Ionothermal ^{17}O Enrichment of Oxides using Microlitre Quantities of Labelled Water

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Supporting Information

Solid-State NMR Experimental Details.

Solid-state NMR experiments were performed using Bruker Avance III spectrometers operating at magnetic field strengths of 14.1 and 20.0 T. ^{13}C, ^{31}P and ^{27}Al solid-state NMR experiments were performed at 14.1 T using a Bruker 4-mm MAS probe, at MAS rates of between 10 and 12.5 kHz. ^{17}O solid-state NMR experiments were performed at 20.0 T using a Bruker 3.2-mm MAS probe and a Samoson DOR probe. Chemical shifts are reported in ppm relative to TMS for ^{13}C, 85 wt% H_3PO_4 for ^{31}P, 1 M $Al(NO_3)_3$ for ^{27}Al and H_2O for ^{17}O. For ^{13}C, transverse magnetisation was obtained by cross polarisation (CP) from ^{1}H using a contact pulse duration of between 1 and 2.5 ms (ramped for ^{1}H). Two-pulse phase modulation (TPPM) ^{1}H decoupling was applied during acquisition. ^{27}Al triple-quantum MAS NMR spectra were recorded using a phase-modulated split-t_1 shifted-echo pulse sequence (S1), with the third pulse chosen to be selective for the central transition. ^{17}O DOR NMR spectra were acquired using an odd-order sideband suppression sequence, (S2) together with a double frequency sweep (DFS) pulse (S3) for signal enhancement. An outer rotor spinning frequency of 1600 Hz was used, with the frequency of the inner-rotor set to 5.2 times the outer rotor spinning frequency. Spinning sidebands in the DOR spectra were identified by comparison with spectra recorded at an outer rotor frequency of 1300 Hz. ^{17}O MAS and triple-quantum MAS NMR spectra were recorded at a MAS frequency of 20 kHz. ^{17}O triple-quantum MAS NMR experiments were recorded using an amplitude-modulated z-filtered pulse sequence, with a DFS reconversion pulse for increased signal sensitivity. The scales of the isotropic axes of the sheared MQMAS spectra are plotted according to the conventions described in Refs. (S4 and S5). For NMR spectra shown in the main text, the number of coadded transients and recycle intervals, and for ^{17}O MQMAS NMR experiments the number and size of t_1 increments, are summarised in Table S1. Further experimental details for spectra shown in Supporting Information are given in the relevant figure captions.

Table S1. Experimental parameters for solid-state NMR spectra shown in the main text.

Sample	Experiment	Number of coadded transients	Recycle interval / s	Number of t_1 increments	Duration of t_1 increment / µs
SIZ-4(EMIMBr)					
	^{13}C CP MAS NMR	10556	5	-	-
	^{31}P MAS NMR	400	10	-	-
	^{27}Al MAS NMR	64	0.5	-	-
SIZ-4(EMIMCl)					
	^{13}C CP MAS NMR	456	10	-	-
	^{31}P MAS NMR	8	10	-	-
	^{27}Al MAS NMR	128	0.5	-	-
^{17}O-enriched SIZ-4 (as-prepared, EMIMCl)					
	^{17}O MAS NMR	14192	3	-	-
	^{17}O MQMAS NMR	1920	3	52	50
	^{17}O DOR NMR	21284	3	-	-
^{17}O-enriched SIZ-4 (calcined)					
	^{17}O MAS NMR	41912	0.5	-	-
	^{17}O MQMAS NMR	7680	0.5	54	50
	^{17}O DOR NMR	34424	0.5	-	-

First-Principles Calculations Details.

Calculations of NMR parameters were carried out using the CASTEP DFT code (S6), employing the gauge including projector augmented wave (GIPAW) algorithm (S7) allowing the reconstruction of the all-electron wave function in the presence of a magnetic field. The generalised gradient approximation (GGA) PBE functional (S8) was employed and core-valence interactions were described by ultrasoft pseudopotentials (S9). A planewave energy cut-off of 50 Ry (680 eV) was used and integrals over the Brillouin zone were performed using a k-point spacing of 0.04 Å^{-1}. Calculations generate the electric field gradient (EFG) tensor ($\mathbf{V}$) and the absolute shielding tensor ($\boldsymbol{\sigma}$) in the crystal frame. The isotropic chemical shift, δ_{iso}, can be obtained from the isotropic chemical shielding, σ_{iso}:

$$\sigma_{iso} = (1/3)\mathrm{Tr}\{\boldsymbol{\sigma}\} \qquad (1)$$

$$\delta_{iso} = -(\sigma_{iso} - \sigma_{ref}) \ , \qquad (2)$$

where σ_{ref} is a reference isotropic shielding. Values for σ_{ref} of 169.4, 553.2, 277.0 and 258.0 ppm were used for ^{13}C, ^{27}Al, ^{31}P and ^{17}O, respectively. For ^{13}C, ^{31}P and ^{17}O, σ_{ref} values were determined from comparison of the calculated NMR parameters with the experimental data in this work. For ^{27}Al, a σ_{ref} value determined in previous work was found to be suitable (S10, S11).

The quadrupolar interaction is characterised by a magnitude, C_Q, and asymmetry parameter, η_Q:

$$C_Q = eQV_{ZZ}/h \qquad (3)$$

$$\eta_Q = (V_{XX} - V_{YY})/V_{ZZ} \ , \qquad (4)$$

where V_{II} are the principal components of the electric field gradient (EFG) tensor, ordered such that $|V_{ZZ}| \geq |V_{YY}| \geq |V_{XX}|$, e is the electronic charge, Q is the nuclear quadrupole moment, and h is Planck's constant. Although the sign of C_Q is often difficult to determine experimentally, the signs of calculated C_Q values are included in tabulated data. For the

NMR calculations, the initial atomic positions and unit cell parameters were taken from literature diffraction structures (S12, S13). Prior to calculation of the NMR parameters, however, full geometry optimisations were performed (also using a cut-off energy of 50 Ry and *k*-point spacing of 0.04 $Å^{-1}$), where both the lattice parameters and internal atomic coordinates were allowed to vary. Calculations were performed using the EaStCHEM Research Computing Facility, which consists of 136 AMD Opteron 280 dual-core processors running at 2.4 GHz, partly connected by Infinipath high speed interconnects.

Solid-State NMR of Ordered and Disordered SIZ-4.

As described in the main text, SIZ-4 can be prepared in forms that contain either 1-ethyl-3-methyl imidazolium (EMIM) or 1,3-dimethyl imidazolium (DMIM) cations within the pores, depending on the synthesis method used. Although both cations give structures with the same topology, important structural differences are associated with the two types of guest species. Within the pores of the framework, EMIM cations occupy a disordered arrangement, while DMIM cations are fully ordered. These structural differences are clearly evident in ^{13}C CPMAS NMR spectra of (unenriched) SIZ-4 samples, prepared using EMIMBr and EMIMCl, shown in Figures S1a and S1b. For SIZ-4(EMIMBr), a complex spectrum is observed, with considerable line broadening and multiple splittings present for most of the resonances. This results from disorder of the EMIM cations within the pores of the framework. In particular, the two CH_2 resonances observed at 46 and 49 ppm, and the broadened methyl resonance at 15 ppm indicate multiple configurations of the ethyl chain, in agreement with single-crystal X-ray diffraction measurements. In contrast, the ^{13}C CPMAS NMR spectrum of SIZ-4(EMIMCl) exhibits sharp, well-resolved resonances as a result of the ordered incorporation of the DMIM cations in the structure.

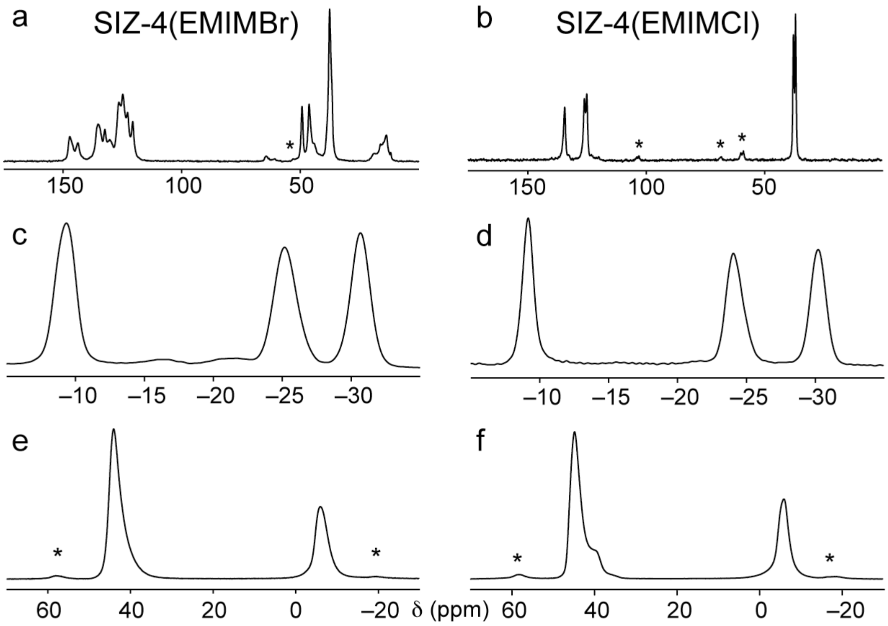

Figure S1. (a, b) ^{13}C, (c, d) ^{31}P and (e, f) ^{27}Al (14.1 T) MAS NMR spectra of (a, c, e) SIZ-4(EMIMBr) and (b, d, f) SIZ-4(EMIMCl). Spinning sidebands are denoted by asterisks.

Importantly, the differences in ordering of the EMIM and DMIM cations significantly affect solid-state NMR spectra of the surrounding framework species. ^{31}P MAS NMR spectra for the two materials, shown in Figures S1c and S1d, both exhibit three resonances, in agreement with the crystal structure; however, for SIZ-4(EMIMBr), the disorder in the structure results in broader line widths of between 340 – 480 Hz, as compared to line widths of 220 – 340 Hz for SIZ-4(EMIMCl), and a significant shift in one of the resonances. Broadening resulting from the disorder of the template is also apparent in a ^{27}Al MAS NMR spectrum of SIZ-4(EMIMBr), shown in Figure S1e. In this spectrum, resonances are observed at approximately –6 and 45 ppm, in the typical ranges for six- and four-coordinate aluminium, respectively. However, the Al^{IV} resonance appears to exhibit a characteristically broadened lineshape, indicative of disorder in the structure. This contrasts with the spectrum for SIZ-4(EMIMCl), shown in Figure S1f, where the Al^{IV} resonance exhibits a clear 'shoulder' consistent with the presence of two unresolved quadrupolar-broadened lineshapes. Indeed, the presence of two distinct Al^{IV} sites in both structures is confirmed by ^{27}Al MQMAS NMR spectra, shown in Figure S2. In both spectra, a single Al^{VI} site and two distinct Al^{IV} sites are observed. However, poorer resolution is obtained for SIZ-4(EMIMBr) owing to the disordered structure. For the resonance corresponding to the six-coordinate site and one of the resonances corresponding to the four-coordinate sites, quadrupolar parameters C_Q and η_Q were determined from lineshape analysis of cross-sections taken through the MQMAS spectrum. The composite parameter P_Q (= $C_Q(1+\eta_Q/3)^{½}$) was also determined through analysis of the position of the centre-of-mass of the lineshape in the δ_1 and δ_2 dimensions. For the remaining six-coordinate site, the C_Q value was too small to be measured directly from the spectrum, so only P_Q was determined. These values are summarised in Table S2.

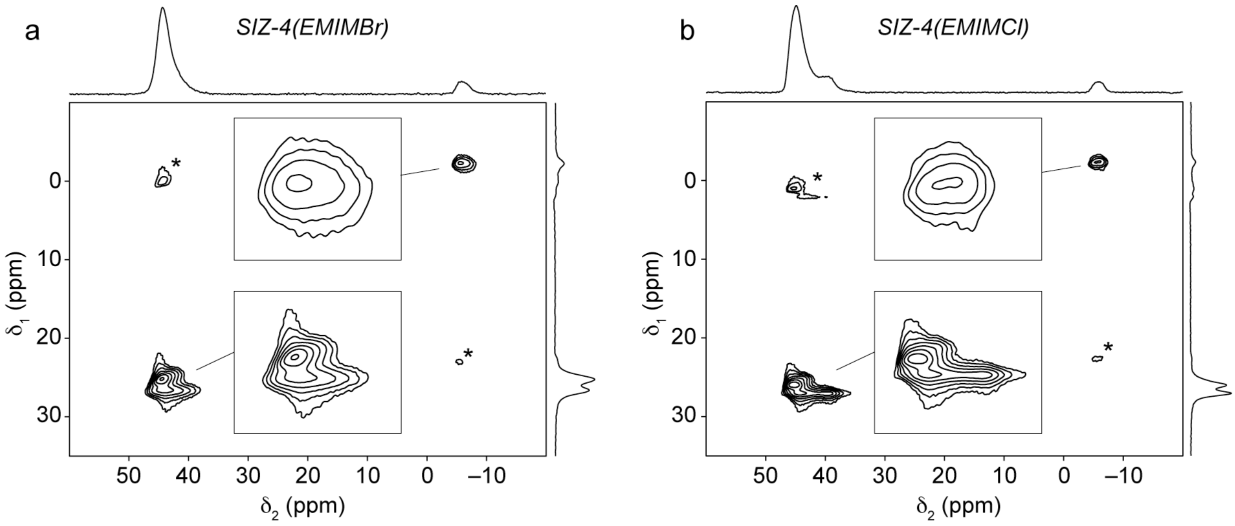

Figure S2. ^{27}Al (14.1 T) split-t_1 triple-quantum shifted-echo MAS NMR spectra of (a) SIZ-4(EMIMBr) and (b) SIZ-4(EMIMCl). Spectra were recorded at a MAS frequency of 10 kHz, with 288 transients separated by a recycle interval of 0.5 s for each of the (a) 200 and (b) 256 t_1 increments of 50 μs. Spinning sidebands are denoted by asterisks.

Table S2. Experimental ^{13}C, ^{31}P and ^{27}Al isotropic chemical shifts, δ_{iso}^{exp}, ^{27}Al quadrupolar products, P_Q^{exp}, ^{27}Al quadrupolar coupling constants, C_Q^{exp}, and ^{27}Al asymmetry parameters, η_Q^{exp}, for as-prepared and calcined SIZ-4(EMIMCl).

Assignment	δ_{iso}^{exp} (ppm)	P_Q^{exp} / MHz	C_Q^{exp} / MHz	η_Q^{exp}
As-prepared SIZ-4(EMIMCl)				
C1	37.5(2)	-	-	-
C2	134.3(2)	-	-	-
C3	126.0(3)	-	-	-
C4	125.0(3)	-	-	-
C5	36.6(2)	-	-	-
P1	–28.5(5)	-	-	-
P2	–22.3(5)	-	-	-
P3	–7.4(5)	-	-	-
Al1	–4.4 (5)	2.0(2)	2.3(1)	0.4(1)
Al2	46.4(5)	2.2(2)	-	-
Al3	47.1(5)	4.5(2)	4.6(1)	0.2(1)
Calcined SIZ-4				
Al1	39.4(5)	3.4(1)	2.9(1)	1.0(1)
P1	–30.1(5)	-	-	-

Figure S3 compares ^{27}Al and ^{31}P 14.1 T MAS NMR spectra of as-prepared and calcined samples of unenriched and ^{17}O-enriched SIZ-4. For calcined SIZ-4, the ^{27}Al and ^{31}P MAS NMR spectra both exhibit a single resonance, in agreement with the crystal structure. Spectra of the ^{17}O-enriched samples are observed to be identical to those obtained for the unenriched samples. This shows that the ~4% abundance of ^{17}O in the enriched structures is sufficiently low that interactions with directly-bonded P and Al species (*e.g.*, dipolar or *J*-couplings) is not evident in NMR spectra. Experimental ^{27}Al and ^{31}P NMR parameters for as-prepared and calcined SIZ-4 are summarised in Table S2.

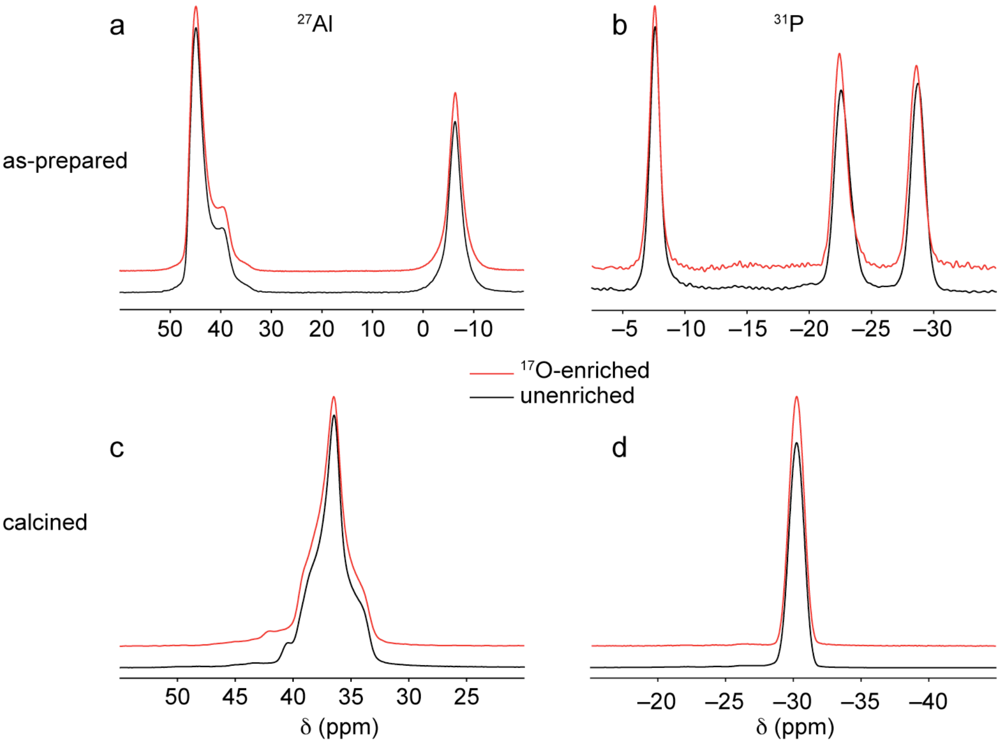

Figure S3. Comparison of ^{27}Al and ^{31}P (14.1 T) MAS NMR spectra for ^{17}O-enriched (shown in red) and natural abundance (shown in black) samples of (a, b) as-prepared SIZ-4 and (c, d) calcined SIZ-4. Spectra were recorded at 12.5 kHz MAS and are the result of coadding 16 transients separated by recycle intervals of 3 s (^{27}Al) and 60 s (^{31}P).

A ^{17}O 20.0 T DOR MAS NMR spectrum of SIZ-4 recorded with ~30 kHz ^1H continuous-wave dipolar decoupling is compared to the non-decoupled spectrum in Figure S4. The ^1H-decoupled spectrum shows no apparent increase in resolution, indicating that ^1H dipolar couplings to the template molecule do not contribute significantly to the observed linewidth at the spinning rate used. However, owing to probe limitations we were unable to investigate whether higher power decoupling could lead to any reduction in linewidth.

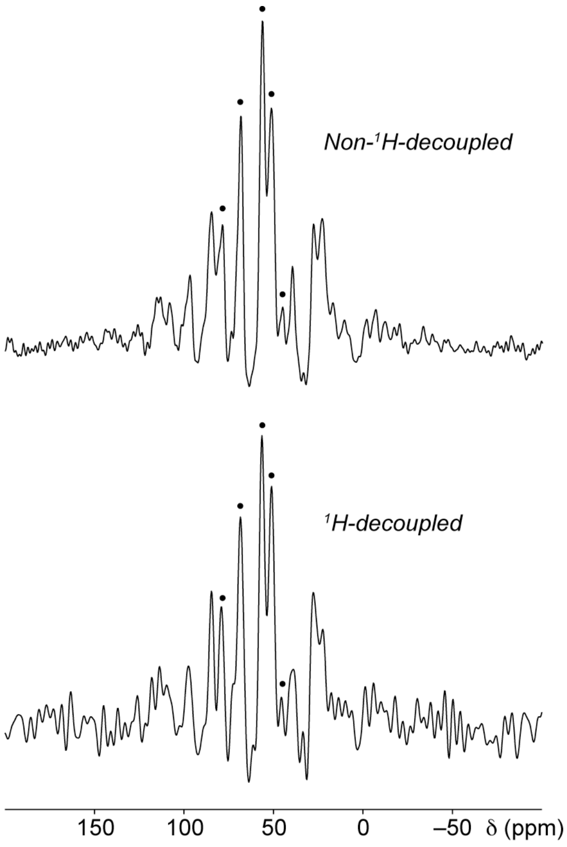

Figure S4. ^{17}O (20.0 T) DOR NMR spectrum of SIZ-4 acquired with approximately 30 kHz ^1H dipolar decoupling. The spectrum is the result of coadding 1952 transients separated by a recycle interval of 3 s. Isotropic resonances are indicated by •.

First-Principles Calculations of ^{31}P and ^{27}Al NMR parameters.

Calculated ^{13}C, ^{31}P and ^{27}Al NMR parameters for as-prepared and calcined SIZ-4 are given in Table S3. The calculations for as-prepared SIZ-4 were performed using the ordered crystal structure containing the 1,3-dimethyl imidazolium cation (referred to in previous work as SIZ-10c (S13)). The NMR parameters were determined after full geometry optimisation of the crystal structures, with the unit cell dimensions allowed to vary. Considering the 1,3-dimethyl imidazolium cations, the calculated ^{13}C isotropic chemical shifts enable assignment of the chemically equivalent but crystallographically-distinct methyl and aromatic CH carbons that exhibit slightly different chemical shifts in the experimental spectrum shown in Figure S1b. For the as-prepared framework, the calculated ^{31}P isotropic chemical shifts enable assignment of the three distinct P sites in the structure. For P1 and P2, calculated chemical shifts of –31.1 and –25.2 ppm are in good agreement with the resonances observed at –28.5 and –22.3 ppm in the experimental spectrum. For P3, the calculated chemical shift of –7.0 ppm is in good agreement with the resonance observed experimentally at –7.4 ppm. The similarity in chemical shift of P1 and P2, and the relatively large difference in chemical shift of P3 reflects the differences in numbers of four- and six-coordinate Al sites in the second coordination sphere around each site. The three distinct Al sites in the structure can also be assigned using both the calculated isotropic chemical shifts and quadrupolar parameters. In particular, although having very similar chemical shifts, the four-coordinate Al2 and Al3 species can be distinguished on the basis of the significant difference in C_Q. For Al3, the larger calculated C_Q of 4.71 MHz is in good agreement with the value of 4.5 MHz measured experimentally. The calculated C_Q value of 2.30 MHz for Al2 is consistent with the experimental P_Q value of 2.2 MHz. For the six-coordinate Al1, the calculated C_Q of 2.54 MHz is a little overestimated compared to the experimental value of 2.3 MHz, but the large difference in isotropic chemical shift relative to Al2 and Al3 is well reproduced. For calcined SIZ-4, the calculated ^{31}P and ^{27}Al NMR parameters are also in good agreement with the experimental values.

Table S3. Calculated ^{13}C, ^{31}P and ^{27}Al isotropic chemical shifts, δ_{iso}^{calc}, ^{27}Al quadrupolar products, P_Q^{calc}, ^{27}Al quadrupolar coupling constants, C_Q^{calc}, and ^{27}Al asymmetry parameters, η_Q^{calc}, for as-prepared and calcined SIZ-4(EMIMCl).

Site	δ_{iso}^{calc} (ppm)	P_Q^{calc} / MHz	C_Q^{calc} / MHz	η_Q^{calc}
As-prepared SIZ-4(EMIMCl)				
C1	35.0	-	-	-
C2	134.7	-	-	-
C3	128.8	-	-	-
C4	126.6	-	-	-
C5	34.0	-	-	-
P1	–31.1	-	-	-
P2	–25.2	-	-	-
P3	–7.0	-	-	-
Al1	–1.2	2.64	2.54	0.48
Al2	47.0	2.46	2.30	0.66
Al3	46.7	–4.74	–4.71	0.21
Calcined SIZ-4				
Al1	39.3	3.47	3.06	0.87
P1	–32.7	-	-	-

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