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Simulation of 3QMAS NMR Spectra for Mordenite with the Point Charge Model

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Abstract: ^{27}Al triple quantum magic angle spinning (3QMAS) NMR spectra of several mordenite (MOR) samples were simulated with the point charge model method and compared with experimental 3QMAS spectra. Signal positions from different tetrahedral (T) sites in 3QMAS spectra are mainly governed by local structures of T sites such as T-O-T angles and T-O bond lengths. When preparation methods, cations in addition to Si/Al ratios vary, the local structures of T sites in MOR change enough to alter signal patterns in 3QMAS of MOR. This inhibits to study the of Al distribution variation over 4 different T sites in mordenite during process such as dealumination by 3QMAS spectra.

Keywords : mordenite, ^{27}Al MQMAS, NMR, point charge model, simulation

INTRODUCTION

Al in the framework of aluminosilicate zeolites is known to behave as Brø nsted acid sites. Thus it is not surprising that many properties of aluminosilicate zeolites are strongly influenced by the distribution patterns of Al over the available tetrahedral (T) sites even in a given zeolite framework structure as well as Al contents in the framework. Hence, local ordering of Al atoms in these porous materials has been the main research subject for systematic development of aluminosilicate zeolites.[1-4] However, if Al in the zeolites are substituted randomly or nonrandomly has not been clear until experimental ^{27}Al nuclear magnetic resonance (NMR) evidence for nonrandom distribution in ZSM-5 was reported.[5]

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Mordenite has only 4 crystallographically nonequivalent T sites while ZSM-5 has 12 T sites. Smaller number of T sites might improve spectral resolution in 2-dimensional (2D) ^{27}Al triple quantum magic angle spinning (3QMAS) NMR spectra taken to prove the nonrandom distribution of Al in ZSM-5 although the general low crystallinities of mordenites can deteriorate the spectral resolution. Mordenite has been extensively used for catalysts in petroleum process.[6,7] If Al in the framework of mordenite is eliminated preferentially from certain T sites or randomly during dealumination process, has not been known yet. Before probing this with 3QMAS NMR technique, it is necessary first to check if the signal patterns of 3QMAS spectra are sturdy enough with spectral simulation of known mordenite structures with various Si/Al ratios. So far only limited number of mordenite crystal structures were reported so that the Si/Al ratios we could take was in the range of 4.7 ~ 10. In this work, the point charge model (PCM) methods[8] was applied to simulate 2D 3QMAS spectra and the simulated spectra compared experimental spectra.

EXPERIMENTAL

Simulation Procedure

Single crystal X-ray diffraction (SXRD) or neutron powder diffraction (NPD) data were used to simulate 3QMAS NMR spectra at a 600 MHz NMR instrument. T-O-T angles and coordinates of 4 nearest neighbor oxygens for Al sitting at origin (0,0,0) were taken to calculate isotropic chemical shifts and quadrupole parameters with PCM.[5] From these values, peak positions in 2-dimensional 3QMAS spectra can be predicted in the assumption of equal population of Al at 4 different T sites as previously described in detail in reference 5.

Materials

For simulation, NPD data of D-nat-5.5, D-syn-5.6 and D-syn-10 were taken from reference 9, and likewise SXRD data of H-nat-4.7 and H-nat-5.1 from references 10 and 11. H and D denote non-frame cations in the mordenite samples, syn and nat mean synthesized and natural, respectively, and the numbers at the end indicate Si/Al ratios in the framework.

For acquiring experimental ^{27}Al 3QMAS NMR spectra, Na-syn-6.5 (CBV10 in their catalog) purchased from Zeolyst International (U.S.A.) was used without any further treatment.

NMR Spectroscopy

All the ^{27}Al NMR experiments were carried out on an INOVA 600 MHz system (Varian Inc., U.S.A.) with a 14.1 Tesla wide-bore magnet and a CP-MAS probe equipped with 4 mm zirconia rotors. Typical sample spinning rate was 12.5 kHz and its stability was within ± 4 Hz.

The first, second, and third pulse length in the 3QMAS pulse sequence with 2 hard pulses and 1 soft pulse for zero quantum transition filtering was 4, 1.4, and 17 μs, respectively, and t1 was incremented in step of 20 μs up to 1262 μs with an initial value of 2 μs. Spectral width was 200 and 50 kHz for F2 and F1 dimension, respectively. Scan number of each FID was 96 and repetition time was 2 s. In addition to ordinary double Fourier transformation for 2D data, shearing was applied to get final spectra.[12-14] This shearing amount for triple quantum transition is 19:12 = F2:F1 for ^{27}Al nuclei of I=5/2.[14] Chemical shift was referenced to external 1M aqueous solution $AlCl_3$.

RESULTS AND DISCUSSION

Calculated NMR parameters for Al at 4 different T sites of 5 different mordenite samples are summarized in Table 1. The notations employed in the Table 1 are the same with those in reference 5. With these parameters ^{27}Al 3QMAS NMR simulation spectra of D-nat-5.5, D-syn-5.6, D-syn-10, H-nat-4.7, and H-nat-5.1 are generated as shown in Fig. 1.

Simulated 3QMAS spectra of D-syn-10 and D-syn-5.6 are very similar although the samples have very different Si/Al ratios. On the other hand, simulated 3QMAS spectra of D-syn-5.5 and D-syn-5.6 have very different peak positions especially for T1 and T4 sites even though they have almost the same Si/Al ratios. In contrast, simulated spectra of H-nat-4.7 and H-nat-5.1 differently prepared from each other but with similar Si/Al ratios are similar. The mordenite samples of Si/Al close to 5, i.e. D-nat-5.5, D-syn-5.6, H-nat-5.1, and H-nat-

4.7 do not show similar 3QMAS spectral patterns, which implies the local structures of the samples with the same Si/Al ratio could be different.

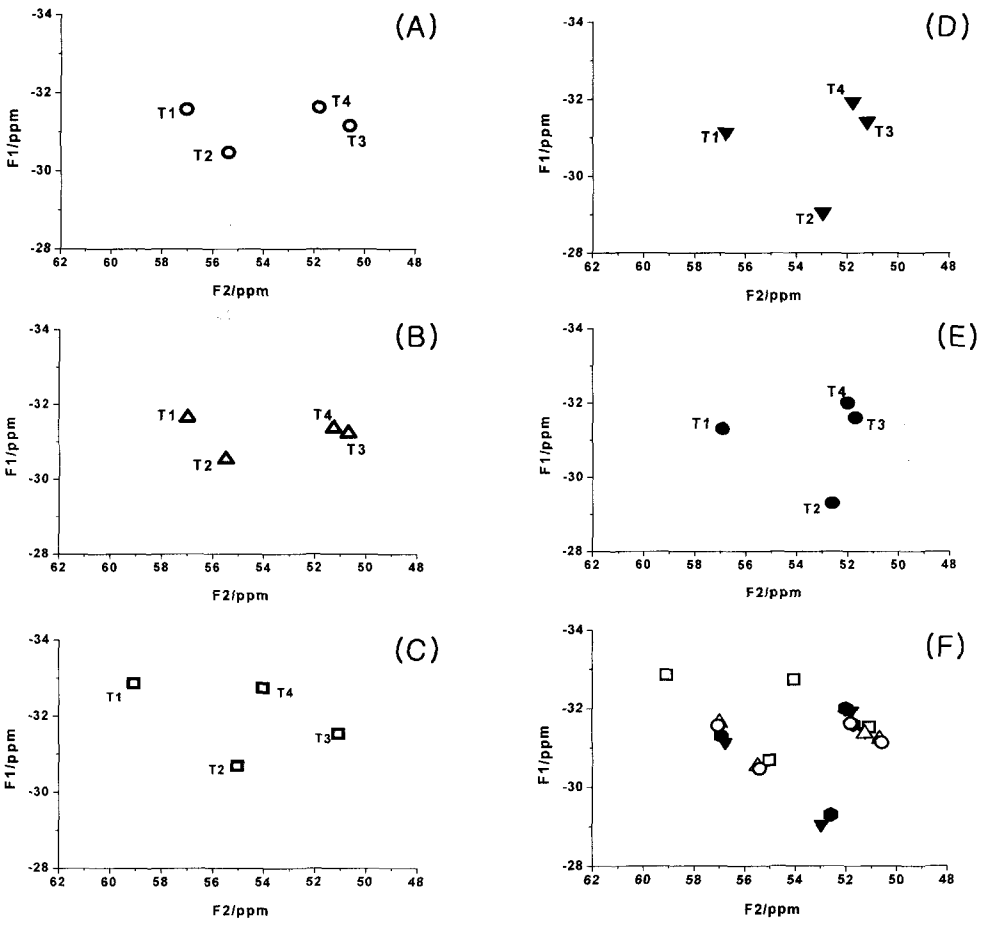

Fig. 1. Simulated ^{27}Al 3QMAS spectra of D-syn-10 (A), D-syn-5.6 (B), D-nat-5.5 (C), H-nat-4.7 (D), and H-nat-5.1 (E), and of all the 5 mordenites (F).

Table 1. Calculated NMR parameters for Al at 4 different T sites of 5 different mordenites

parameters	Al Site	H-nat-4.7	H-nat-5.1	D-nat-5.5	D-syn-5.6	D-syn-10
mean T-O-T Angle (°)	T1	150.4	150.1	144.8	149.0	149.3
	T2	158.1	157.7	152.8	152.8	153.0
	T3	153.9	153.1	153.8	154.8	155.0
	T4	152.3	152.1	148.8	154.0	153.0
δ_{iso}[a] (ppm)	T1	56.8	57.0	59.6	57.5	57.4
	T2	53.0	53.1	55.6	55.6	55.5
	T3	55.1	55.5	55.1	54.6	54.5
	T4	55.9	56.0	57.6	55.0	55.5
C_Q[b] (MHz)	T1	0.3	0.3	1.5	1.4	1.1
	T2	0.2	1.3	1.4	0.7	0.6
	T3	3.5	3.5	3.7	3.6	3.6
	T4	3.6	3.6	3.6	3.4	3.4
η[c]	T1	0.3	0.9	0.1	0.3	0.6
	T2	0.2	0.8	0.8	0.7	0.9
	T3	0.9	0.9	0.8	0.8	0.8
	T4	0.9	0.9	0.6	1.0	0.9
$C_{Q\eta}$[d] (MHz)	T1	0.3	0.4	1.5	1.5	1.2
	T2	0.2	1.5	1.5	0.7	0.6
	T3	3.9	3.9	4.1	4.0	4.0
	T4	4.1	4.0	3.8	3.9	3.9
δ_{CG2}[e] (ppm)	T1	56.8	56.9	59.1	57.0	57.0
	T2	53.0	52.6	55.0	55.5	55.4
	T3	51.2	51.7	51.1	50.7	50.6
	T4	51.8	52.0	54.1	51.2	51.8
δ_{CG1}[f] (ppm)	T1	-31.2	-31.3	-32.9	-31.7	-31.6
	T2	-29.1	-29.3	-30.7	-30.5	-30.5
	T3	-31.4	-31.6	-31.5	-31.2	-31.2
	T4	-31.9	-32.0	-32.8	-31.4	-31.6

[a]Isotropic ^{27}Al chemical shifts calculated from the average T-O-T angles of the 4 distinct T sites by using the equation of Lippmaa et al.[15] [b]Quadrupole coupling constants calculated from the coordinates of the four nearest oxygen atoms of each T site by using point charge model. [c]Asymmetry parameters calculated by the same method described in [b]. [d]Second order quadrupole effects ($C_Q(1+ \eta^2/3)^{1/2}$) calculated by using the C_Q and η values listed in this table. [e]Shifts of center of gravity on the F2 axis of a simulated 3QMAS NMR spectrum, calculated from the $C_{Q\eta}$ and δ_{iso} values given in this table by using Equation 71 in the reference 14. [f]Shifts of center of gravity on the F1 axis of a simulated 3QMAS NMR spectrum, calculated by using Equation 70 in the reference 14.

In general, local structures of mordenites can be changed by preparation procedures, cations, as well as Si/Al ratios. As shown in the simulated 3QMAS spectra, all these factors would influence T-O-T angles and T-O bond lengths enough to vary the peak positions in 3QMAS spectra. As a result, it is difficult to detect the intensity variation of Al at each T site from different Si/Al ratios although simulated spectra match with experimental spectra reasonably well as shown in Fig. 2.

In summary, ^{27}Al 3QMAS NMR spectra of mordenites with different Si/Al ratios, preparation, and cations were simulated to check the possibility to study Al distribution at T sites in the framework of modernites with ^{27}Al 3QMAS NMR. The local structures of T sites were varied enough to change 3QMAS spectral patterns by all those factors. As a result, the resonance position or intensity variation in the 3QMAS NMR spectra of mordenites is difficult to be correlated with Al distributions at 4 different T sites.

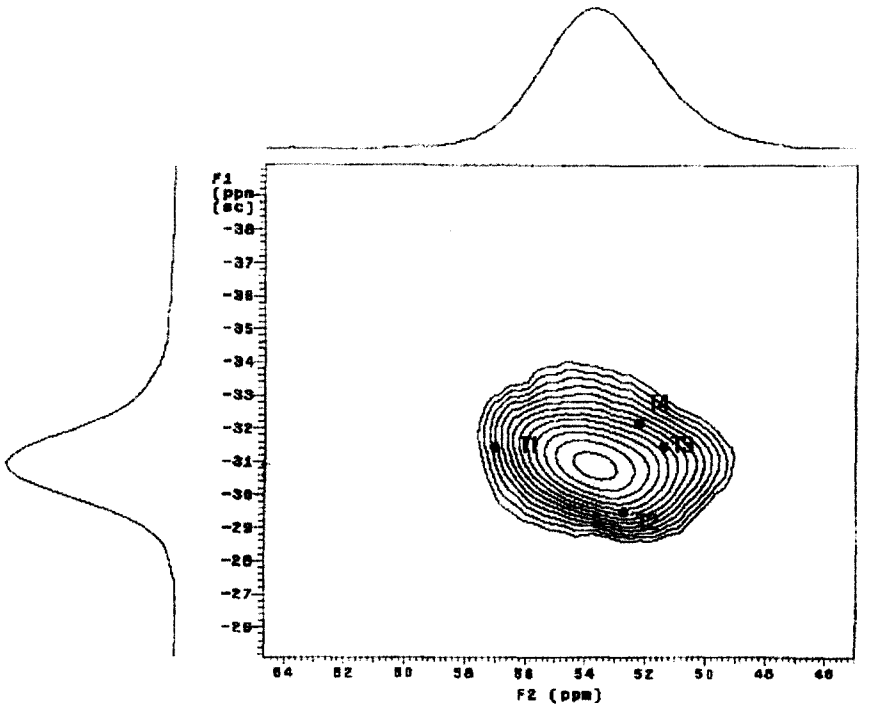

Fig. 2. Simulated positions for 4 T sites of H-nat-5.1 overlapped on the experimental ^{27}Al 3QMAS spectrum of Na-syn-6.5.

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