

Facile, Room-Temperature ^{17}O Enrichment of Zeolite Frameworks Revealed by Solid-State NMR Spectroscopy

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ABSTRACT: A new approach for room-temperature ^{17}O enrichment of zeolites reveals a surprisingly dynamic and labile framework, where rapid and reversible bond breaking takes place. ^{17}O NMR spectroscopy shows that although O sites in both framework Si-O-Al and Si-O-Si linkages are enriched simply on exposure to $\text{H}_2^{17}\text{O}(\text{l})$, the enrichment of Si-O-Al species is more rapid, with a more uniform framework enrichment observed at longer durations. We demonstrate that this unexpected enrichment can be observed for two different framework topologies and for Na-exchanged (*i.e.*, non-acidic) zeolites, as well as their protonic forms, confirming that the Brønsted acid proton is not necessary for isotopic exchange into the framework. This work not only offers new opportunities for structural characterization of these chemically and industrially important materials using NMR spectroscopy, but suggests that further investigation of the rate and position of enrichment in zeolite frameworks could provide new insight into their chemical reactivity and their stability in aqueous-based applications such as ion exchange and catalysis.

Introduction

Aluminosilicate zeolites are some of the most commonly used catalysts in industrial heterogeneous catalysis, as a result of their shape selectivity and tunable acidity.¹ Understanding the structure-property relationships in these important materials by diffraction techniques is challenging, because of the lack of long-range order that results from the inclusion of Al in the framework. This leads to disorder in the location of extra-framework cations and adsorbed molecules within the pores. In this context, solid-state NMR spectroscopy provides a powerful tool for structural characterisation, complementary to diffraction, owing to its sensitivity to the local structural environment.²⁻³ For aluminosilicate zeolites, ^{29}Si (spin $I = 1/2$, 4.7% abundant) and ^{27}Al ($I = 5/2$, 100% abundant) NMR spectra have been widely exploited for characterisation of the framework, providing information on the neighbouring and next-nearest neighbour (NNN) environments, while ^1H ($I = 1/2$, 100%) and ^{13}C ($I = 1/2$, 1%) NMR spectra can provide information on host-guest interactions with the species within the pores.³⁻⁴ However, despite making up nearly 2/3 of the zeolite framework, oxygen has been studied much less by NMR spectroscopy, owing to the extremely low natural abundance of the NMR-active isotope, ^{17}O ($I = 5/2$, 0.037%). Even routine ^{17}O MAS NMR experiments require costly isotopic enrichment to be feasible on reasonable timescales, and more complex experiments (involving magnetisation transfer between the nuclear spins) remain challenging unless enrichment levels are high.⁵ Conventionally, ^{17}O enrichment of zeolites has been carried out post synthesis, using either (i) exchange with $^{17}\text{O}_2(\text{g})$ ⁶⁻⁹ or (ii) steaming with $\text{H}_2^{17}\text{O}(\text{g})$,¹⁰⁻¹³ both involving high temperatures (typically 400-600 °C for 4-72 h), which could potentially lead to degradation and/or dealumination of the framework. Although alternative lower-temperature en-

richment approaches (*e.g.*, ionothermal synthesis) have been demonstrated for zeotypic materials,¹⁴⁻¹⁶ these have not been widely implemented for zeolites owing to their greater synthetic challenge.

Recent work on the ADOR (Assembly, Disassembly, Organization and Reassembly) process,^{17,18} where the chemically-selective disassembly of hydrolytically-unstable parent frameworks produces novel “daughter” zeolites that cannot be synthesized directly by standard hydrothermal methods, has shown that using $\text{H}_2^{17}\text{O}(\text{l})$ in the hydrolysis results in the incorporation of ^{17}O within the bulk zeolitic layers,¹⁹ suggesting a much more significant rearrangement of the framework than first thought. The chemical nature of “ADOR-able” zeolites, which include hydrolytically-sensitive dopant elements such as Ge, are different from conventional aluminosilicate zeolites, as are the acidic conditions under which most hydrolyses are carried out, and the driving force for the reaction. However, when taken in conjunction with a recent preliminary observation of ^{17}O enrichment of a chabazite (topology type CHA) framework upon hydration with $\text{H}_2^{17}\text{O}(\text{l})$,²⁰ the extensive enrichment seen in ADOR raises more general questions about the lability, flexibility and dynamic nature of zeolite frameworks. In this work, we show that rapid and extensive ^{17}O enrichment of zeolites with two different framework topologies (mordenite, topology type MOR, and ferrierite, FER) is possible simply by room temperature hydration with $\text{H}_2^{17}\text{O}(\text{l})$. This surprising observation not only provides a cost-effective, low-temperature and simple route to ^{17}O enrichment of zeolites, but raises important questions about the chemical reactivity of these industrially important solids, and their applications in aqueous-based processes such as ion exchange and aqueous phase reactions.^{21,22}

Experimental Methods

Sample preparation and basic characterisation

H-MOR was prepared by deammoniation of $\text{NH}_4\text{-MOR}$ (Zeolyst CBV21a, Si/Al = 11) at 550 °C for 5 h. Na-MOR was prepared by ion exchange of $\text{NH}_4\text{-MOR}$ (0.5 g) in 50 mL 3 M NaCl at 80 °C for ~16 h. H-FER was prepared by deammoniation of $\text{NH}_4\text{-FER}$ (Zeolyst CP914C, Si/Al = 11) at 550 °C for 5 h. Samples were enriched in ^{17}O by condensing ~0.03 L $^{17}\text{O}_2(\text{g})$ (Cortecnet, 70% enriched) into a pre-evacuated quartz vial containing between 0.1 and 0.2 g of zeolite, before heating in a tube furnace at 600 °C for 12 hr (H-MOR) or 550 °C for 24 h (H-FER and Na-MOR) for 12 h. A ramp rate of 5 °C min^{-1} was used for heating and cooling. For *in situ* hydration, zeolites were first dehydrated by heating under vacuum (10^{-3} Torr) at 300 °C for 18 h. A slurry was then prepared by mixing 50 mg of zeolite with 50 μl of $\text{H}_2^{17}\text{O}(\text{l})$ (Cortecnet, 90% enriched), sealed in a disposable PTFE HR MAS insert and placed inside a Bruker 4 mm ZrO_2 rotor. Powder XRD measurements were acquired for the H-MOR sample removed from the sealed HR MAS insert after ~250 days (*i.e.*, after all NMR experiments were completed). The powder was placed in a capillary, and data was acquired in ~80 mins (over a 2θ range of 3-50°) on a STOE STADIP instrument operated in Debye-Scherrer mode equipped with a Cu X-ray tube, a primary beam monochromator ($\text{CuK}_{\alpha 1}$), and a position-sensitive scintillation linear detector.

Solid-state NMR spectroscopy

Solid-state NMR experiments were performed using Bruker Avance III spectrometers equipped with wide-bore magnets operating at a magnetic field strength, B_0 , of 9.4 and 14.1 T, corresponding to ^1H Larmor frequencies, ν_0 , of 400 and 600 MHz, respectively, using a conventional Bruker 4 mm low- γ HX double resonance probe. Powdered samples were either (i) packed into conventional 4 mm ZrO_2 rotor or (ii) slurried with $\text{H}_2^{17}\text{O}(\text{l})$ (see above) and sealed within a HR MAS insert inside a 4 mm ZrO_2 rotor, and rotated at rates between 10 and 14 kHz. Chemical shifts are quoted in ppm relative to $\text{H}_2^{17}\text{O}(\text{l})$, $\text{Al}(\text{NO}_3)_3$ (1 M) and $\text{Si}(\text{CH}_3)_4$, measured using secondary (solid) references of aluminium acetylacetonate ($\text{Al}(\text{acac})_3$, ^{27}Al $\delta_{\text{iso}} = 0$ ppm) and octakis(trimethylsiloxy)silsesquioxane (Q8M8, $\text{OSi}(\text{CH}_3)_3$ $\delta_{\text{iso}} = 11.3$ ppm). ^{29}Si MAS NMR experiments were carried out using nutation frequencies, ν_1 , of 77 kHz (H-MOR, 14.1 T) and 90 kHz (H-FER and Na-MOR, 9.4 T) and a recycle interval of 120 s. ^{27}Al MAS NMR experiments were carried out at 9.4 T, with $\nu_1 = 115$ kHz and a recycle interval of 0.5 s. For ^{17}O , experiments were carried out at 14.1 T with $\nu_1 = 62.5$ kHz, using a recycle interval of 1 s. MQMAS experiments were acquired using a triple-quantum amplitude modulated z-filter pulse sequence, with a final central-transition selective ($\nu_1 \approx 11$ kHz) 90° pulse. Further experimental details for MQMAS spectra are given in the Supporting Information). Spectra are shown after a shearing transformation and referenced using the convention described in Ref. 23. The relative MQMAS efficiencies were simulated for the three pulse z-filter pulse sequence using the SIMPSON²⁴ density matrix simulation program, with the parameters used experimentally, for the C_Q values determined from the experimental spectra.

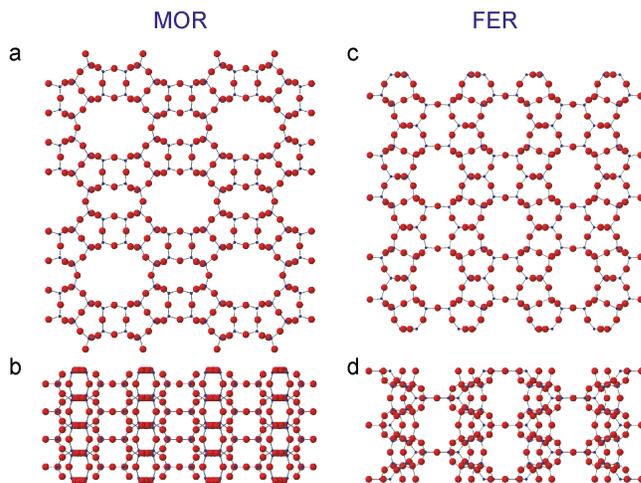


Figure 1. Framework structure of (a, b) mordenite and (c, d) ferrierite, viewed down the (a, c) z and (b, d) y axes, showing the 8 MR and 12 MR channels of MOR down the z axis and the intersecting 10 MR and 8 MR channels of FER.

Results and Discussion

Mordenite (MOR) (Figure 1) contains parallel 8 and 12 membered-ring channels, and is widely used as a heterogeneous solid-acid catalyst.²⁵ Figure 2 shows ^{17}O MAS and multiple-quantum MAS (MQMAS)²⁶⁻²⁸ NMR spectra of a 2-day old slurry of 50 mg of H-MOR with 50 μl of (90% enriched) $\text{H}_2^{17}\text{O}(\text{l})$. The ^{17}O MAS NMR spectrum is dominated by a signal from $\text{H}_2^{17}\text{O}(\text{l})$ at ~0 ppm, but a shoulder at higher shift suggests other ^{17}O species may be present. These can be resolved in the MQMAS spectrum (where the second-order quadrupolar broadening is removed to give a high-resolution, or isotropic, spectrum).²⁶⁻²⁸ The MQMAS spectrum in Figure 2b shows two clear resonances, in addition to the residual signal from water (marked *), which has negligible quadrupolar coupling and so should not appear in the MQMAS spectrum. Note, it is not possible to resolve signals from the crystallographically distinct O species, owing to the disorder introduced both by Al substitution into the framework and the presence of H_2O within the pores. The presence of 10 distinct O species (and disorder introduced by Al substitution) leads to a small distribution of chemical shifts (and a corresponding broadening along an axis of +17/31 in the MQMAS spectrum), more clearly seen in Figure 2 for Si-O-Al species.²⁶⁻²⁸

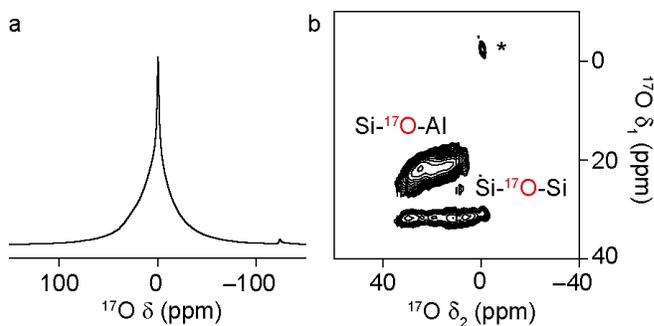


Figure 2. ^{17}O (14.1 T, 10 kHz) (a) MAS and (b) MQMAS spectra of a 50 μl /50 mg of H-MOR/ $\text{H}_2^{17}\text{O}(\text{l})$ left for 2 days. * denotes signal from $\text{H}_2^{17}\text{O}(\text{l})$. Total acquisition times of (a) ~1 and (b) ~18 h.

Table 1. Average ^{17}O NMR parameters extracted from the MQMAS spectrum in Figure 2b.

Species	$\langle\delta_i\rangle$ (ppm)	$\langle\delta_{\text{iso}}\rangle$ (ppm)	$\langle P_Q\rangle^a$ / MHz	$\langle C_Q\rangle$ / MHz
Si- ^{17}O -Al	22.4(5)	33(1)	3.9(5)	3.8(5)
Si- ^{17}O -Si	31.7(5)	43(1)	5.2(5)	5.0(5)

$$^a P_Q = C_Q(1 + \eta_Q^2/3)^{1/2}$$

The (average) NMR parameters extracted from the centre-of-gravity of the spectral lineshapes²⁹ are given in Table 1 (see also Supporting Information), and confirm the assignment of the two signals as framework Si- ^{17}O -Al and Si- ^{17}O -Si species.⁶⁻¹³ The NMR parameters are in broad agreement with those obtained in a previous ^{17}O NMR study of H-MOR,⁹ although this was carried out on a dehydrated zeolite (enriched post synthesis by exchange with $^{17}\text{O}_2(\text{g})$).

Figure 2 suggests that significant ^{17}O enrichment of the zeolite framework has been obtained simply by mixing dehydrated H-MOR with $\text{H}_2^{17}\text{O}(\text{l})$ for 2 days. This result is more notable in that there has been no heating of the sample (beyond the frictional heating from sample rotation during the experiment, estimated to be ~ 5 - 8 °C for MAS at 10 kHz), and there is no additional acid present (unlike the conditions typically used in ADOR reactions). There is no spectral evidence for Si- $^{17}\text{O}(\text{H})$ -Al species, confirming (as would be expected) that the Brønsted acid H is not attached to the framework in the hydrated zeolite, but is associated with water. This is not the case for the dehydrated H-MOR studied in previous work, where signals from Si- $^{17}\text{O}(\text{H})$ -Al species were seen.⁹ From the high-resolution (δ_i) projection of the MQMAS spectrum in Figure 2b, relative Si- ^{17}O -Al:Si- ^{17}O -Si intensities of $\sim 3.1:1$ are obtained. Although MQMAS is inherently non-quantitative,²⁶⁻²⁸ the intensities of the spectral resonances can be corrected by simulating the expected relative efficiencies for multiple-quantum excitation and conversion (estimated, using SIMPSON²⁴ as described above, as $\sim 1:0.42$ for Si- ^{17}O -Al:Si- ^{17}O -Si, respectively). This gives a corrected Si- ^{17}O -Al:Si- ^{17}O -Si ratio of $\sim 1.3:1$ for the spectrum in Figure 2b. This is not in agreement with the ideal ratio of $\sim 0.2:1$ (calculated using Si/Al = 11 and assuming only Si- ^{17}O -Al (*i.e.*, not Si- $^{17}\text{O}(\text{H})$ -Al) are present), suggesting that, at this short slurring time the enrichment is preferred for Si-O-Al bonds.

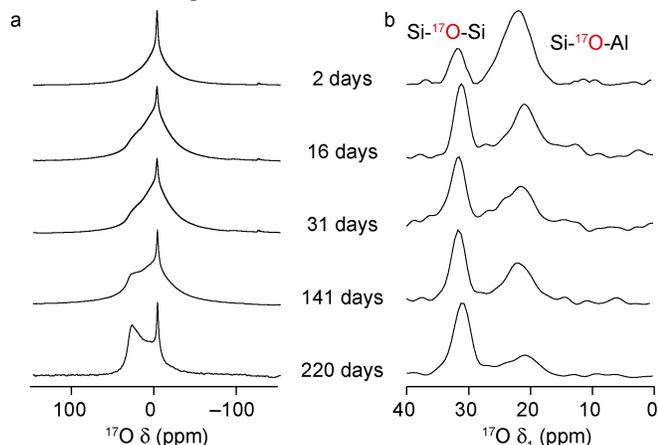


Figure 3. ^{17}O (14.1 T) (a) MAS and (b) isotropic projections of MQMAS NMR spectra of a 50 $\mu\text{l}/50$ mg slurry of H-MOR/ $\text{H}_2^{17}\text{O}(\text{l})$ after varying times. Spectra are shown normalised.

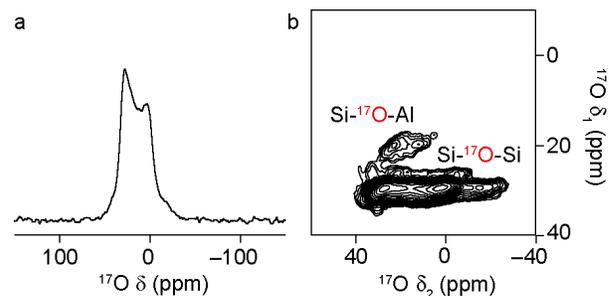


Figure 4. ^{17}O (14.1 T, 14 kHz) (a) MAS and (b) MQMAS NMR spectra of H-MOR enriched post synthesis by exchange with $^{17}\text{O}_2(\text{g})$.

Figure 3 shows ^{17}O MAS and isotropic MQMAS spectra of the same zeolite slurry, acquired after varying times. Although the signal from $\text{H}_2^{17}\text{O}(\text{l})$ is present in all MAS NMR spectra, the signals at higher shift become relatively more intense as the hydration time increases. Figure 3b reveals a clear preference for enrichment of the Si-O-Al species at shorter hydration times, but the Si- ^{17}O -Al:Si- ^{17}O -Si ratio reflects more uniform enrichment at longer slurring times. However, the final level (and position) of enrichment may be limited by the initial volume of $\text{H}_2^{17}\text{O}(\text{l})$ added to the slurry. The faster replacement of O atoms in Si-O-Al linkages than in Si-O-Si bonds indicates at least two mechanisms are operating in this process. It seems likely that the H_2O interacts more strongly at sites near framework Al either by interaction with the Al itself, with Brønsted acid species associated with it, or *via* hydrogen bonding to the adjacent O atoms, and that this interaction facilitates faster exchange.

Figure 4 shows ^{17}O MAS and MQMAS spectra of H-MOR enriched post synthesis by exchange with $^{17}\text{O}_2(\text{g})$ (at 600 °C for 12 h). Given the high temperature used in this process it might be expected that the enrichment would be more uniform for this sample. The MQMAS spectrum is very similar (see overlay in Supporting Information), confirming extensive framework enrichment in both cases. It can be seen that the Si- ^{17}O -Si signal is slightly shifted and a little broader in the sample enriched using gas exchange, suggesting there are some Si-O-Si species (at lower δ_i) that are more difficult to enrich under the slurring conditions used. However, it is not clear if the hydration level (and therefore the exact framework geometry) of the two zeolites is identical. A Si- ^{17}O -Al:Si- ^{17}O -Si ratio of $\sim 0.18:1$ (after correction of the MQMAS intensities) is observed for the gas-enriched H-MOR, in much better agreement with that expected in the ideal case. Although it is difficult to directly compare (and, indeed, to measure) absolute levels of enrichment for the samples enriched using the two approaches (particularly as one enrichment is carried out *in situ*), the signal intensity in the ^{17}O MAS NMR spectra (after accounting for the mass differences) suggests the level of enrichment for the two is of the same order of magnitude, with the sample enriched by room temperature exchange with $\text{H}_2\text{O}(\text{l})$ giving ~ 2 - 3 times more signal. From previous work on zeolites¹⁹ where enrichment levels were measured using mass spectrometry, we can estimate the enrichment level to be 15-25% (with a maximum possible level, assuming no water was lost and equilibrium was reached, of $\sim 50\%$).

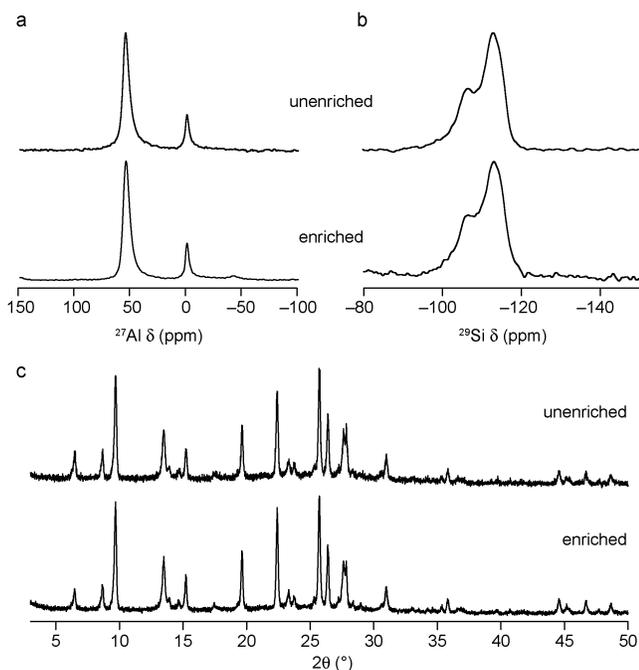


Figure 5. (a) ^{27}Al (14.1 T, 14 kHz) and (b) ^{29}Si (14.1 T, 14 kHz) MAS NMR spectra of H-MOR prior to enrichment and of a H-MOR/ $\text{H}_2^{17}\text{O}(\text{l})$ slurry, after (a) 60 days and (b) 218 days. (c) Powder XRD patterns of H-MOR prior to enrichment and of a sample of H-MOR slurred with $\text{H}_2^{17}\text{O}(\text{l})$ for 250 days.

The observation of significant ^{17}O enrichment of the zeolite framework simply by exposure to $\text{H}_2^{17}\text{O}(\text{l})$ is perhaps surprising given the role of many zeolites in catalysis and ion exchange, and suggests that the bonds within the framework are unexpectedly labile, even at room temperature. However, as shown in Figure 5, bond breakage appears reversible, as the ^{29}Si and ^{27}Al MAS NMR spectra show little change to the material (*i.e.*, no framework degradation or dealumination), and powder XRD patterns of the sample before and after enrichment are very similar. This is in contrast to the hydrolysis and framework breakdown seen (and indeed actively promoted) during the ADOR process.¹⁷⁻¹⁹ The bond breaking and formation appears extremely facile, allowing approach to an equilibrium isotopic distribution, and any activation barrier must be relatively low. No evidence for the formation of Q^3 (*i.e.*, Si-OH) species is seen by ^{29}Si NMR spectroscopy (see the Supporting Information for additional cross polarization experiments), confirming any reaction is rapid on the NMR timescale and no framework degradation occurs. Although Al(VI) species are seen in the ^{27}Al MAS NMR spectrum, these are formed reversibly upon hydration of mordenite, as they have been shown to be in other zeolites, such as Beta.³⁰⁻³³ While such “framework-associated” Al(VI) sites may represent a first step towards dealumination, they are not the result of removal from the framework or framework breakdown, and, as is clear from Figure 5b, are present both before and after reaction with $\text{H}_2\text{O}(\text{l})$.

This room temperature ^{17}O enrichment of zeolite frameworks is not specific to H-MOR, as shown in Figure 6, where a similar observation is made for slurries of Ferrierite (H-FER). As shown in Figure 1, the FER and MOR structures are similar, with FER containing orthogonal 8 and 10 membered-ring channels, but lacking the single 4 membered-ring subunit, which could potentially provide a point of strain within the

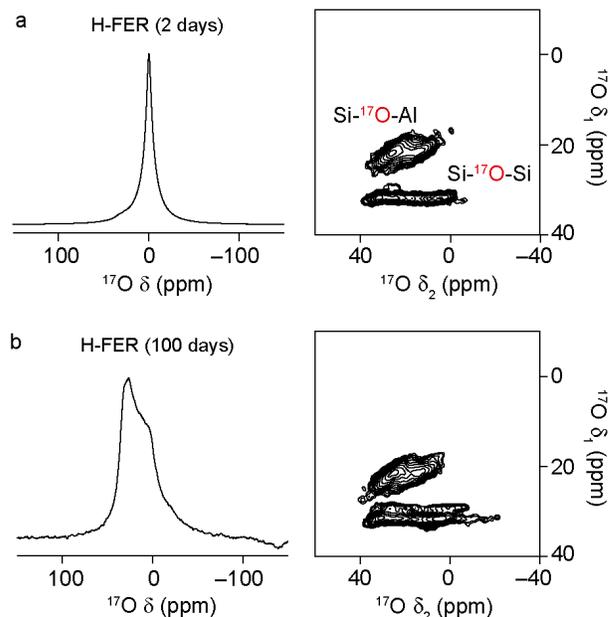


Figure 6. ^{17}O (14.1 T, 10 kHz) MAS and MQMAS spectra of a 50 μl /50 mg slurry of H-FER/ $\text{H}_2^{17}\text{O}(\text{l})$ left for (a) 2 days and (b) 100 days.

structure.²⁵ Figure 6 shows ^{17}O MAS and MQMAS spectra of a slurry of 50 mg of H-FER with 50 μl of (90% enriched) $\text{H}_2^{17}\text{O}(\text{l})$, after 2 and 100 days of reaction. At shorter hydration times the ^{17}O MAS spectrum is dominated by water, although there are additional signals at higher δ . These can be clearly resolved in ^{17}O MQMAS spectra, where preferential enrichment of Si-O-Al is observed after 2 days hydration, but an increasing amount of Si-O-Si is seen after 100 days of exposure (see also Supporting Information). As observed for MOR, additional Si-O-Si signals are seen (at lower δ_1) at the longer times, suggesting some framework sites enrich more slowly. As for MOR, a distribution of chemical shifts (resulting from the differences in the distinct O environments) leads to broadening in the isotropic spectrum. The isotropic shifts observed are also slightly different to MOR, reflecting the different framework topologies and consequent differences in the bond angles. The ^{27}Al and ^{29}Si MAS NMR spectra before and after enrichment (shown in the Supporting Information) are very similar, confirming no framework breakdown is observed.

Figure 7 shows ^{17}O MAS and MQMAS spectra of a 50 μl /50 mg slurry of Na-MOR/ $\text{H}_2^{17}\text{O}(\text{l})$, left for 25 days, and also demonstrates enrichment of both Si-O-Al and Si-O-Si framework linkages. This is of interest because it suggests the Brønsted acid H is not required for bond breaking and remaking to occur. As shown in the Supporting Information, there is little difference in ^{27}Al and ^{29}Si MAS NMR spectra before and after enrichment, confirming once again that this process does not result in any framework breakdown. However, unlike H-MOR, no Al(VI) species are present in the ^{27}Al MAS NMR spectra of Na-MOR, suggesting that while these framework associated Al could play some role in the enrichment process for H-MOR, they are not crucial for framework lability, implying that different mechanistic processes may be active in different forms of the zeolite. As shown in the Supporting Information, it does appear from our preliminary results that the enrichment is slower for Na-MOR, with enrichment primarily of only Si-O-Al species seen after 2 days, but more

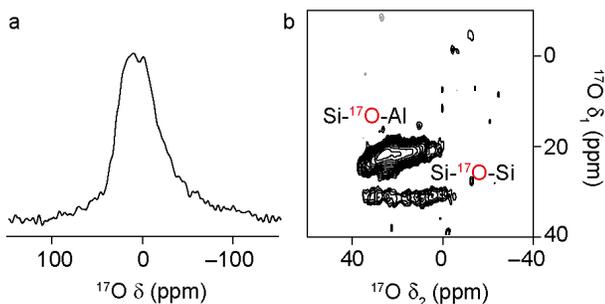


Figure 7. ^{17}O (14.1 T, 10 kHz) MAS and MQMAS spectra of a 50 μl /50 mg slurry of Na-MOR/ $\text{H}_2^{17}\text{O}(\text{l})$ left for 25 days.

systematic and quantitative measurements would be required to investigate this observation more fully.

^{17}O enrichment of solid-state materials has been demonstrated using a number of different approaches, including hydrolysis of reactive precursors, ionothermal enrichment, dry gel conversions reactions, low-temperature steaming, mechanochemistry and higher temperature gas exchange.^{5,14-16,34-39} In all cases, the cost-effective and atom-efficient nature of the procedure is a key driver (given the high cost of isotopically enriched reagents), but the method of choice varies according to the chemical nature of the material of interest. For zeolites specifically, as discussed above, most prior approaches have utilized high temperature reactions (with either $^{17}\text{O}_2(\text{g})$ or $\text{H}_2^{17}\text{O}(\text{g})$). It is clear that high temperature routes have potential disadvantages regarding energy costs, and they can result in partial framework decomposition and/or dealumination as the temperature increases.^{1,40-42} However, the enrichment obtained using these approaches is more likely to be uniform (as seems to be the case for the zeolites studied in this work). In contrast, the very simple nature of enrichment by exposure to water at room temperature requires no specialist equipment at all, can be carried out on the bench, appears to be widely applicable (unlike *e.g.*, ionothermal approaches¹⁶) and is cost-effective both in terms of energy and reagents. We have demonstrated here that the early stages of the reaction result in less quantitative enrichment (although one could argue that this in itself provides information on chemical reactivity and mechanism, facilitating *in situ* studies in a way that the high-temperature approaches cannot). More uniform enrichment is seen at longer hydration times, and the system may well be able to reach equilibrium if sufficient liquid water is delivered.

Recent computational work on a CHA zeolite system,²⁰ predicted low energy barriers for the breaking of Si-O-Si and Si-O-Al bonds in hydrated zeolites, suggesting that these bonds could be labile even at room temperature. We were able to confirm lability by demonstrating reversible ^{17}O exchange in the system (although this requires additional mechanistic steps than the initial bond breakage considered computationally). Computation suggested that bond breakage involved a chain of four water molecules and proton shuttling, and the work determined that the energy barrier for hydrolysis of Si-O-Al linkages was lower (by a factor of ~ 2) than that for Si-O-Si bonds, in good agreement with our experimental observations here for more complex framework systems. Here, we have demonstrated that framework lability in zeolites is more general, and not restricted to systems containing 4MR (as in CHA), but that extensive and rapid enrichment is seen in systems with different framework topologies and ring sizes. MOR is considerably more complex than CHA, with 4 different T

sites on which Al could be substituted (as opposed to 1), 10 (rather than 4) distinct O sites (which enrich at different rates), and exhibits Al(IV) and Al(VI) upon hydration; suggesting different mechanisms may well be relevant for framework lability. Furthermore, the observation of ^{17}O enrichment in Na-MOR, where no Brønsted acid protons are present, suggest that enrichment in this system proceeds *via* a different mechanistic pathway than that proposed previously. The complexity of the MOR/FER frameworks (in comparison to CHA) increases the challenge of computation in these cases, but future computational work (alongside more extensive and quantitative experimental measurements) may be required to understand and exploit the chemical reactivity of these systems.

Conclusions

In this work we have explored an unexpectedly facile and cost-effective route for room-temperature ^{17}O enrichment of zeolite frameworks. Rapid enrichment of framework O species was seen in zeolites with different topologies, with preferential enrichment of Si-O-Al species at shorter hydration times and a more uniform enrichment at the longer durations. We have shown that ^{17}O enrichment is rapid, with hydration for < 24 h providing sufficient sensitivity to acquire ^{17}O MQMAS spectra in 24 h. Similar results are obtained for H-MOR and H-FER, demonstrating the comparable lability of zeolites with different framework topologies. The observation of similar enrichment in Na-MOR is perhaps more surprising, and suggests that a Brønsted acid H is not required for bonds to be broken and remade, and that there are likely to be different mechanisms operating in different forms of the zeolite.

Facile room-temperature ^{17}O enrichment of zeolites is of interest for subsequent structural characterisation using NMR spectroscopy and, in particular, will provide useful information on the reactivity of Brønsted acid sites directly. However, the ease with which this process occurs shows that many zeolitic frameworks are significantly more dynamic and their bonds more labile than expected, even at room temperature, raising interesting questions about their chemical reactivity and the roles they play in solution-based catalysis, adsorption processes and ion-exchange reactions. Further work is clearly required to gain a more detailed insight into the mechanism of enrichment. The rate and preferred position(s) of enrichment in different framework structures will need to be investigated systematically, as will any differences observed for other zeolitic forms (*i.e.*, Na-, Cu-, K- or NH_4 -) or for zeolites with varying Si/Al ratios.

In situ analysis of isotopic exchange for ^{17}O has long been used in solution-state NMR to provide mechanistic information,⁴³⁻⁴⁴ and interaction with water has, more recently, been used for surface-selective enrichment of solid oxides (mostly *ex situ*) and of nanoparticles.⁴⁵⁻⁴⁸ Our work shows that NMR spectroscopy can be used to also follow O exchange *in situ* in zeolites, and that rapid enrichment of frameworks with different topologies and acidities is possible. In order to understand and investigate the different mechanisms that are active in more detail, a wider investigation will need to be carried out alongside computational studies; this can both aid spectral assignment and interpretation (necessary to understand which O species are enriched more quickly or more slowly) and predict energy barriers for hydrolysis of particular types of bonds in specific frameworks. The role (if any) that is played by Al(VI) in the enrichment kinetics will need to be determined

(although the results shown here on Na-MOR and initial observations on CHA²⁰ suggest these species are not required for framework lability. In addition, the effect of varying the overall and relative volumes of H₂O(l) in both *in situ* and *ex situ* experiments will need to be investigated. While it may be difficult to obtain answers some of these questions (particularly in a quantitative manner), it will be vital to explore this enrichment reaction in more detail if this surprising reactivity of these widely used materials is to be understood and their use in aqueous processes optimised and controlled.

ASSOCIATED CONTENT

Supporting Information

Information on experimental NMR parameters, spectral analysis, and further NMR spectra of H-MOR, H-FER and Na-MOR are given in the Supporting Information. The Supporting Information is available free of charge on the ACS Publications website.

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Author Contributions

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REFERENCES

1. Wright, P. A. *Microporous Framework Solids*; RSC Publishing: Cambridge, 2008.
2. Ashbrook, S. E.; Dawson D. M.; Griffin, J. M. *Solid-State NMR in Local Structural Characterisation*, Eds D.W. Bruce, D. O'Hare and R.I. Walton, John Wiley & Sons Ltd, 2014, Chichester, UK.
3. Ashbrook, S. E.; Dawson, D. M.; Seymour, V. R. Recent Developments in Solid-State NMR Spectroscopy of Crystalline Microporous Materials. *Phys. Chem. Chem. Phys.* 2014, 16, 8223-8242.
4. Mafra, L.; Klinowski, J. Molecular Sieves: Crystalline Systems. *eMagRes*, 2013, 2, 89-108, DOI: 10.1002/9780470034590.emrstm1325.
5. Ashbrook, S. E.; Smith, M. E. Solid state ¹⁷O NMR - An Introduction to the Background Principles and Applications to Inorganic Materials. *Chem. Soc. Rev.* 2006, 35, 718-735.
6. Peng, L.; Liu, Y.; Kim, N.; Readman, J. E.; Grey, C. P. Detection of Brønsted Acid Sites in Zeolite HY with High-Field ¹⁷O-MAS-NMR Techniques. *Nature Mater.* 2005, 4, 11-14
7. Peng, L.; Huo, H.; Gan, Z.; Grey, C. P. ¹⁷O MQMAS NMR Studies of Zeolite HY. *Micropor. Mesopor. Mater.* 2008, 109, 156-162.
8. Bull, L. M.; Cheetham, A. K.; Anupold, T.; Reinhold, A.; Samoson, A.; Sauer, J.; Bussemer, B.; Lee, Y.; Gann, S.; Shore, J.; Pines, A.; Dupree, R. A High-Resolution ¹⁷O NMR Study of Siliceous Zeolite Faujasite. *J. Am. Chem. Soc.* 2002, 120, 3510-3511.
9. Huo, H.; Peng, L.; Gan, Z.; Grey, C. P. Solid-State MAS NMR Studies of Brønsted Acid Sites in Zeolite H-Mordenite. *J Am Chem Soc* 2012, 134, 9708-9720.
10. Ernst, H.; Freude, D.; Kanellopoulos, J.; Loeser, T.; Prochnow, D.; Schneider, D. Has ¹⁷O NMR Been Established as a Spectroscopic Tool for Zeolite Characterisation? *Stud. Surf. Sci. Catal.* 2007, 154, 1173-1179.
11. Pingel, U.-T.; Amoureux, J.-P.; Anupold, T.; Bauer, F.; Ernst, H.; Fernandez, C.; Freude, D.; Samoson, A. High-Field ¹⁷O NMR Studies of the SiOAl Bond in Solids. *Chem. Phys. Lett.* 1998, 294, 345-350.
12. Freude, D.; Loeser, T.; Michel, D.; Pingel, U.; Prochnow, D. ¹⁷O NMR Studies of Low Silicate Zeolites. *Solid State Nucl. Magn. Reson.* 2001, 20, 46-60.
13. Amoureux, J. P.; Bauer, F.; Ernst, H.; Fernandez, C.; Freude, D.; Michel, D.; Pingel, U. T. ¹⁷O Multiple-Quantum and ¹H MAS NMR Studies of Zeolite ZSM-5. *Chem. Phys. Lett.* 1998, 285, 10-14.
14. Parnham E. R.; Morris, R. E. 1-Alkyl-3-methyl Imidazolium Bromide Ionic Liquids in the Ionothermal Synthesis of Aluminium Phosphate Molecular Sieves. *Chem. Mater.* 2006, 18, 4882-4887
15. Cooper, E. R.; Andrews, C. D.; Wheatley, P. S.; Webb, P. B.; Wormald P.; Morris, R. E. Ionic Liquids and Eutectic Mixtures as Solvent and Template in Synthesis of Zeolite Analogues. *Nature*, 2004, 430, 1012-1016.
16. Griffin, J. M.; Clark, L.; Seymour, V. R. Aldous, D. W.; Dawson D. M.; Iuga, D.; Morris R. E.; Ashbrook S. E. Ionothermal ¹⁷O Enrichment of Oxides using Microlitre Quantities of Labelled Water. *Chem. Sci.* 2012, 3, 2293-2300.
17. Roth, W. J.; Nachtigall, P.; Morris, R. E.; Wheatley, P. S.; Seymour, V. R.; Ashbrook, S. E.; Chlubná, P.; Grajciar, L.; Polozij, M.; Zukal, A.; Shvets, O.; Čejka, J. A Family of Zeolites with Controlled Pore Size Prepared Using a Top-Down Method. *Nature Chem.* 2013, 5, 628-633.
18. Eliášová, P.; Opanasenko, M.; Wheatley, P. S.; Shamzhy, M.; Mazur, M.; Nachtigall, P.; Roth, W. J.; Morris, R. E.; Čejka, J. The ADOR Mechanism for the Synthesis of New Zeolites. *Chem. Soc. Rev.* 2015, 44, 7177-7206.
19. Bignami, G. P. M.; Dawson D. M.; Seymour, V. R.; Wheatley P. S.; Morris R. E.; Ashbrook S. E. Synthesis, Isotopic Enrichment and Solid-State NMR Characterization of Zeolites Derived from the Assembly, Disassembly, Organisation, Reassembly Process. *J. Am. Chem. Soc.* 2017, 139, 5140-5148.
20. Heard, C. J.; Grajciar, L.; Rice, C. M.; Pugh, S. M.; Nachtigall, P.; Ashbrook, S. E.; Morris, R. E. Fast Room Temperature Lability of Aluminosilicate Zeolites. *Nat. Commun.* 2019, 10, 4690.
21. Vjunov, A.; Fulton, J. L.; Camaioni, D. M.; Hu, J. Z.; Burton, S. D.; Arslan, I.; Lercher, J. A. Impact of Aqueous Medium on Zeolite Framework Integrity. *Chem. Mater.* 2015, 27, 3533-3545.
22. Prodingler, S.; Shi, H.; Eckstein, S.; Hu, J. Z.; Olarte, M. V.; Camaioni, D. M.; Derewinski, M. A.; Lercher, J. A. Stability of Zeolites in Aqueous Phase Reactions. *Chem. Mater.* 2017, 29, 7255-7262.
23. Pike, K. J.; Malde, R. P.; Ashbrook, S. E.; McManus, J.; Wimpey, S. Multiple-Quantum MAS NMR of Quadrupolar Nuclei. Do Five-, Seven- and Nine-Quantum Experiments Yield Higher Resolution than the Three-Quantum Experiment? *Solid State Nucl. Magn. Reson.* 2000, 16, 203-215.
24. Bak, M.; Rasmussen, J. T.; Nielsen, N. C. SIMPSON: A General Simulation Program for Solid-State NMR Spectroscopy. *J. Magn. Reson.* 2000, 147, 296-330.
25. Baerlocher C.; McCusker L. B.; Olson D. H. *Atlas of Zeolite Framework Types 6th edition*; Elsevier: Oxford, 2007.
26. Frydman, L.; Harwood, J. S. Isotropic Spectra of Half-Integer Quadrupolar Spins from Bidimensional Magic-Angle Spinning NMR. *J. Am. Chem. Soc.* 1995, 117, 5367-5368.
27. Amoureux, J. P.; Fernandez, C.; Steuernagel, S. Z-Filtering in MQMAS NMR. *J. Magn. Reson. A* 1996, 123, 116-118.
28. Ashbrook S. E.; Sneddon, S. New Methods and Applications in Solid-State NMR Spectroscopy of Quadrupolar Nuclei. *J. Am. Chem. Soc.* 2014, 136, 15440-15456.
29. Moran, R. F.; Dawson, D. M.; Ashbrook S. E. Exploiting NMR Spectroscopy for the Study of Disorder in Solids. *Int. Rev. Phys. Chem.* 2017, 36, 39-115.

30. van Bokhoven, J. A.; van der Eerden, A. M. J.; Koningsberger, D. C. Flexible Aluminium Coordination of Zeolites as Function of Temperature and Water Content, an In-Situ Method to Determine Aluminium Coordinations. *Stud. Surf. Sci. Catal.* **2002**, *142*, 1885-1890.
31. van Bokhoven, J. A.; van der Eerden, A. M. J.; Koningsberger, D. C. Three-Coordinate Aluminum in Zeolites Observed with In situ X-ray Absorption Near-Edge Spectroscopy at the Al K-edge: Flexibility of Aluminum Coordinations in Zeolites. *J. Am. Chem. Soc.* **2003**, *125*, 7435-7442.
32. Abraham, A.; Lee, S.-H.; Shin, C.-H.; Hong, S. B.; Prins, R.; van Bokhoven, J. A. Influence of Framework Silicon to Aluminium Ratio on Aluminium Coordination and Distribution in Zeolite Beta Investigated by ^{27}Al MAS and ^{27}Al MQMAS NMR. *Phys. Chem. Chem. Phys.* **2004**, *6*, 3031-3036.
33. Ravi, M.; Sushkevich, V. L.; van Bokhoven, J. A. Lewis Acidity Inherent to the Framework of Zeolite Mordenite. *J. Phys. Chem. C.* **2019**, *123*, 15319-15144.
34. Flambard A.; Montagne L.; Delevoye L. A new ^{17}O Isotopic Enrichment Method for the NMR Characterization of Phosphate Compounds. *Chem. Comm.* **2006**, *32*, 3426-3428.
35. Keeler E. G.; Michaelis V. K.; Griffin R. G. ^{17}O NMR investigation of Water Structure and Dynamics *J. Phys. Chem. B.* **2016**, *120*, 7851-7858.
36. Bignami G. P. M.; Davis Z. H.; Dawson D. M.; Morris S. A.; Russell S. E.; McKay D.; Parke R.E.; Iuga D.; Morris R. E.; Ashbrook S. E. Cost-Effective ^{17}O Enrichment and NMR Spectroscopy of Mixed-Metal Terephthalate Metal-Organic Frameworks. *Chem. Sci.* **2018**, *9*, 850-859.
37. He P.; Xu J.; Terskikh V. V. Sutrisno A.; Nie H.-Y.; Huang Y. Identification of Non-equivalent Framework Oxygen Species in Metal-Organic Frameworks by ^{17}O Solid-State NMR. *J. Phys. Chem. C.* **2013**, *117*, 16953-16960.
38. Métro T.-X.; Gervais C.; Martinez A.; Bonhomme C.; Laurencin D. Unleashing the potential of ^{17}O NMR Spectroscopy Using Mechanochemistry. *Angew. Chem.* **2017**, *129*, 6907-6911.
39. Chen B.; Huang Y. ^{17}O Solid-State NMR Spectroscopic Studies For The Involvement of Water Vapor in Molecular Sieve Formation by Dry-Gel Conversion. *J. Am. Chem. Soc.* **2016**, *128*, 6437-6446.
40. Yu, Z.; Zheng, A.; Wang, Q.; Chen, L.; Xu, J.; Amoureux, J. P.; Deng, F. Insights into the Dealumination of Zeolite HY Revealed by Sensitivity-Enhanced ^{27}Al DQ-MAS NMR Spectroscopy at High Field. *Angew. Chemie - Int. Ed.* **2010**, *49*, 8657-8661.
41. Müller, M.; Harvey, G.; Prins, R. Comparison of the Dealumination of Zeolites Beta, Mordenite, ZSM-5 and Ferrierite by Thermal Treatment, Leaching with Oxalic Acid and Treatment with SiCl_4 by ^1H , ^{29}Si and ^{27}Al MAS NMR. *Microporous Mesoporous Mater.* **2000**, *34*, 135-147.
42. Kanellopoulos, J.; Unger, A.; Schwieger, W.; Freude, D. Catalytic and Multinuclear MAS NMR Studies of a Thermally Treated Zeolite ZSM-5. *J. Catal.* **2006**, *237*, 416-425.
43. Klemperer, W. G. ^{17}O -NMR Spectroscopy as a Structural Probe. *Angew. Chem.* **1978**, *17*, 246-254.
44. Balogh, E.; Casey, W. H. High-Pressure ^{17}O NMR Studies on Some Aqueous Polyoxoions in Water. *Prog. Nucl. Magn. Reson. Spectrosc.* **2008**, *53*, 193-207.
45. Wang, M.; Wu, X.-P.; Zheng, S.; Zhao, L.; Li, L.; Shen, L.; Gao, Y.; Xue, N.; Guo, X.; Huang, W.; Gan, Z.; Blanc, F.; Yu, Z.; Ke, X.; Ding, W.; Gong, X.-Q.; Grey, C. P.; Peng, L. Identification of Different Oxygen Species in Oxide Nanostructures with ^{17}O Solid-State NMR Spectroscopy. *Sci. Adv.* **2015**, *1*, e1400133.
46. Li, Y.; Wu, X.-P.; Jiang, N.; Shen, L.; Sun, H.; Wang, Y.; Wang, M.; Ke, X.; Yu, Z.; Dong, L.; Guo, X.; Hou, W.; Ding, W.; Gong, X.-Q.; Grey, C. P. Peng, L. Distinguishing Faceted Oxide Nanocrystals with ^{17}O Solid-State NMR Spectroscopy. *Nat. Commun.* **2017**, *8*, 581.
47. Du, J. H.; Peng, L. Recent Progress in Investigations of Surface Structure and Properties of Solid Oxide Materials with Nuclear Magnetic Resonance Spectroscopy. *Chin. Chem. Lett.* **2018**, *29*, 747-751.
48. Champouret Y.; Coppel Y.; Kahn M. L. Evidence for Core Oxygen Dynamics and Exchange in Metal Oxide Nanocrystals from In Situ ^{17}O MAS NMR *J. Am. Chem. Soc.* **2016**, *138*, 16322-16328.
49. Pugh S. M.; Wright P. A.; Law, D. J.; Thompson, N.; Ashbrook, S. E. Facile, Room-Temperature ^{17}O Enrichment of Zeolite Frameworks Revealed by Solid-State NMR Spectroscopy. Dataset. University of St Andrews Research Portal <https://doi.org/10.17630/9671bf64-5774-4116-a0c9-e7fbd83716b>, 2019.

TOC Graphic

