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^{17}O MQMAS NMR studies of Na-A and Ca-A†

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We report, for the first time, ^{17}O MQMAS and $^{17}O/^{23}Na$ double resonance NMR studies on calcium-exchanged zeolite sodium-A; the results show that the isotropic shifts of the framework sites are strongly affected by factors including the hydration level and nature of the charge-balancing cations.

Zeolites and other related microporous materials, such as aluminium phosphates, have many applications ranging from molecular sieves and drying agents, to catalysts and catalytic supports. In order to develop new or to improve existing catalytically-active and gas separation materials it is important to understand the interactions that occur in the pores and channels of the zeolite between the zeolite framework and the absorbed molecules. Most of the NMR studies of zeolite frameworks carried out to date have concentrated on the silicon and aluminium spins. However, oxygen constitutes a major part of the zeolite framework and it is *via* the oxygen atoms that many absorbed species bind to the zeolite framework. Little work has been performed in this area due to both the low natural abundance of the NMR-active $I = 5/2$ nucleus, ^{17}O, and the broad ^{17}O resonances typically observed for the framework sites caused largely by the 2nd order-quadrupolar interaction. This latter interaction can, however, be removed by using the multiple quantum magic angle spinning (MQMAS) NMR method introduced by Frydman and Harwood.[1] The method produces 2D spectra with a so-called 'isotropic dimension' free of the 2nd order quadrupole interaction and an 'anisotropic dimension' with the 2nd-order quadrupolar lineshapes. ^{17}O MQMAS NMR spectroscopy has now been used to resolve different framework sites in zeolites with similar quadrupole coupling constants (QCC's), studies to date focussing on hydrated and dehydrated Na-A and K-A, hydrated Sr-A and Tl-A, alkali metal exchanged LSX and also purely siliceous zeolites.[2–6] Pingel *et al.*[2] have reported that the ^{17}O isotropic shift decreases with increasing Si–O–Al angle while Stebbins and co-workers have shown that the hydration level affects the shifts.[6]

The work described here concentrates on the hydrated and dehydrated forms of Na-A and Ca-A. Zeolite A was chosen for study as it has a Si/Al ratio of 1 : 1 and therefore contains only Si–O–Al linkages. Therefore, the distribution in chemical shifts and QCCs that results from the presence of both Si–O–Al and Si–O–Si linkages is minimised. Further experimental details are described below.‡

Sodium zeolite A (Na-A) has the formula $Na_{12}(Si_{12}Al_{12}O_{48})\cdot 27H_2O$ for the 12 Å pseudo-cell. The structure consists of β-cages linked together by double 4-rings, with larger α-cages formed by the voids between the β-cages. β-Cages are formed by 6-rings and 4-rings while α-cages also consist of 8-rings. Three crystallographically distinct framework oxygen sites are present: O(1) forms part of the 8-ring and the 4-ring, O(2) the 8-ring and the 6-ring and finally O(3) the 6-ring and the 4-ring. The crystallographic ratios are 1 : 1 : 2 for the O(1), O(2) and O(3) sites, respectively. There are eight 6-rings per β-cage and six 8-rings per α-cage, however, due to cation repulsion and symmetry considerations a maximum of three cations can occupy the 8-ring site per unit cell. Although little detailed structural work has been carried out on hydrated Na-A, the main sodium site is believed to be located in the 6-ring and therefore eight Na are coordinated to the O(3) and to the more distant O(2) sites.[7] The remaining sodium ions are distributed among the water sites in the α-cage. Hence, every framework oxygen is coordinated to a sodium ion. Structural studies of Ca-A $Ca_6(Si_{12}Al_{12}O_{48})$ indicate that the six Ca^{2+} ions should lie in the 6-rings bound to O(3) and the more distant O(2) sites.[8] Hydrogen-bonded water molecules are coordinated to O(1) and O(2) in the 8-ring.

The ^{17}O 1-pulse spectra of dehydrated and hydrated NaA and CaA show that the ^{17}O spectra are strongly affected by the level of dehydration. Furthermore, the shifts of the ^{17}O resonances on hydration do not appear to correlate with any simple predictions made on the basis of changes in Si–O–Al bond angles. MQMAS spectra of both systems were, therefore, acquired to examine these phenomena in greater detail. (The 1-pulse spectra, and a discussion of effect of dehydration on the bond angles and ^{17}O spectra of NaA are provided in the ESI†).

Three distinct sites can be seen in the MQMAS spectrum of Ca-A (Fig. 1), which shift noticeably upon dehydration (Fig. 2). Several different structural studies of dehydrated Ca-A have been carried out and they all show that the Si–O(3)–Al angle does not change significantly upon dehydration.[9, 10] The Si–O(1)–Al angle increases from 143 to 148 or 152°, depending on the refinement, while the Si–O(2)–Al angle either remains the same at 165° or increases to 175°, again depending on the refinement. Using the correlation of Pingel *et al.*,[2] the O(3) chemical shift should remain unchanged in both the hydrated and dehydrated samples, the O(1) site should shift to lower frequencies upon dehydration, and the O(2) shift should either remain the same or shift to lower frequencies depending on the

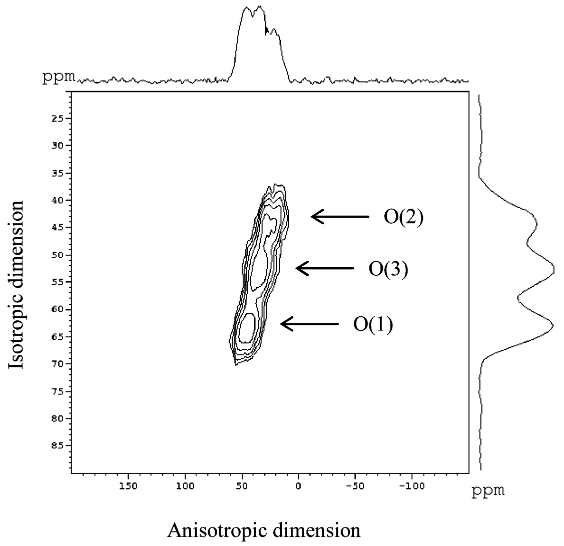

Fig. 1 ^{17}O MQMAS NMR spectrum of hydrated Ca-A.

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† Electronic supplementary information (ESI) available: Fig. S1: schematic structure of zeolite A. Fig. S2: ^{17}O 1-pulse spectra. Fig. S3: ^{17}O MQMAS NMR spectra. Comparison of hydrated and dehydrated Na-A. See http://www.rsc.org/suppdata/cc/b2/b208356f/

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refinement used. Contrary to these predictions, a significant increase in the isotropic shift of one of the sites is seen upon dehydration, which implies that either, there is a reduction in one of the bond angles or that there is another important contribution to the chemical shift. The structural refinements show little change in the positions of the Ca^{2+} ions upon dehydration and, therefore, the main structural change is associated with the loss of the water molecules. This suggests that the highest frequency resonance, centered at approximately 64 ppm in the isotropic dimension of hydrated Ca-A (and 50 ppm in the anisotropic dimension), which is affected the most on dehydration (shifting to 71 ppm in the isotropic dimension), may tentatively be assigned to O(1), since the O(1) environment will be affected the most by the loss of the hydrogen-bonded water molecules. The remaining two peaks are assigned based on their bond angles to O(2) (35 ppm, largest bond angle) and O(3) (broad peak at 49 ppm).

As there are eight possible 6-ring cation sites per unit cell and only six Ca^{2+} ions, there will also be 'bare' O(2) and O(3) atoms, *i.e.*, oxygen atoms with no cation or waters bound to them. This may account for the fact that the intensities in the isotropic dimension of the dehydrated Ca-A MQMAS spectrum deviate from the expected ratio of 1 : 1 : 2 for O(1) : O(2) : O(3), based on the crystallographic results, since the 'bare' O(2) and O(3) atoms may contribute to the O(1) peak. T_1 effects, preferential enrichment of different oxygen sites and the difficulty in exciting all the resonances equally in MQMAS experiments, may also contribute to the differences in intensities.

In order to test the hypothesis that the bare O(1) site may be assigned to the '71 ppm' resonance, a mixed Ca,Na-A sample with the composition Ca_4Na_4-A was prepared. Previous crystallographic work on the dehydrated sample by Seff and Shoemaker[11] showed that both the Ca^{2+} and Na^+ ions are located in the 6-ring, coordinated to O(3) and O(2). In addition, all the 6-rings have an ion coordinated to them, potentially reducing the ^{17}O chemical shift distribution. The MQMAS spectrum of dehydrated Ca_4Na_4-A (ESI†) is very similar to that of dehydrated CaA, although the intensity of the resonance assigned to O(1) has decreased. A $^{17}O/^{23}Na$ transfer of populations in double resonance (TRAPDOR) experiment[12] was then performed on this sample to probe the ^{23}Na–^{17}O dipolar couplings (Fig. 3). Since the dipolar coupling is directly related to the Na–O distance, this experiment should allow us to determine which oxygen peaks correspond to oxygen (O(2) and O(3) sites) coordinated to Na^+. A noticeable decrease in intensity is observed for the resonance at approximately 25 ppm in the 1-dimensional echo spectrum on applying ^{23}Na irradiation, indicating that at least some of the oxygen atoms that contribute to the intensity of this resonance are bound to sodium. Thus, part of the intensity of this resonance arises from the 6-ring oxygen atoms O(2) and O(3) coordinated to Na^+. The resonance at approximately 50 ppm is essentially unaffected by ^{23}Na irradiation, indicating that this site may be assigned to site that is not bound to Na^+.

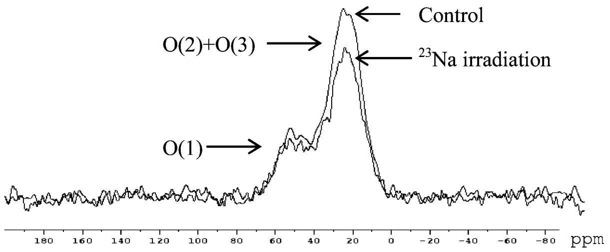

Fig. 3 $^{17}O/^{23}Na$ TRAPDOR NMR spectrum of dehydrated Ca_4Na_4-A. A spinning speed of 10 kHz and ^{23}Na rf power of 96 kHz were used.

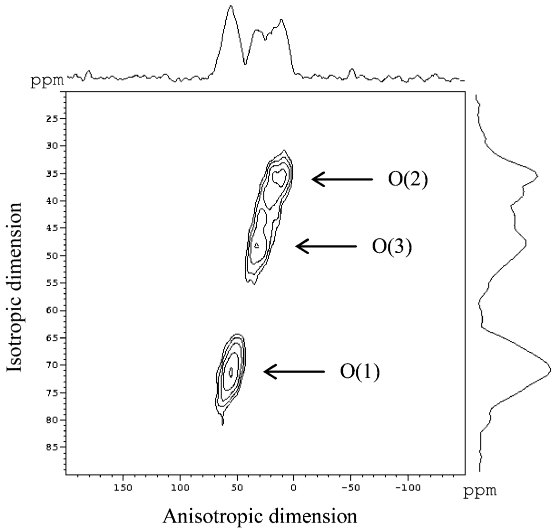

Fig. 2 ^{17}O MQMAS NMR spectrum of dehydrated Ca-A. A spinning speed of 13 kHz was used and tentative assignments are as indicated.

The TRAPDOR results for the resonance at 50 ppm are consistent with either 'bare' oxygen sites *or* O(3) atoms coordinated to Ca^{2+} ions. In order to test the latter suggestion, we prepared samples of both the hydrated and dehydrated forms of Sr_6-A and Sr_4Na_4-A and the hydrated form of Zn_6-A.[13] Very similar results were obtained suggesting that changes in the divalent cation have less of an effect on the ^{17}O spectra than the effects due to dehydration in these systems. Our assignments of the oxygen sites for the spectra of the hydrated M^{2+} exchanged materials are in agreement with those of Stebbins and coworkers for Sr-A, which were made partially on the basis of the intensities of the different resonances.[6]

In conclusion, we suggest that although the ^{17}O isotropic shift is affected by the Si–O–Al bond angle, simple correlations only seen to hold in systems where all the oxygen atoms are bound to cations or water molecules, for example hydrated Na-A. However, large perturbations in chemical shifts are observed when the sodium ions are replaced by a divalent cations such as Ca^{2+} and the chemical shifts in these systems become strongly dependent on the level of hydration. Double resonance experiments can help in the assignments of the different oxygen sites.

Notes and references

‡ Calcium ion-exchange was carried out using conventional aqueous ion-exchange methods.[7] ^{17}O isotopic enrichment was achieved by exposing the dehydrated zeolite (500 °C for 16 h under vacuum) to $^{17}O_2$ gas at approximately atmospheric prssure and the resulting closed system was the heated to 580 °C for 16 h. ^{17}O MAS NMR experiments were performed on a Bruker DMX 600 MHz spectrometer equipped with a 4 mm probe, with a $\pi/6$ of 1.4 μs. The triple-quantum MAS experiments were carried out using two high power pulses (4.5 and 2.0 μs) followed by a weak z-filter pulse (32 μs).[14]

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