiO_2^e	∞	100	5.3	0.0	44	0			

^{a}Calculated percentage from Si/Al mole ratio. ^{b}Quadrupole coupling constant in MHz. ^{c}Electric field gradient tensor asymmetry parameter. ^{d}Isotropic chemical shift in ppm from external tap water. $^e SiO_2$, low cristobalite.

expect the spectrum to be dominated by the different second-order quadrupole interactions in the Si[^{17}O]Al and Si[^{17}O]Si fragments, as is indeed found to be the case. In this section, we shall use the results on Na-A (Si[^{17}O]Al linkages) and dealuminated Y (Si[^{17}O]Si linkages) to help interpret our results.

Fourth, we consider the effects of the Si/Al ratio on the observed ^{17}O NMR spectrum, and the effects of (Ba^{2+}) ion exchange of the nonframework cations on the various NMR parameters (δ_i, e^2qQ/h, and η).

Sodium A Zeolite. We show in Figure 1A the 48.8-MHz static ^{17}O NMR spectrum of a sample of [^{17}O]Na-A zeolite prepared by direct synthesis. The resonance consists of a broad, second-order quadrupole split doublet for the Si[^{17}O]Al group, which can be characterized by $\delta_i = 32$ ppm, $e^2qQ/h = 3.8$ MHz, and $\eta = 0.2$, as shown in the spectral simulation of Figure 1B (static parameters are given in Table II). The results of Figure 1A do not reveal the three crystallographically nonequivalent oxygens, although these sites may give a small distribution of quadrupole coupling constants and chemical shifts. Similarly, at 11.7 T (tesla), the static ^{17}O NMR spectrum and its simulation, Figure 1C,D yield no evidence for more than one oxygen site, the spectrum being well described by a one-component simulation having $\delta_i = 33$ ppm, $e^2qQ/h = 4.2$ MHz, and $\eta = 0.2$. The results of the static spectra (Figure 1A,C) indicate that the ^{17}O NMR spectrum of [^{17}O]Na-A is overwhelmingly dominated by the second-order quadrupole interaction. Finally, MASS NMR yields a single-component spectrum which may be simulated using $\delta_i = 32$ ppm, $e^2qQ/h = 3.2$ MHz, and $\eta = 0.2$, as shown in Figure 1E,F (MASS parameters are given in Table III).

We have noticed that the quadrupole coupling constants, e^2qQ/h, calculated from the simulated spectra have the relationship e^2qQ/h (static, 67.8 MHz) > e^2qQ/h (static, 48.8 MHz) > e^2qQ/h (MASS, 67.8 MHz). The static high-field e^2qQ/h is as much as 24% larger than the MASS value, while δ_i and η are very consistent. This effect must arise from broadening mechanisms which are averaged out under the MASS condition or are reduced at lower field. The most probable cause is the chemical shift anisotropy interaction. This effect is also observed in the other zeolites investigated, Na-Y, NH_4-Y, and Ba,Na-Y. In addition, a distribution of NMR parameters due to crystallographically nonequivalent oxygen sites, and a small orientation-dependent dipolar broadening in the rigid lattice, may further broaden the static spectra more than the MASS spectra. Nevertheless, static spectra better reveal second-order broadened features and give better resolution for spectra with chemically distinct sites. Thus for zeolites which have two chemically distinct oxygens, we first obtain asymmetry parameters and isotropic chemical shifts from the static spectra, then simulate the MASS spectra on the basis of these parameters. For this reason, we report both the static (Table II) and MASS (Table III) NMR parameters separately and discuss the quadrupole coupling constants,

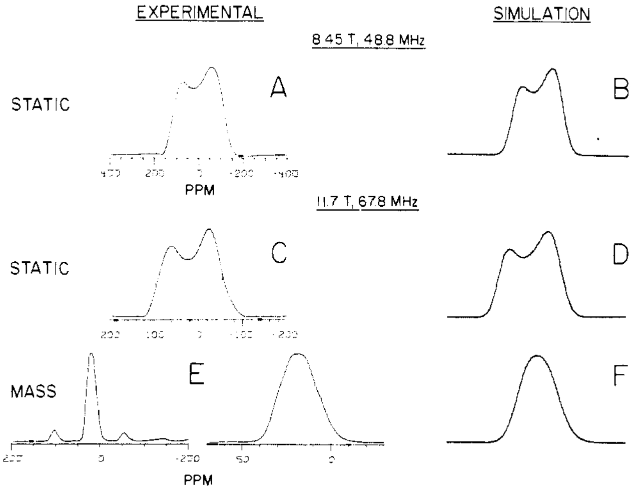

Figure 1. ^{17}O NMR spectra and spectral simulations of Na-A zeolite: (A) static, at 8.45 T, 2115 scans, recycle time 30 s; (B) spectral simulation of A; (C) static, at 11.7 T, 1000 scans, recycle time 60 s; (D) spectral simulation of C; (E) 11.7 T, 5.2-kHz MASS, 3599 scans, recycle time 10 s; (F) spectral simulation of E. Line broadenings for simulations are 400 Hz for MASS and 1150 Hz for static spectra.

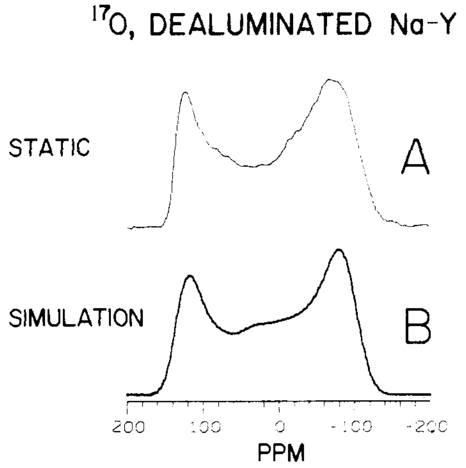

Figure 2. ^{17}O NMR spectrum and a spectral simulation of dealuminated Na–Y zeolite: (A) static, at 67.8 MHz, 3599 scans, recycle time = 15 s; (B) spectral simulation of A.

e^2qQ/h, obtained from the MASS data (in the absence of chemical shift anisotropy (CSA) effects).

The e^2qQ/h value for Na–A (3.2 MHz, from MASS) is in excellent agreement with the 3.2 MHz predicted on the basis of a 51% ionicity for the Si–O bond and 63% ionicity for the O–Al bond, and the empirical correlation presented previously.[10] Thus, in at least one respect, the ^{17}O NMR results presented in Figure 1 have the advantage over previous studies of quadrupolar nuclei in zeolites (e.g., of ^{23}Na and ^{27}Al) in that we are, at least to a first approximation, able to *predict* what the e^2qQ/h values should be, on the basis of simple structural considerations.[10]

Dealuminated Na–Y Zeolite. We show in Figure 2A the 67.8 MHz (11.7 Tesla) static NMR spectrum of a sample of Na–Y zeolite which has been dealuminated as described in the Experimental Section. The spectrum is very similar to that of low cristobalite[10] (static and MASS data are given in Table II and III, respectively), e^2qQ/h = 5.7 MHz, η = 0.1, and δ_i = 47 ppm for static and e^2qQ/h = 5.2 MHz, η = 0.2, and δ_i = 45 ppm for MASS. As expected, the significantly more covalent Si[^{17}O]Si bond yields a larger e^2qQ/h than in the case of the Si[^{17}O]Al bond in Na–A (Figure 1).

The ^{29}Si MASS NMR spectrum of this dealuminated Na–Y (data not shown) has a narrow (ca. 1.0 ppm at half-height) resonance at −107.8 ppm, indicating predominantly Si(0Al) sites. Framework Si linked to AlO_4 tetrahedra are not detected above the noise level (5%). Klinowski et al.[17] have demonstrated that reaction of Na–Y zeolite with $SiCl_4$ yields an essentially aluminum-free faujasite with a chemical shift of −107.4 ppm, and a line width at half-height of about 0.5 ppm. Our chemical shift is almost identical with theirs, but our line is slightly broader. This may result from either ^{17}O dipolar broadening effects or a small ^{17}O chemical shift distribution.

The ^{27}Al spectrum of the dealuminated sample is similar to that of Klinowski et al.,[18] there being two peaks. The peak at 58.1 ppm corresponds to a very small amount (<5%) of framework aluminum remaining in the lattice after dealumination. The second peak, at 0.3 ppm, corresponds to an even smaller amount (~1–2%) of nonframework octahedral aluminum, this peak being generated by the hydrolysis of extra-lattice aluminum. However, because the ^{27}Al signals are both very weak, and there is no evidence of a Si(1Al) line in the ^{29}Si spectrum, we are confident these species do not contribute appreciably to the ^{17}O spectrum of Figure 2A.

Na–Y Zeolite. We show in Figure 3 the static, MASS, and 75°-VASS NMR spectra of a sample of [^{17}O]Na–Y zeolite having Si/Al = 2.74. Contrary to our initial hopes, the MASS and VASS spectra *do not* resolve the Si[^{17}O]Si and Si[^{17}O]Al fragments, because their chemical shifts are very similar. In sharp contrast, however, the *static* spectra do indicate the presence of two, overlapping, second-order quadrupolar broadened features, which on the basis of the e^2qQ/h values for Na–A (Si[^{17}O]Al, e^2qQ/h = 3.2 MHz), and dealuminated Na–Y (Si[^{17}O]Si, e^2qQ/h = 5.2 MHz), can be assigned to the two types of chemically nonequivalent oxygens in the Na–Y lattice.

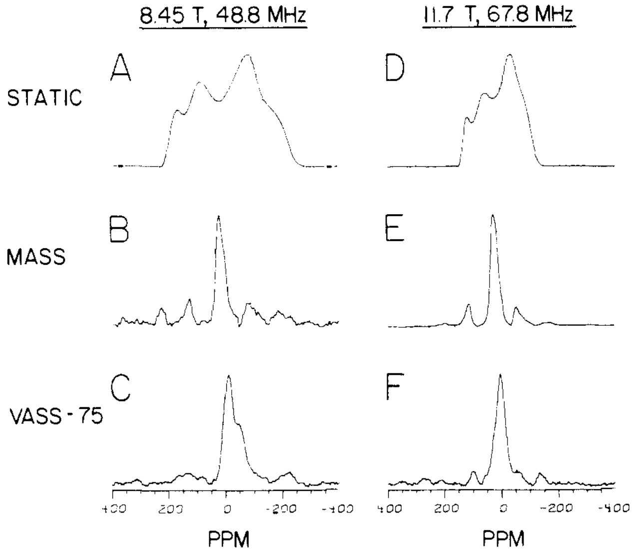

Figure 3. ^{17}O Fourier transform NMR spectra of ^{17}O-enriched Na–Y zeolite. At 8.45 T: (A) static, 2911 scans, recycle time = 30 s, (B) MASS at 4.8 kHz, 3627 scans, recycle time = 1 s; (C) 75°-VASS at 3.8 kHz, 3744 scans, recycle time = 10 s. At 11.7 T: (D) static, 1000 scans, recycle time = 30 s; (E) MASS at 5.2 kHz, 3599 scans, recycle time = 10 s; (F) 75°-VASS at 4.2 kHz, 3599 scans, recycle time = 1 s.

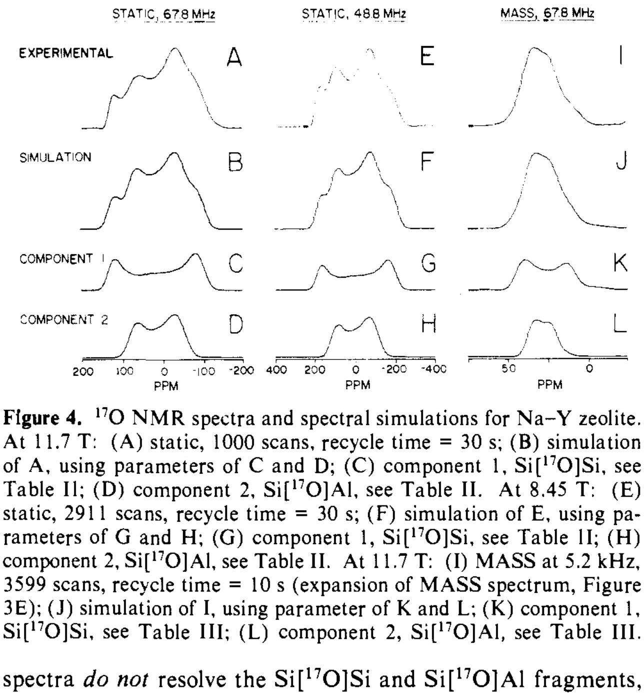

Figure 4. ^{17}O NMR spectra and spectral simulations for Na–Y zeolite. At 11.7 T: (A) static, 1000 scans, recycle time = 30 s; (B) simulation of A, using parameters of C and D; (C) component 1, Si[^{17}O]Si, see Table II; (D) component 2, Si[^{17}O]Al, see Table II. At 8.45 T: (E) static, 2911 scans, recycle time = 30 s; (F) simulation of E, using parameters of G and H; (G) component 1, Si[^{17}O]Si, see Table II; (H) component 2, Si[^{17}O]Al, see Table II. At 11.7 T: (I) MASS at 5.2 kHz, 3599 scans, recycle time = 10 s (expansion of MASS spectrum, Figure 3E); (J) simulation of I, using parameter of K and L; (K) component 1, Si[^{17}O]Si, see Table III; (L) component 2, Si[^{17}O]Al, see Table III.

We show the static 67.8-MHz ^{17}O NMR spectrum of [^{17}O] Na–Y and its computer simulation in Figure 4, parts A and B, respectively. The spectrum consists of contributions from the Si[^{17}O]Si fragment (46.5%, based on the Si/Al ratio, e^2qQ/h = 5.7 MHz, η = 0.1, δ_i = 46 ppm,) and from the Si[^{17}O]Al fragment (53.5%, e^2qQ/h = 4.2 MHz, η = 0.2, δ_i = 31 ppm). Very similar results are obtained at 48.8 MHz (8.45 T), as shown in Figure 4E–H (46.5% Si[^{17}O]Si, e^2qQ/h = 5.3 MHz, η = 0.1, δ_i = 48 ppm; 53.5% Si[^{17}O]Al, e^2qQ/h = 4.0 MHz, η = 0.2, δ_i = 32 ppm). The results of these two spectral simulations are very close to those which can be obtained by addition of the Na–A (Si[^{17}O]Al) and dealuminated Na–Y (Si[^{17}O]Si) results shown in Figures 1 and

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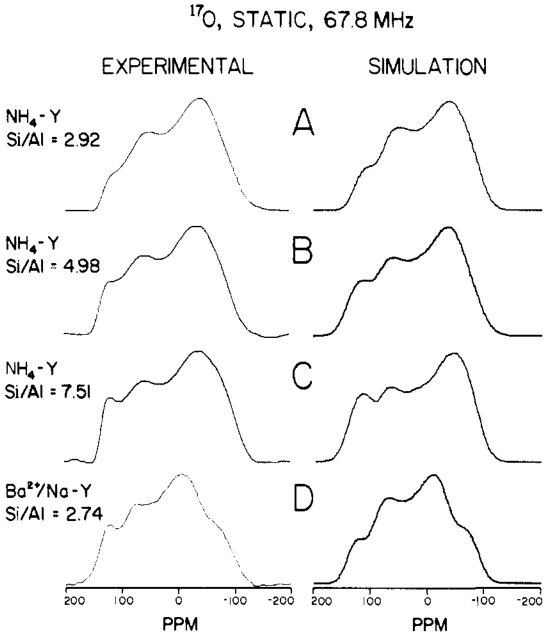

Figure 5. Static ^{17}O NMR spectra and spectral simulations of NH_4^+ and Ba,Na-Y zeolites. At 67.8 MHz, 30 s recycle time: (A) NH_4-Y with Si/Al = 2.92, 1880 scans, plus spectral simulation; (B) NH_4-Y with Si/Al = 4.98, 404 scans, plus spectral simulation; (C) NH_4-Y with Si/Al = 7.51, 552 scans, plus spectral simulation; (D) Ba^{2+} exchanged Na-Y with Si/Al = 2.74, 1000 scans, plus spectral simulation.

2. Further support for the correctness of our assignments is to be found in the NH_4-Y results as a function of Si/Al ratio, shown in Figure 5.

Using the e^2qQ/h, η, and δ_i values obtained in Figure 4 (parts C,D,G,H), we are now better able to interpret the MASS NMR spectra of Na-Y zeolite. The 67.8-MHz spectrum and its simulation are shown in Figure 4I-L. The simulation consists of a line from the Si[^{17}O]Si fragment (46.5%, e^2qQ/h = 4.6 MHz, $\eta = 0.1$, δ_i = 44 ppm; Figure 4K) and a line from the Si[^{17}O]Al fragment (53.5%, e^2qQ/h = 3.1 MHz, $\eta = 0.2$, δ_i = 31 ppm; Figure 4L). The results of the MASS NMR experiment permit a more accurate determination of the isotropic chemical shifts of the Si[^{17}O]Si and Si[^{17}O]Al fragments (44 and 31 ppm, respectively), because of the decreased spectral line widths. However, the e^2qQ/h values in the MASS NMR simulation are up to 15% smaller than those obtained from the static spectrum, which could indicate small anisotropic chemical shielding and/or dipolar contribution to the static breadth. The effects are, however, too small for us to accurately assess and will require even higher magnetic field strengths (and perhaps single-crystal studies) to be determined with any accuracy.

We believe the results we have presented above to be of considerable interest since they provide the first confirmation, in a zeolite, of the general applicability of the empirical relationship presented previously:[10]

$$e^2qQ/h \text{ (MHz)} = -0.203I + 14.78$$

where I is the mean ionicity, expressed in percent, obtained from the Pauling electronegativities (EN). Using EN values of Al = 1.5, Si = 1.8, and O = 3.5, we can compute e^2qQ/h = 3.2 MHz for the Si[^{17}O]Al fragment (57% ionic), and e^2qQ/h = 4.4 MHz for the Si[^{17}O]Si fragment (51% ionic). These values are in accord with the ~3.2- and ~4.6-MHz values found in the present work and represent the first successful prediction of e^2qQ/h values in zeolites.

Silicon to Aluminum Ratios and Cation Effects. For a given Si/Al mole ratio (from the ^{29}Si MASS NMR spectrum), it is possible to compute quantitatively the intensities of the two components which are due to chemically distinct oxygen sites, provided that Loewenstein's rule is obeyed, as it is with A and Y zeolites. Taking the basic lattice fragment as $^1/_4T - O - {}^1/_4T$ where T is Si or Al, each Si-O-Si linkage is equivalent to (2Si + 0Al)/4 per oxygen atom, and each Si-O-Al linkage to (1Si + 1Al)/4 per oxygen atom. The resulting Si/Al mole ratio in the tetrahedrally bonded anionic framework is given by:

$$\frac{\text{Si}}{\text{Al}} \equiv \frac{2[\text{SiOSi}] + [\text{SiOAl}]}{[\text{SiOAl}]} \equiv \frac{2(\frac{1}{4}I_1) + \frac{1}{4}I_2}{\frac{1}{4}I_2}$$

I_1 is the percentage of Si-O-Si sites, and I_2 the percentage of Si-O-Al sites; $I_1 + I_2 = 100$.

We show, in Figure 5, static 67.8-MHz ^{17}O NMR spectra of three NH_4-Y zeolite samples of differing Si/Al ratio, together with the spectrum of a Ba^{2+} exchanged Na-Y (Si/Al = 2.74). Also shown are the spectral simulations obtained using the Si/Al ratios deduced from the ^{29}Si MASS NMR spectra of the same samples (parameters are given in Table II). There is generally good agreement between the experimental and simulated spectra, supporting our assignments of Si[^{17}O]Si and Si[^{17}O]Al fragments.

The results of Figure 5 and additional ^{17}O MASS NMR spectra (data not shown, parameters are given in Table III) yield not only nuclear quadrupole coupling constant (and asymmetry parameter) information, but also show a nonframework cation dependence of the ^{17}O chemical shift, which results in rather a different static ^{17}O NMR spectrum for Ba,Na-Y, as compared with Na-Y or NH_4-Y (Figure 5). For example, for Ba,Na-Y, the isotropic chemical shift of the Si[^{17}O]Al fragment is more deshielded (~12-14 ppm) from its position in the Na^+ and NH_4^+ forms than that of the Si[^{17}O]Si fragment (~2-11 ppm), due presumably to the close proximity of Ba^{2+} (larger cation radius) to the AlO_4^- center.

Concluding Remarks

The results presented in this paper represent our first attempts at using ^{17}O solid-state NMR to probe the structure of zeolites. Our results indicate, as expected, that the second-order quadrupole interaction overwhelmingly dominates the observed line shapes. Apparent e^2qQ/h parameters obtained from the chemically distinct Si[^{17}O]Si and Si[^{17}O]Al fragments show a small field dependence, indicating the presence of a small chemical shift anisotropy contribution. MASS averages this CSA interaction and permits an accurate measure of the e^2qQ/h values for both types of oxygen. We find an e^2qQ/h range of 4.6-5.2 MHz for the Si[^{17}O]Si fragments, and 3.1-3.2 MHz for the Si[^{17}O]Al fragments, in good agreement with results based on the empirical ionicity-e^2qQ/h correlation presented previously.[10] Further work is in progress to try to determine the CSA values more accurately, by simulation of static spectra using both quadrupole and CSA interactions. We believe the results we have obtained above indicate a promising future for ^{17}O solid-state NMR studies of the structures of zeolites and related systems. Further experimental results on $AlPO_4$-n materials and related systems, and a theoretical discussion, are presented in the following paper.

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