

Determination of the $\text{Al}^{\text{T1}}/\text{Al}^{\text{T2}}$ Ratio in MAZ Zeolites Using Line Shapes of MQ MAS NMR

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Received: May 25, 1999; In Final Form: June 29, 1999

The MQ MAS NMR is used to evaluate the real, individual line shape of the Al signals in the 1D ^{27}Al MAS NMR spectrum of zeolite materials. By the application of these real line shapes, an improved deconvolution of the 1D MAS NMR spectrum is achieved. This methodology was applied to the two tetrahedrally coordinated Al sites in mazzite zeolite, resulting in an accurate determination of the $\text{Al}^{\text{T1}}/\text{Al}^{\text{T2}}$ ratio. The method proposed here yields significant higher $\text{Al}^{\text{T1}}/\text{Al}^{\text{T2}}$ ratios than those obtained from the classical deconvolution of the 1D ^{27}Al MAS NMR by two Lorentzian shaped lines. This implies an enrichment of Al in the 12-membered channel compared to the ratio proposed earlier in the literature.

Introduction

In 1967, Union Carbide patented the synthesis of the zeolite omega.¹ The framework structure, originally proposed by Barrer, consists of gmelinite cages that joined in columns by shared six-ring faces. The columns run parallel to the *c*-axis. The columns themselves are linked laterally by a 6-fold axis to form a 12-membered ring (Figure 1).² More recently the structure refinement was improved by Rinaldi et al. Instead of the simple 6-fold axis suggested by Barrer, a 6-fold screw axis linked the columns to form the 12-ring window.³ Zeolite omega is therefore isostructural with the mineral mazzite.

Out of the 36 tetrahedral atoms that build up the unit cell, 24 tetrahedral sites are located in the four-membered rings in the gmelinite cages (crystallographically labeled as T1) while the six-membered rings through which the cages are linked to form the columns comprise 12 tetrahedral atoms per unit cell (crystallographic T2 site).

In the past, both ^{29}Si and ^{27}Al MAS NMR have extensively been used to elucidate the Al distribution over the two crystallographically distinct tetrahedral sites of the omega zeolite.^{4–9} By deconvolution of the ^{29}Si MAS NMR spectrum estimates of this aluminum distribution over the two different tetrahedral sites were calculated.^{5,6} The accuracy of this approach is however limited by the coincidence of the Si(*n*Al) bands belonging to T1 and T2.

When studying the mazzite zeolite with ^{27}Al MAS NMR, a rather unique feature is observed. Even at a magnetic field of 9.4 T a clear separation of two Al bands, at nearly 61 and 54 ppm, is encountered for the tetrahedral framework aluminum sites. These were assigned to the Al atoms incorporated in the T1 and T2 crystallographic site, respectively.⁴ The relative ratio between the 61 and 54 ppm signal will then obviously yield the $\text{Al}^{\text{T1}}/\text{Al}^{\text{T2}}$ ratio. Both the groups of Fyfe⁵ and Klinowski⁶ measured the same industrial zeolite omega sample ($\text{Si}/\text{Al} = 4.2$) from Union Carbide, but their analysis resulted in a slightly different $\text{Al}^{\text{T1}}/\text{Al}^{\text{T2}}$ ratio. To determine the relative peak intensities, Lorentzian shaped lines were fitted to the spectrum. Whereas Fyfe et al. performed their measurements at 14.1 T,

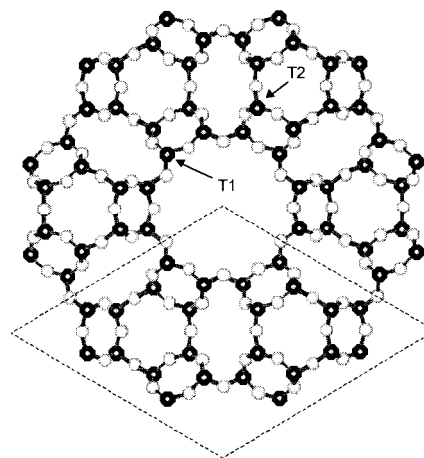


Figure 1. Projection of the MAZ along the *c*-axis. Black circles are T atoms, light circles are the oxygen atoms.

Klinowski et al. used a lower magnetic field of 11.7 T. Later on, the same methodology to evaluate the $\text{Al}^{\text{T1}}/\text{Al}^{\text{T2}}$ distribution was applied to 1D ^{27}Al MAS NMR data obtained at 9.4 T, which generally resulted in a lower $\text{Al}^{\text{T1}}/\text{Al}^{\text{T2}}$ numerical ratio.⁸ Substantial narrowing of the two tetrahedral Al lines in the 1D ^{27}Al MAS NMR spectrum is present when increasing the magnetic field from 9.4 to 14.1 T.⁵ This suggests that quadrupolar interactions are playing a part in the NMR line shapes.

In this paper we show that a quadrupolar interaction is present for the two sites, whereas the resulting influence is the largest for the T1 signal compared to T2. The newly developed MQ MAS method will be used to determine the real, individual line shape of the two tetrahedral sites, on the basis of which the 1D ^{27}Al MAS NMR spectrum can be simulated better. The resulting $\text{Al}^{\text{T1}}/\text{Al}^{\text{T2}}$ ratios are substantially different from those previously assumed in the literature.

Experimental Section

Two mazzite-type materials were synthesized from gels having the following molar chemical composition: 10 SiO_2 , 2.4 Na_2O , 1.0 Al_2O_3 , 0.24 TMA_2O , 110 H_2O and 10 SiO_2 , 2.4 Na_2O , 0.60 Al_2O_3 , 0.24 TMA_2O , 0.97 18-crown-6 crown-ether,

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1.0 1,6-diaminohexane, 110 H₂O, respectively. A detailed description of the synthesis of these materials is given in ref 10. They will be labeled MAZ (3.67) and MAZ (4.03) according to their Si/Al ratio.

The 1D ²⁷Al MAS NMR spectra were recorded on a BRUKER AMX 300 (7 T) and a BRUKER MSL 400 (9.4 T) spectrometer with a resonance frequency for Al of 78.21 and 104.26 MHz, respectively. For the 1D MAS NMR measurements, the pulse lengths were 0.3 and 0.6 μs for the AMX 300 and the MSL 400, respectively, this in order to fulfill the condition for the quantitative measurement of quadrupolar nuclei.¹¹ The 2D MQ(3Q) MAS NMR spectra were obtained using the three-pulse, amplitude-modulated, split-*t*₁ sequence described by Brown and Wimperis in their Figure 14a.¹² This pulse sequence provides directly a sheared spectrum that contains isotropic resolution along the F1 dimension. For the MQ measurements on the BRUKER MSL 400 (9.4 T), 512 spectra were acquired in the F1 dimension. An increment of 10 μs between two successive spectra was used. The pulse lengths were optimized to obtain a maximal signal intensity in the time domain. Pulse lengths of 3.5, 1.5, and 0.6 μs for the three successive pulses were applied. A 0.5 M Al(NO₃)₃ solution was used as the external chemical shift reference.

Results and Discussion

Although a clear separation between the two distinct tetrahedral Al sites in the mazzite samples is obtained in the 1D ²⁷Al MAS NMR spectrum at 9.4 T, the 2D MQ MAS NMR technique was applied to these materials. The 2D ²⁷Al MQ MAS NMR spectrum of MAZ(3.67), measured at 9.4 T, is given in Figure 2a. As is expected for this sample, two well-resolved peaks are observed in the 2D spectrum. A small distortion is seen for the T1 site, which does not influence the isotropic projection. Slices parallel to the F2 dimension can be used to obtain the individual quadrupolar parameters of the various sites.¹³ In these zeolite samples, this is however a difficult procedure due to a distribution of both the quadrupolar coupling constants and the chemical shift which results in a broadening of the NMR powder pattern. Here the slices will mainly be utilized to simulate the experimental 1D spectrum to derive a better Al^{T1}/Al^{T2} ratio. The position of the slices used are indicated in Figure 2a by the labels S1 and S2; the individual line shapes S1 and S2 are given in Figure 2b. No overlap of the two signals is encountered for these slices, as was seen from the 3-dimensional MQ picture of the MAZ(3.67)

The applicability of these slices in the deconvolution of the 1D spectrum is determined by whether the intensity of the line is faithful across the entire slice since the excitation response can be dependent on the orientation of the crystallites, and second whether one slice can give an accurate representation of the 1D line shape.

The octahedral Al line in the spectrum of the aluminophosphate VPI-5 was used to evaluate the intensity across the slices of the MQ MAS spectrum. This signal has a quadrupolar coupling constant QCC of 3 to 3.5 MHz, which is 3 times the value estimated for the T sites in MAZ (vide infra). It can be expected that deviating intensities occur with increasing QCC. Slices across the octahedral Al signal were compared to the theoretical line shape of the powder pattern. Each of these slices was accurately simulated by one quadrupolar powder pattern with a coupling constant of 3.3 MHz, implying the intensity across the slice is not affected by the excitation profile. Correct phasing of the MQ spectrum in the F1 dimension is important in the fitting procedure.

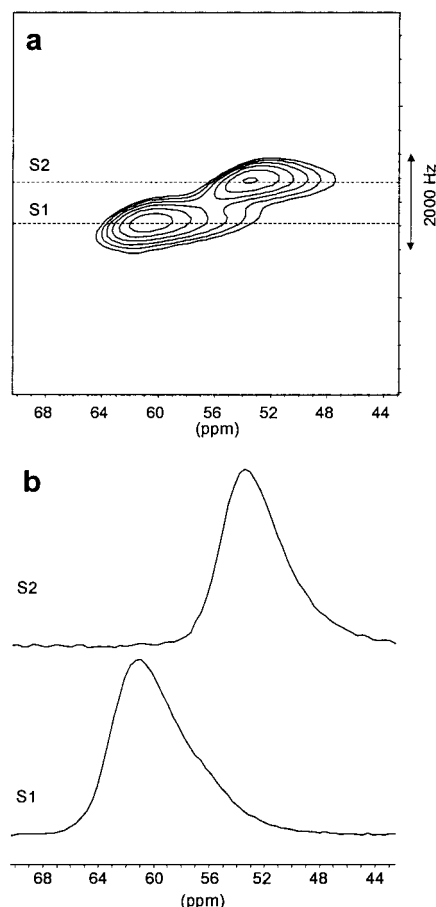


Figure 2. (a) 2D ²⁷Al 3Q MAS NMR spectrum of the MAZ(3.67) sample. (b) 1D projection of the slices S1 and S2.

Several slices through both the T1 and T2 Al MQ MAS NMR line of the MAZ(3.67) sample were compared. The shapes remained identical when no overlap of T1 and T2 was encountered. A small shift (0.3 ppm), due to the distortion of the signal in the 2D MQ spectrum, was observed. A slightly improved line shape can be obtained when a summation of several slices for each of the T sites is made. However, caution regarding the overlap of the T1 and T2 lines is then required for slices between S1 and S2 of Figure 2a. Therefore it is chosen to use only one slice across each T site in the MQ MAS NMR spectrum.

From the slices in Figure 2b, it can easily be seen that the real line shape of the two tetrahedral sites deviates from the Lorentzian shape that was previously used to simulate the spectrum.^{4–9} It is even so that the T1 site exhibits a stronger asymmetry than the T2 site.

The result of the simulation, applying the real line shapes, is given in Figure 3. The 1D ²⁷Al MAS NMR spectrum of the MAZ(3.67) sample, at 9.4 T, can be deconvoluted into two bands with an intensity ratio of 1.75 ± 0.06 to 1 for the T1 to the T2 site. The goodness of fit *R* is 7.6×10^{-3} , where *R* is calculated by sum of the squared differences of the experimental to the fitted data points divided by the sum of the squares of the experimental data. An attempt was also made to deconvolute this spectrum by means of the two Lorentzian shape lines as suggested by Klinowski et al.⁴ A ratio of 0.87 ± 0.06 was obtained, while a less accurate fitting of the experimental spectrum was achieved then ($R = 77 \times 10^{-3}$). This latter ratio corresponds well with the results of Massiani et al. for a similar sample.⁹

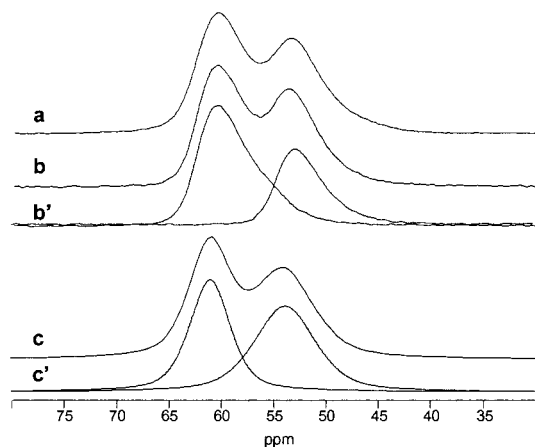


Figure 3. (a) 1D ^{27}Al MAS NMR of MAZ(3.67). (b) Fitted spectrum using the slices (b') S1 and S2 ($R = 7.6 \times 10^{-3}$). (c) Fitted spectrum using (c') two Lorentz lines ($R = 77 \times 10^{-3}$).

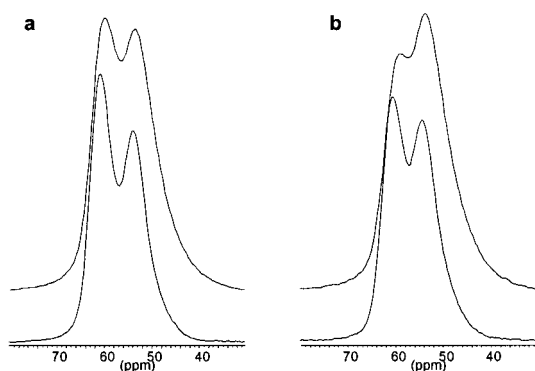


Figure 4. Influence of the magnetic field on the appearance of the 1D ^{27}Al MAS NMR spectra of (a) MAZ(3.67) and (b) MAZ(4.03). Top spectra are measured at 7 T, bottom spectra at 9.4 T.

The origin of this difference in the Al^{T1}/Al^{T2} distribution ratio can be deduced from Figure 4. Here the 1D ^{27}Al MAS NMR spectra of both the MAZ(3.67) and the MAZ(4.03) are displayed. At 9.4 T, for both the MAZ(3.67) and MAZ(4.03), the Al atoms in T1 are found at 61.0 ppm while the T2 Al atoms have their maximum signal intensity at 54.0 ppm. At a magnetic field of 7 T, however, the maximum intensities are at 60.2 and 53.8 ppm, respectively. Furthermore the lowering of the external magnetic field is accompanied by a broadening of the spectral lines. This together with the changes in chemical shift are the driving forces for the apparent changes in the relative Al^{T1}/Al^{T2} ratio seen in Figure 4. This intensity change is most pronounced for the MAZ(4.03) sample.

Both the induced chemical shift and the line broadening are typical properties of quadrupolar nuclei. Under magic angle spinning conditions, the quadrupole-induced chemical shift (QIS) for Al is expressed by eq 1:¹⁴

$$\text{QIS (in ppm)} = \delta_{\text{CG}} - \delta_{\text{iso}} = -6000 (\text{QCC}^2/\nu_Z^2)(1 + \eta^2/3) \quad (1)$$

In this expression the QCC stands for quadrupole coupling constant (in Hz), η for the asymmetry parameter, and ν_Z for the Zeeman frequency of Al (in Hz), whereas δ_{CG} and δ_{iso} represent the center of gravity and the isotropic chemical shift (in ppm), respectively. Since the isotropic chemical shift is field independent, the difference in chemical shift when measuring the sample in different magnetic fields can be used to evaluate the QCC. Depending on the asymmetry parameter, an average

QCC of 1.2 to 1.4 MHz can be calculated for the aluminum in the T1 site while the range for T2 is from 0.6 to 0.7 MHz.

Furthermore, the width of the line is directly proportional to the square of QCC and inversely related to the Zeeman frequency. This explains the difference in the line width measured for the two slices in Figure 2b. Since T1 possesses the largest QCC, a broader signal is encountered compared to the T2 line. The apparent increase of the T2 site in the spectra measured at 7 T to those obtained at 9.4 T is the combined result of the induced chemical shift which is largest for T1 and the increased line width due to the lower Zeeman frequency.

The higher QCC for the T1 compared to the T2 site can be confirmed when the local geometry of the T1 and T2 sites is considered. According to Ghose and Tsang there is a positive correlation between the quadrupole coupling constant and the shear strain $|\psi|$.¹⁵

$$|\psi| = \Sigma |\tan(\theta_i - \theta_0)| \quad (2)$$

θ_i is the individual O—Al—O angle; θ_0 represents the ideal bond angle, being 109.5° in a tetrahedron. Using the refined atomic positions of Rinaldi et al.,³ the shear strain for the T1 and T2 site is 0.3 and 0.2, respectively. Although the atomic positions are obtained from a dehydrated sample, it confirms the larger QCC for the T1 tetrahedral aluminum site.

In the frame of this knowledge, the difference in the Al^{T1}/Al^{T2} ratio determined by Klinowski et al.⁶ and Fyfe et al.⁵ on the same MAZ sample can consequently be explained by the difference in external magnetic field in which the sample was measured. Increasing the field to 14.1 T, as Fyfe et al. did, strongly reduces not only the line width but also the overlap of the T1 and T2 Al signal yielding a more accurate Al^{T1}/Al^{T2} ratio.

The Al distribution in zeolites in general and the Al^{T1}/Al^{T2} ratio in MAZ in particular are essential parameters determining the properties such as Brönsted acidity and cation siting. On the basis of the present, more accurate determination of the Al^{T1}/Al^{T2} ratio, an enrichment of the Al content in the 12-ring channel of the MAZ samples is determined.

Conclusion

A methodology to deconvolute the 1D MAS NMR spectrum of zeolites is presented here. By application of this approach, the Al distribution over the T1 and T2 crystallographic sites of MAZ-type materials was reinvestigated. The real, individual line shape of the individual Al sites, which was determined from the sheared MQ spectrum, not only allowed a better fitting of the 1D ^{27}Al MAS NMR spectrum but indicated a larger quadrupole coupling constant for the Al atoms in the T1 site than those in T2.

Acknowledgment. This work was supported by the Flemish Fund for Scientific Research (FWO—Vlaanderen) and by a G.O.A. project of the Flemish Government. A.M.G is grateful to I.W.T for a research grant, and P.J.G acknowledges the FWO for a position as Research Director.

References and Notes

- (1) Union Carbide Co., *Dutch Patent* 6,710,729, August 3, 1967.
- (2) Barrer, R. M.; Villiger, H. J. *Chem. Soc., Chem. Commun.* **1969**, 659.
- (3) Rinaldi, R.; Pluth, J. J.; Smith, V. *Acta Crystallogr. Sect. B* **1975**, *31*, 1603.

- (4) Klinowski, J.; Anderson, M. W.; Thomas, J. M. *J. Chem. Soc., Chem. Commun.* **1983**, 525.
- (5) Fyfe, C. A.; Gobbi, G. C.; Kennedy, G. J.; Graham, J. D.; Ozubko, R. S.; Murphy, W. J.; Bothner-By, A.; Dadok, J.; Chesnick, A. S. *Zeolites* **1985**, 5, 179.
- (6) Klinowski, J.; Anderson, M. W. *J. Chem. Soc., Faraday Trans. 1* **1986**, 82, 569.
- (7) Massiani, P.; Chauvin, B.; Fajula, F.; Figueras, F.; Gueguen, C. *Appl. Catal.* **1988**, 42, 105.
- (8) Massiani, P.; Fajula, F.; Figueras, F.; Sanz, J. *Zeolites* **1988**, 8, 332.
- (9) Chauvin, B.; Massiani, P.; Dutartre, R.; Figueras, F.; Fajula, F.; Des Courieres, T. *Zeolites* **1990**, 10, 174.
- (10) Goossens, A. M.; Feijen, E. J.; Verhoeven, G.; Wouters, B. H.; Grobet, P. J.; Jacobs, P. A.; Martens, J. A. Submitted.
- (11) Lippmaa, E.; Samoson, A.; Mägi, M. *J. Am. Chem. Soc.* **1986**, 108, 1730.
- (12) Brown, S. P.; Wimperis, S. J. *Magn. Reson.* **1997**, 128, 42.
- (13) Massiot, D.; Touzo, B.; Trumeau, D.; Coutures, J. P.; Virlet, J.; Florian, P.; Grandinetti, P. J. *Solid State Nucl. Magn. Reson.* **1996**, 6, 73.
- (14) Kentgens, A. P. M. *Geoderma* **1997**, 80, 271.
- (15) Ghose, S.; Tsang, T. *Am. Mineral.* **1973**, 58, 748.