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Solid-state NMR evidence for the presence of two crystallographically distinct tetrahedral sites in zeolite merlinoite†

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Two crystallographically distinct tetrahedral sites in zeolite merlinoite are identified by ^{29}Si MAS NMR and 2D ^{27}Al quadrupole nutation NMR spectroscopies.

Since the initial work of Lippmaa and Engelhardt in 1981,[1] the use of multi-nuclear solid-state NMR techniques in the characterization of zeolites and related materials has provided many new insights into the structure and chemistry of this important class of microporous solids, particularly in the short-range order. For instance, ^{29}Si MAS NMR can detect the relative populations of five distinct Si environments, *i.e.* $Si(OSi)_n(OAl)_{4-n}$ with $n = 0–4$.[2] When all tetrahedral atoms (T-atoms) in the zeolite framework are crystallographically equivalent with avoidance of Al–O–Al linkages, therefore, the quantitative framework Si/Al ratio can be easily calculated from the ^{29}Si resonance intensities. However, many of the already known zeolite structures contain two or more crystallographically distinct T-sites characterized by different T–O–T and O–T–O bond angles and T–O bond lengths. This allows the Si atoms situated in these sites to exhibit different ^{29}Si chemical shifts, even for the same $Si(OSi)_n(OAl)_{4-n}$ environments, making it difficult to accurately determine the framework Si/Al ratio from the spectra. When structurally distinct lines overlap heavily with one another, in particular, it is not possible to directly deconvolute the ^{29}Si NMR spectra.

Merlinoite (MER topology) is a small-pore, low-silica zeolite that is rarely found in nature.[3] Amongst the early zeolite discoveries, in addition, zeolites W and K-M are known to be synthetic counterparts of MER zeolite.[4,5] The structure of this zeolite is characterized by a three-dimensional pore system consisting of intersecting 8-ring channels.[6] To date, there are three reported ^{29}Si MAS NMR spectra of MER-type zeolites prepared *via* different synthetic routes.[7–9] In all cases, the interpretation and assignment of the spectra have been made based on the implicit assumption that only one crystallographically distinct T-site exists in the zeolite framework. A recurring question is the fact that the Si/Al ratios calculated from the ^{29}Si NMR spectra are not in reasonable agreement with those determined from elemental analysis. This implies that each line in the ^{29}Si MAS NMR spectra of MER zeolites previously reported may be misunderstood. Here we present the ^{29}Si MAS NMR and 2D ^{27}Al quadrupole nutation NMR results showing that two crystallographically distinct T-sites are present in the framework of MER-type zeolites.

An MER zeolite with Si/Al = 1.8 was prepared by heating an aluminosilicate gel with the oxide composition of $1.2Na_2O\cdot 4.8K_2O\cdot 1.0Al_2O_3\cdot 10SiO_2\cdot 150H_2O$ at 100 °C for 18 d. The powder XRD of MER zeolite prepared here reveals that the solid is a highly crystalline MER zeolite and no reflections other than those from MER are observed.[10] This pattern was indexed as orthorhombic with unit-cell dimensions of $a = 14.13(1)$, $b = 14.24(2)$ and $c = 10.10(1)$ Å. A combination of elemental and thermal analyses of the as-synthesized Al-MER sample gives a unit cell composition of $K_{11.1}Na_{0.3}Al_{11.4}Si_{20.6}O_{64}\cdot 17.8H_2O$. The ^{27}Al MAS NMR spectrum of this zeolite exhibits only one line at 58.5 typical of tetrahedral Al sites in zeolites.

Fig. 1 shows the ^{29}Si MAS NMR spectrum of our MER zeolite together with the simulated spectrum and its deconvoluted components. Five well-resolved ^{29}Si lines at −85.1, −89.4, −94.0, −98.7 and −103.2 ppm are observed. The general feature of this spectrum is very similar to the case of zeolite structures having only one T-site such as LTA and FAU zeolites with high Al contents. As seen in Fig. 1, however, curve deconvolution reveals that there is an additional low-intensity shoulder around −108 ppm, reflecting the presence of more than one crystallographically distinct T-site in the framework of MER zeolite. This clearly shows that the ^{29}Si NMR spectra for Al-MER zeolites cannot be interpreted following the manner that the individual lines are implicitly regarded as single Si environments, which has been repeatedly employed in the literature.[7–9] Actually, an attempt to deconvolute the ^{29}Si NMR spectrum of our Al-MER material by assigning the first five lines to $Si(OSi)_n(OAl)_{4-n}$ species with $n = 0–4$ and by ignoring the presence of the high-field line, due to its low intensity, gave a $(Si/Al)_{NMR}$ value of 2.3 that is fairly larger than the bulk Si/Al

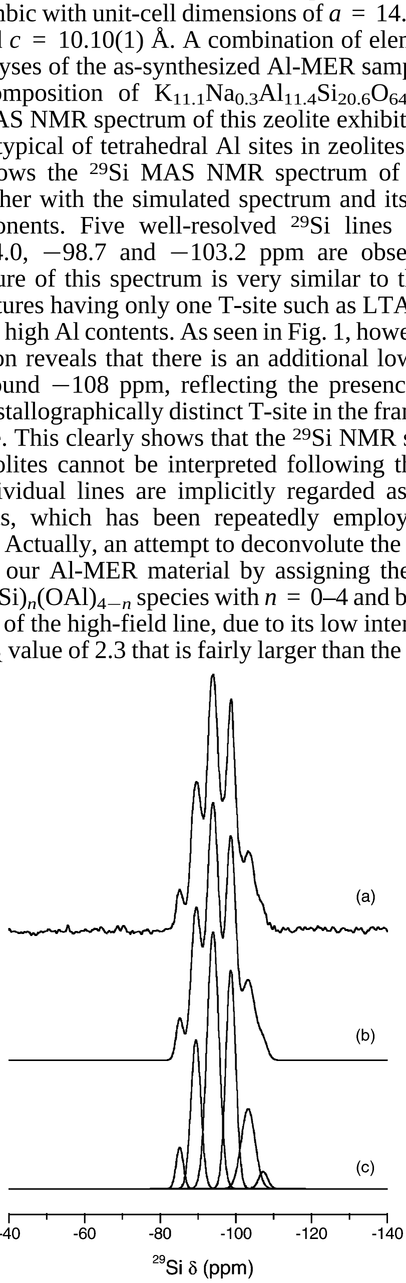

Fig. 1 ^{29}Si MAS NMR spectra of MER zeolite prepared: (*a*) experimental, (*b*) simulated and (*c*) deconvoluted components. Spectrum recorded on a Bruker DSX 400 at 12 kHz spinning rate, 60 s recycle delay, 79.459 MHz, 2.0 μs pulse length (π/5 rad), 1200 scans.

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† Electronic supplementary information (ESI) available: powder XRD and ^{27}Al MAS NMR spectrum of the MFR zeolite. See http://www.rsc.org/suppdata/cc/b0/b004748l/

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Table 1 Chemical shifts, intensities, and assignments of the ^{29}Si NMR resonances in MER zeolite prepared here

Chemical shift (ppm from TMS)	Relative intensity (%)	Assignment	Average T–O–T angle[11]	
			Si_I–O–T	Si_{II}–O–T
−85.1	3.6	$Si_I(OAl)_4$	142.1	
−89.4	17.8	$Si_I(OSi)(OAl)_3 + Si_{II}(OAl)_4$	140.3	148.8
−94.0	37.1	$Si_I(OSi)_2(OAl)_2 + Si_{II}(OSi)(OAl)_3$	139.0	147.2
−98.7	26.1	$Si_I(OSi)_3(OAl) + Si_{II}(OSi)_2(OAl)_2$	137.8	145.7
−103.2	13.5	$Si_I(OSi)_4 + Si_{II}(OSi)_3(OAl)$	136.4	144.0
−107.5	1.9	$Si_{II}(OSi)_4$		142.1

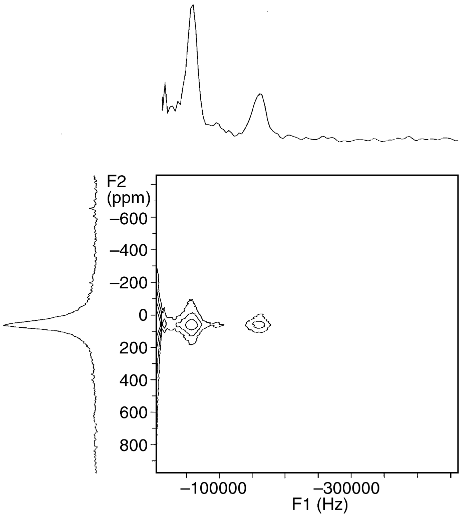

Fig. 2 1D and 2D ^{27}Al quadrupole nutation spectra of MER zeolite recorded on a Varian Unity Inova 200 with an ω_{rf} of 53 kHz. 512 data points were collected in the t_1 dimension in increments of 0.25 μs.

ratio (1.8) from chemical analysis. Although the topological symmetry for the MER framework was initially found to be the tetragonal subgroup *I*4/*mmm*, on the other hand, it has recently been shown that a better refinement is achieved from the orthorhombic subgroup *Immm*.[8,9] In this space group two crystallographically distinct sites T_1 and T_2 with 1 : 1 distribution exist in the unit cell. Considering that the average shift difference in the six ^{29}Si lines of Fig. 1 is 4.5 ppm, the shift effect due to site non-equivalence in the MER framework may be comparable in magnitude to the effect of Al substitution in the first tetrahedral coordination sphere of Si (*ca*. 5 ppm). If such is the case, structurally distinct lines should be superimposed upon one another and a deceptively simple spectrum could be observed as that in Fig. 1(a). A list of the positions, relative intensities, and assignments of the six deconvoluted components of the spectrum is given in Table 1, together with the average Si–O–T angles calculated using the relationship of Ramdas and Kinowski[11] for every resolved Si site. Based on the assignment in Table 1 and assuming a random Al distribution over the two T-sites with avoidance of Al–O–Al linkages, the Si/Al ratio derived from the intensities of the deconvoluted components of 1.9 was calculated to be very close to that from elemental analysis. This result supports the validity of our ^{29}Si NMR interpretation for MER-type zeolites based on the presence of two different T sites in this type of zeolites, which can be further evidenced by the fact that the average Si–O–T angle (142.6°) in our MER zeolite calculated from ^{29}Si MAS NMR data in Table 1 is in good agreement with the value (143.5°) in an MER zeolite with Si/Al = 2.1 from powder XRD Rietveld refinement.[8]

To obtain more firm evidence for the speculation given above, the static ^{27}Al quadrupole nutation NMR spectra[12] for MER zeolite prepared here have been measured with a radiofrequency field (ω_{rf}) of *ca*. 53 kHz, which was previously determined with an $Al(H_2O)_6^{3+}$ solution. Like the MAS spectrum, the 1D ^{27}Al static NMR spectrum exhibits one single line at 58 ppm with the full width at half-maximum of about 4 kHz. As seen in Fig. 2, however, the 2D nutation NMR spectrum consists of two distinct lines at 57 and 162 kHz along the axis F_1. Thus, the two lines corresponding to tetrahedral environments for Al atoms, which overlap in the ordinary MAS NMR spectrum, are further resolved by 2D quadrupole nutation. This reveals the presence of two different quadrupolar environments for framework Al atoms in the MER framework. The line at 57 kHz, which is similar to ω_{rf}, has a negligible quadrupolar interaction and can be attributed to framework Al atom at the site of spherical symmetry.[12] By contrast, the line at 162 kHz, which is about 3 times larger than ω_{rf}, has a quadrupole coupling constant (C_Q) of $\geqslant$ 12 MHz. Thus, it can be assgined to the Al site that is severely distorted from spherical symmetry. This clearly shows that the second Al site is crystallographically different from the first Al site. We believe that the asymmetric parameter (η) of the second Al site must be close to unity, since only one sharp peak is observed in the MAS and static ^{27}Al NMR spectra without any trace of a broad second order quadrupole powder pattern with several singularities typical for site with $C_Q \geqslant 12$ MHz and $\eta < 1$.[13] In parallel with the ^{29}Si MAS NMR evidence, in conclusion, it is clear that two crystallographically distinct T-sites are present in the framework of MER-type zeolites.

The results shown here clearly deomonstrate that if the Si/Al ratios calculated from the ^{29}Si MAS NMR spectra for zeolites, especially for novel materials, do not match well with those from elemental analysis, one must use caution in the interpertation of the spectra obtained. This is because we cannot rule out the possibility that structurally distinct lines are superimposed upon one another, yielding the deceptively simple spectra. In addition, the overall results of this study show that the ^{27}Al quadrupole nutation NMR technique can be very useful for determining the presence of crystallographically different T-sites in the zeolite framework, which is difficult to ascertain by other analytical methods.

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