Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Calculating NMR Parameters in Aluminophosphates: Evaluation of Dispersion Correction Schemes

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Supporting Information

S1. Experimental ^{31}P and ^{27}Al NMR of as-made and calcined AlPOs

^{31}P MAS NMR spectra were acquired using a Bruker Avance III 600 MHz spectrometer equipped with a 14.1 T widebore magnet, at a Larmor frequency of 242.9 MHz. Samples were packed in conventional 4-mm ZrO_2 rotors and rotated at an MAS rate of 14 kHz. Chemical shifts are referenced to 85% H_3PO_4 for ^{31}P using BPO_4 (–29.6 ppm)[S1] as a secondary reference. Where necessary, cw ^{1}H decoupling was employed to improve spectral resolution, with a typical radiofrequency field strength ($\gamma B_1/2\pi$) of ~100 kHz (^{1}H). For AlPO-14, low-power cw ^{27}Al decoupling[S2] was also employed (($\gamma B_1/2\pi$) of ~10 kHz). All spectra were acquired using a recycle interval of 30 s.

Table S1.1. Experimental ^{31}P isotropic chemical shifts, δ_{iso}, for as-made AlPOs.

	^{31}P δ_{iso} (ppm)				
	AlPO-14[S3]	AlPO-15[S4]	JDF-2[S5]	AlPO-34[S6]	SIZ-4[S7]
P1	–20.3 (1)	–11.9 (1)	–24.9 (2)	–29.8 (1)	–28.5 (1)
P2	–5.4 (1)	–18.19 (1)	–13.4 (1)	–23.8 (1)	–22.5 (1)
P3	–24.1 (1)		–24.9 (1)	–7.6 (1)	–7.6 (1)
P4	–19.6 (1)				

Table S1.2. Experimental ^{31}P isotropic chemical shifts, δ_{iso}, for calcined AlPOs.

	^{31}P δ_{iso} (ppm)				
	AlPO-14[S8]	AlPO-53[S9]	AlPO-34[S10]	AlPO-17[S11]	AlPO-18[S12]
P1	–21.3 (1)	–29.9 (1)	–30.3 (1)	–26.1 (1)	–27.6 (3)[a]
P2	–27.1 (1)	–31.5 (1)		–37.1 (1)	–27.6 (3)[a]
P3	–31.3 (1)	–26.8 (1)			–27.6 (3)[a]
P4	–26.1 (1)				

[a] Although three crystallographically-distinct sites are predicted from the crystal structure only one resonance is seen in the ^{31}P MAS spectrum.

For calcined AlPO-17 and calcined AlPO-18, ^{27}Al MAS NMR spectra were acquired using Bruker Avance III 400 and 600 MHz spectrometers equipped with 9.4 T and 14.1 T widebore magnets, at Larmor frequencies of 104.3 MHz and 156.4 MHz. Samples were packed in a conventional 4-mm ZrO_2 rotor and rotated at an MAS rate of 14 kHz. Chemical shifts are referenced 1 M $Al(NO_3)_3$ (aq). Triple-quantum MAS NMR experiments were carried out using a phase-modulated split-t_1 shifted-echo pulse sequence,[S13] with the efficiency of the conversion of triple- to single-quantum coherences enhanced by the use of soft-pulse-added-mixing (SPAM).[S14] The final (180°) pulse was chosen to be selective for the central transition. The scale in the indirect dimension is referenced according to the convention in Ref. S15. All spectra were acquired using a recycle interval of 1 s.

Examples of ^{27}Al MAS NMR and MQMAS NMR spectra of calcined AlPO-17 and AlPO-18 are shown in Figures S1.1 and S1.2, respectively. For AlPO-17, two distinct sites are resolved using MQMAS and the NMR parameters extracted from the spectra are given in Table S1.3. A small amount of an unknown impurity phase is also present, denoted by *.

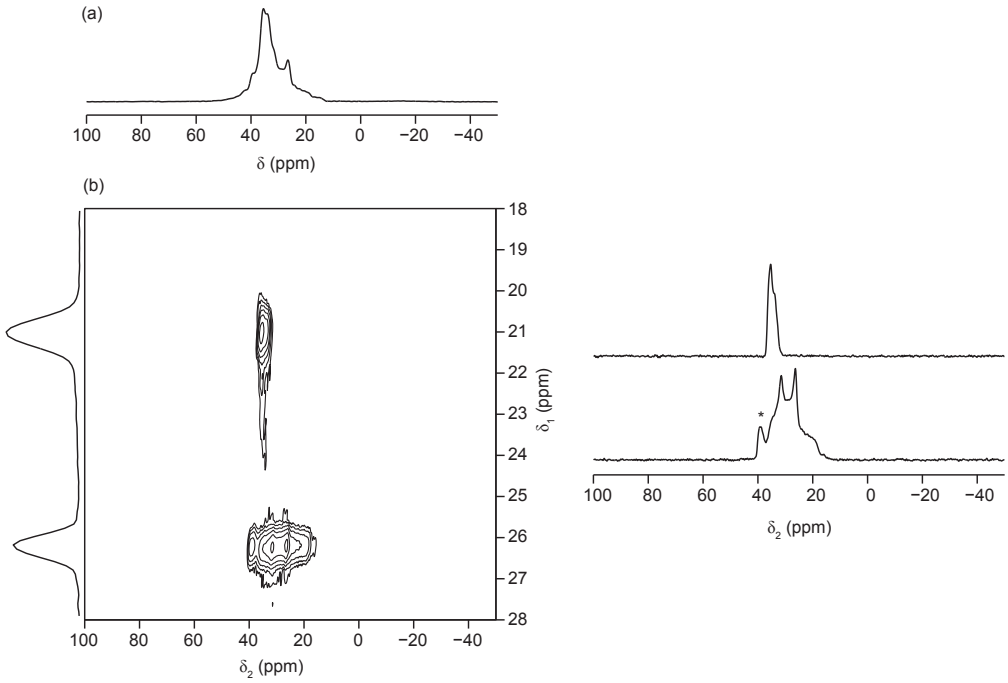

Figure S1.1. ^{27}Al (9.4 T, 14 kHz MAS) MAS NMR spectrum and triple-quantum MAS NMR spectrum (with cross sections extracted parallel to δ_2) of calcined AlPO-17. NMR parameters extracted from the spectra are given in Table S1.3.

For AlPO-18, three crystallographically-distinct Al and P sites are expected from the proposed crystal structure. A single broad resonance is observed in the ^{31}P MAS NMR spectrum (see Table S1.2), suggesting that the three sites are very similar. The ^{27}Al MQMAS spectrum also shows a single resonance in the isotropic dimension, and NMR parameters can be determined by fitting a cross section extracted parallel to δ_2 (and are given in Table S1.3). However, it is clear from the MAS spectrum that a small additional broadening is present, most likely resulting from the overlap of very similar resonances from the three formally distinct sites.

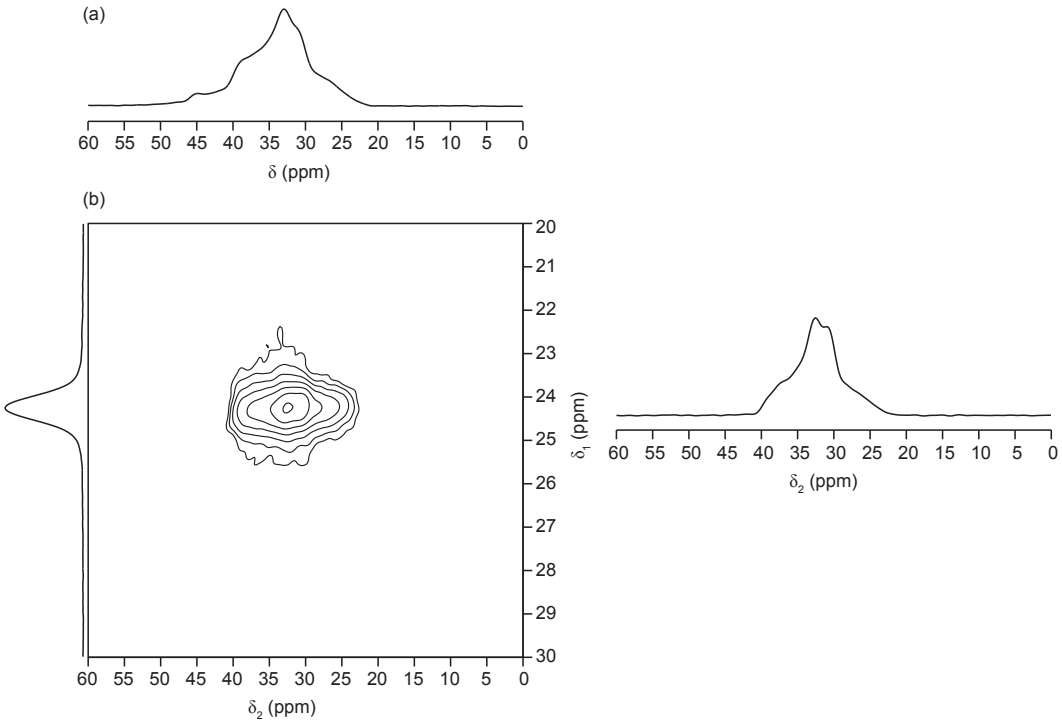

Figure S1.2. ^{27}Al (9.4 T, 14 kHz MAS) MAS NMR spectrum and triple-quantum MAS NMR spectrum (with cross sections extracted parallel to δ_2) of calcined AlPO-18. NMR parameters extracted from the spectra are given in Table S1.3.

Table S1.3. Experimental ^{27}Al NMR parameters (isotropic chemical shift, δ_{iso}, quadrupolar coupling constant, C_Q, asymmetry parameter, η_Q, and quadrupolar product, P_Q) for calcined AlPO-17 and AlPO-18.

	δ_{iso} (ppm)	C_Q / MHz	η_Q	P_Q / MHz
AlPO-17				
Al1	42.6 (1)	4.5 (4)	0.6 (1)	4.6 (4)
Al2	37.5 (1)	2.2 (1)	0.3 (1)	1.8 (1)
AlPO-18				
Al1-3[a]	39.9 (1)[S16]	3.2 (4)	0.7 (3)	3.6 (5)

[a] Although three crystallographically-distinct Al sites are predicted from the crystal structure only one resonance is seen in the isotropic ^{27}Al MAS spectrum.

S2. Initial structural models for as-made AlPOs

Table S2.1. Information on the initial structural models of as-made AlPOs used in this work.

Material	Framework type	SDA	Anion	Space group	Unit cell composition	Diffraction method[b]
AlPO-14[S3]	AFN	isopropylammonium	OH^-	*P*–1	$Al_8P_8O_{32}(C_3H_{10}N)_2(OH)_2(H_2O)_2$	Synchrotron powder XRD
AlPO-15[S4]	[a]	ammonium	OH^-	$P2_1/n$	$Al_8P_8O_{32}(NH_4)_4(OH)_4(H_2O)_8$	Single-crystal XRD
JDF-2[S5]	AEN	methylammonium	OH^-	$P2_12_12_1$	$Al_{24}P_{24}O_{96}(NH_3CH_3)_8(OH)_8$	Single-crystal XRD
AlPO-34[S6]	CHA	morpholinium	F^-	*P*–1	$Al_6P_6O_{24}(C_4H_{10}NO)_2F_2$	Synchrotron single-crystal XRD
SIZ-4[S7]	CHA	dimethylimidazolium	F^-	*P*–1	$Al_6P_6O_{24}(C_5H_9N_2)_2F_2$	Synchrotron single-crystal XRD

[a] No framework code available in IZA database

[b] In most cases H atoms are present in the cif file but their positions have typically been calculated from the geometry of the coordinating atoms

S3. Unit cell parameters for as-made AlPOs pre and post DFT optimisation

Table S3.1. Unit cell parameters for as-made AlPOs pre and post DFT optimisation.

	a / Å	*b* / Å	*c* / Å	volume / Å^3	α	β	γ
AlPO-14[S3]							
[A]	9.6599	9.6639	10.6181	918.2050	74.719	74.140	88.983
[D]	9.6752	9.7569	10.7708	942.6373	74.830	74.190	88.979
[E]	9.5443	9.5706	10.5811	898.2592	75.373	74.101	88.748
[F]	9.5794	9.6261	10.5845	906.3303	75.127	74.182	88.812
AlPO-15[S4]							
[A]	9.5560	9.5630	9.6150	854.0928	90.000	103.580	90.000
[D]	9.6275	9.6603	9.7241	877.8126	90.000	103.924	90.000
[E]	9.5534	9.5284	9.5876	848.8842	90.000	103.430	90.000
[F]	9.5647	9.5260	9.6395	852.7067	90.000	103.862	90.000
JDF-2[S5]							
[A]	10.2810	13.8440	17.0640	2428.7219	90.000	90.000	90.000
[D]	10.3196	14.1501	17.0678	2492.2908	90.000	90.000	90.000
[E]	10.1856	14.0395	16.8507	2409.6665	90.000	90.000	90.000
[F]	10.1900	14.0233	16.8528	2408.2151	90.000	90.000	90.000
AlPO-34[S6]							
[A]	9.3330	9.1830	9.1620	764.6919	88.450	102.570	93.760
[D]	9.4072	9.2988	9.1905	779.2521	88.973	103.551	94.409
[E]	9.3216	9.2190	9.0813	751.9572	89.853	104.619	95.129
[F]	9.3425	9.2153	9.0838	755.4825	89.108	104.287	94.545
SIZ-4[S7]							
[A]	9.074	9.230	9.309	757.1282	76.446	87.343	89.388
[D]	9.1846	9.3401	9.4075	784.9020	76.828	87.291	89.396
[E]	9.0639	9.2301	9.3034	752.1646	75.419	86.981	89.911
[F]	9.0611	9.2360	9.3273	753.7809	75.252	87.150	89.989

S4. Ionic forces for as-made AlPOs optimised using dispersion correction schemes

Table S4.1. Average magnitude of the forces (in eV/Å) upon each atom type, and total energies (in eV), for structural models of a range of as-made AlPOs, post DFT optimisation.

	Ionic forces /(eV/Å)				
	AlPO-14[S3]	AlPO-15[S4]	JDF-2[S5]	AlPO-34[S6]	SIZ-4[S7]
[E] After optimisation using G06 dispersion correction scheme					
H	0.05	0.04	0.04	0.05	0.06
C	0.05		0.05	0.09	0.05
N	0.08	0.01	0.05	0.07	0.02
O	0.04	0.03	0.05	0.05	0.04
Al	0.05	0.08	0.04	0.03	0.03
P	0.06	0.06	0.07	0.05	0.06
F				0.11	0.15
Energy / eV	−20640.98	−23934.12	−58771.79	−16607.80	−17002.99
[F] After optimisation using TS dispersion correction scheme					
H	0.03	0.03	0.02	0.02	0.02
C	0.05		0.01	0.04	0.03
N	0.04	0.04	0.01	0.03	0.01
O	0.02	0.03	0.02	0.03	0.03
Al	0.07	0.10	0.04	0.04	0.03
P	0.04	0.03	0.02	0.03	0.02
F				0.01	0.03
Energy / eV	−20641.08	−23934.16	−58771.80	−16607.85	−17003.02

S5. Initial structural models for calcined AlPOs

Table S5.1. Information on the initial structural models of calcined AlPOs used in this work.

Material	Framework type	Space group	Unit cell composition	Diffraction method[b]
AlPO-14[S8]	AFN	*P*–1	$Al_8P_8O_{32}$	Synchrotron powder XRD (298 K)
AlPO-53(B)[S9]	AEN	*Pbca*	$Al_3P_3O_{12}$	Laboratory powder XRD[b]
AlPO-34[S10]	CHA	*R*–3	$Al_{18}P_{18}O_{72}$	Laboratory powder XRD (310 K)
AlPO-17[S11] [a]	ERI	$P6_3/m$	$Al_{18}P_{18}O_{72}$	Synchrotron powder XRD (300 K)
AlPO-18[S12]	AEI	$C2/c$	$Al_{24}P_{24}O_{96}$	Synchrotron powder XRD (298 K)

[a] The error in the unit cell dimensions in Ref. S11 for calcined AlPO-17 was corrected prior to calculation (with $a = b = 13.89787(7)$ Å corrected to $a = b = 13.089787(7)$ Å)

[b] Temperature not stated but given as room temperature on ICSD

S6. Unit cell parameters pre and post DFT optimisation for calcined AlPOs

Table S6.1. Unit cell parameters for calcined AlPOs pre and post DFT optimisation.

	a / Å	*b* / Å	*c* / Å	volume / Å^3	α	β	γ
AlPO-14[S9]							
[A]	9.7041	9.7361	10.2018	919.8089	77.811	77.504	87.691
[D]	9.7840	9.8389	10.3104	946.3046	77.619	77.462	87.602
[E]	9.7454	9.8071	10.2641	935.9734	77.736	77.533	87.731
[F]	9.7448	9.8012	10.2548	934.3540	77.727	77.498	87.616
AlPO-53(B)[S10]							
[A]	18.0240	13.9170	9.6550	2421.8603	90.000	90.000	90.000
[D]	18.1952	14.0757	9.7654	2501.0043	90.000	90.000	90.000
[E]	18.1535	13.9661	9.7138	2462.7563	90.000	90.000	90.000
[F]	18.1179	13.9754	9.7033	2456.9258	90.000	90.000	90.000
AlPO-34[REF]							
[A]	13.7157	13.7157	14.9273	2431.9174	90.000	90.000	120.000
[D]	13.8103	13.8103	15.0442	2484.8621	90.000	90.000	120.000
[E]	13.7919	13.7919	15.0252	2475.1516	90.000	90.000	120.000
[F]	13.7806	13.7806	15.0093	2468.4509	90.000	90.000	120.000
AlPO-17[S11]							
[A]	13.0898	13.0898	15.3302	2274.8031	90.000	90.000	120.000
[D]	13.2166	13.2166	15.5134	2346.8130	90.000	90.000	120.000
[E]	13.2048	13.2048	15.4548	2333.7620	90.000	90.000	120.000
[F]	13.1944	13.1944	15.4346	2327.0344	90.000	90.000	120.000
AlPO-18[S12]							
[A]	13.7114	12.7314	18.5703	3241.7303	90.000	90.010	90.000
[D]	13.8254	12.8333	18.7095	3319.5244	90.000	89.939	90.000
[E]	13.8098	12.7966	18.6730	3299.8570	90.000	89.913	90.000
[F]	13.7995	12.7791	18.6555	3289.8045	90.000	89.764	90.000

S7. Ionic forces for calcined AlPOs optimised using dispersion correction schemes

Table S7.1. Average magnitude of the forces (in eV/Å) upon each atom type, and total energies (in eV), for structural models of a range of calcined AlPOs, post DFT optimisation.

	Ionic forces /(eV/Å)				
	AlPO-14[S8]	AlPO-53(B)[S9]	AlPO-34[S10]	AlPO-17[S11]	AlPO-18[S12]
[E] After optimisation using G06 dispersion correction scheme					
O	0.04	0.04	0.04	0.04	0.04
Al	0.03	0.04	0.07	0.02	0.02
P	0.02	0.03	0.03	0.01	0.02
Energy / eV	−16965.02	−50895.86	−38172.01	−38171.89	−50895.94
[F] After optimisation using TS dispersion correction scheme					
O	0.03	0.02	0.03	0.04	0.02
Al	0.04	0.05	0.08	0.05	0.05
P	0.04	0.04	0.02	0.03	0.03
Energy / eV	−16965.02	−50895.85	−38171.99	−38171.88	−50895.91

S8. References

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