Synthesis and characterisation of aluminophosphate-based zeotype materials prepared with α, ω -bis(*N*-methylpyrrolidinium)alkane cations as structure-directing agents[†]

Martin J. Maple* and Craig D. Williams

Received 24th April 2007, Accepted 11th July 2007 First published as an Advance Article on the web 31st July 2007 DOI: 10.1039/b706206k

New routes to the preparation of two families of small pore microporous solids are described. Flexible diquaternary alkyl ammonium cations $(C_4H_8)CH_3N^+(CH_2)_nN^+CH_3(C_2H_8)$, n = 3-5, have been found to act as structure directing agents in the synthesis of aluminophosphate-based materials of the ABC-6 group. The templates exhibit considerable selectivity in crystallising phases of the **ERI** or **AFX**-type (MeAPO-17 or MeAPO-56, respectively) from a wide variety of metalloaluminophosphate gels (Me = Mg²⁺, Co²⁺ or Si⁴⁺). For example, from gels containing Mg/P = 0–0.25, 1,4-bis(*N*-methyl-pyrrolidinium)butane cations gave MgAPO-17, and 1,5-bis(*N*-methylpyrrolidinium)pentane cations gave MgAPO-56. Notably, materials could be prepared with levels of metal-substitution tailored to a high degree and distributed non-randomly within the framework. As-prepared solids have been characterised by powder XRD, multinuclear solid state NMR, FT-IR, SEM, and thermal and elemental analysis.

Introduction

Aluminophosphates¹ (AlPO₄-n) are zeotypes containing strictly alternating alumina and phosphate tetrahedra, which cornershare to form open framework structures. The connectivity of the tetrahedra define the topology, or framework type, which is independent of composition. Novel topologies are assigned three letter codes by the International Zeolite Association² and many are found as both aluminosilicates (zeolites) and aluminophosphates. The preparation of such materials often requires the presence of organic amines or quaternary ammonium salts which fill the pores in the as-made materials.³ The inorganic framework crystallises around the organic which remains within the channels after synthesis. The precise role of such structure directing agents (SDAs), or 'templates' is, in many cases, poorly understood. Particular organic moieties may or may not direct the synthesis of materials having the same framework types when added to silicate and phosphate-based preparations. For example, zeolite SSZ-16⁴ shares the AFX topology and may be prepared with the same 1,4-bis(1-azoniabicyclo[2.2.2]octane)butane cations as MgAPO-56 (albeit the latter co-crystallises with STA-2).⁵ In contrast, decamethonium cations template EU-16 (EUO) zeolites, and the magnesioaluminophosphate DAF-17 (DFO), each of which have a different framework structure.

The search for novel topologies or compositions is driven by the need to develop catalysts with new and different shape selectivities and activities. Thus there is considerable interest in the synthesis of microporous aluminophosphates, particularly those in which cations have been aliovalently substituted into framework sites.8 Materials containing metals are designated MeAPOs, while those containing Si are termed SAPOs. Combinations are also possible. Solid acid catalysts are generated by substituting, for example, $Mg^{\scriptscriptstyle 2+}$ for $Al^{\scriptscriptstyle 3+}$ or $Si^{\scriptscriptstyle 4+}$ for $P^{\scriptscriptstyle 5+}.^9$ The charge on the framework is balanced, after the SDA is removed, by protons which form Brønsted acid sites. Additionally, redox properties may be conferred when cations such as Co2+ or Mn2+ are included in place of Al³⁺.¹⁰ Such substitutions invariably, but not exclusively, result in families of isomorphous materials. A notable exception are materials prepared in the presence of 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane: STA-6 (SAS) crystallises in the presence of Mg²⁺ or Si⁴⁺ (amongst others) while STA-7 (SAV) is formed in Co²⁺ or Zn²⁺ containing gels.¹¹ These materials exemplify the need to examine closely details of the gel chemistry as part of the search for novel materials and compositions.

Recently 1,4-bis(*N*-methylpyrrolidinium)butane bromide has been found to template two new aluminosilicate zeolites, TNU-9¹² and TNU-10.¹³ In the work we report here we have applied this template, and two further members of the homologous series (one larger and one smaller), to the crystallisation of aluminophosphate-based materials both pure and also substituted with Mg²⁺, Co²⁺, or Si⁴⁺ cations. Here we describe the preparation of materials with the **ERI** and **AFX** framework types, over a wider range of compositions than previously reported.^{14,15} The cavities present within these solids (Fig. 1) match closely the shape of the SDAs, which we suggest leads to the strong structure directing effect.

Experimental

Divalent α, ω -bis(*N*-methylpyrrolidinium)alkane hydroxide templates (diquat- ω) were synthesised *via* the Menschutkin reaction¹⁶ and ion exchanged from the bromide forms with silver(1) oxide.

School of Applied Sciences, University of Wolverhampton, Wulfruna Street, Wolverhampton, UK WV1 1SB. E-mail: m.maple@wlv.ac.uk; Fax: +44 (0)1902 322714; Tel: +44 (0)1902 322737

 $[\]dagger$ Electronic supplementary information (ESI) available: Structural stereoplots, FT-IR spectra, deconvoluted ^{31}P MAS NMR spectra and simulated XRD patterns. See DOI: 10.1039/b706206k



Fig. 1 Illustrative diagrams showing the principal cavities present in the framework types (a) **ERI** and (b) **AFX**, and the SDA molecules which direct their formation. Only the tetrahedral framework connectivity is shown, the oxygen positions being omitted for clarity.

A slight excess of 1-methylpyrrolidine was refluxed overnight in acetone with either 1,3-dibromopropane, 1,4-dibromobutane, or 1,5-dibromopentane. All organic reagents were obtained from Aldrich (97–99%). The resultant white precipitates were suction filtered and washed with acetone to remove unreacted amine. Before addition to the aluminophosphate gels the required amount of template was converted to the hydroxide form by stirring with Ag₂O (Alfa Aesar, 99%) in distilled water for 15 min. Solid material was removed by filtration and the residue washed with distilled

water until the pH of the filtrate leaving the filter approached 7. The resultant aqueous solution contained the template and was concentrated on a rotary evaporator before being added to the synthesis gel.

Gels were made up by dissolving orthophosphoric acid (85%, BDH) in distilled water and adding either magnesium acetate tetrahydrate (Aldrich, 98%), cobalt acetate tetrahydrate (BDH, 97%), Ludox TMA colloidal silica (Aldrich) or fumed silica (Aldrich, 99.8%), followed by hydrated aluminium hydroxide (Aldrich) and the template. The mixture was stirred for 15 min, until homogeneous, before being transferred to PTFE-lined stainless steel autoclaves and heated under autogeneous pressure at 190 °C for 48-72 h (for MeAPOs) or 96 h (for SAPOs prepared with colloidal silica) or 168 h (for SAPOs prepared with fumed silica). Initial gel pH were ca. 7. For comparison, aluminophosphate gels were prepared without additional metal cations, and with or without the addition of aqueous hydrofluoric acid (Fluka, 40%). These gels were all treated in the same way as the MeAPOs. In all cases the crystalline products were suction filtered, washed with distilled water and dried before being characterised. Further experimental details are given in Table 1.

For phase identification, materials were analysed by XRD on a Philips PW1050/81 diffractometer operating in Bragg– Brentano geometry with Cu-K α X-radiation and secondary monochromation. Theta compensating divergence slits were used giving a constant irradiated sample length of 12.5 mm. Materials were placed on an aluminium plate sample holder and data collected in 40 min over the 2 θ range 3–50°, with a 0.02° step.

Table 1 Summary of synthesis gel compositions, product identification and selected materials' framework compositions

	Synthesis gel composition			Inorganic composition		
Run No.	Cation ratio	Fluoride ratio	Template ^a	Product solid ^b	ICP-OES	³¹ P MAS NMR
1	1.0 A1 : 1.0 P		diquat-3	ERI + A		
2	1.0 A1 : 1.0 P	0.8	diquat-3	$\mathbf{ERI} + \mathbf{A}$		
3	0.1 Mg : 0.9 Al : 1.0 P		diquat-3	ERI + B		
4	0.1 Co : 0.9 Al : 1.0 P		diquat-3	ERI	Co _{0.11} Al _{0.89} PO ₄	
5	0.1 Si : 1.0 Al : 0.9 P		diquat-3	ERI + B		
6	0.2 Si : 1.0 Al : 0.8 P		diquat-3	ERI + B		
7	1.0 A1 : 1.0 P		diquat-4	$\mathbf{ERI} + \mathbf{A}$		
8	1.0 A1 : 1.0 P	0.8	diquat-4	ERI	AlPO ₄	
9	0.1 Mg : 0.9 Al : 1.0 P		diquat-4	ERI		
10	0.15 Mg : 0.85 Al : 1.0 P		diquat-4	ERI	Mg _{0.14} Al _{0.86} PO ₄	$Mg_{0.33}Al_{0.67}PO_4$
11	0.2 Mg : 0.8 Al : 1.0 P		diquat-4	ERI	-	-
12	0.25 Mg : 0.75 Al : 1.0 P		diquat-4	ERI	Mg _{0.17} Al _{0.83} PO ₄	$Mg_{0.31}Al_{0.69}PO_4$
13	0.5 Mg : 0.5 Al : 1.0 P		diquat-4	ERI + C	$Mg_{0.39}Al_{0.61}PO_4$	$Mg_{0.22}Al_{0.78}PO_4$
14	0.1 Co : 0.9 Al : 1.0 P		diquat-4	ERI	Co _{0.11} Al _{0.89} PO ₄	-
15	0.1 Si : 1.0 Al : 0.9 P		diquat-4	ERI		
16	0.2 Si : 1.0 Al : 0.8 P		diquat-4	ERI ^c		
17	1.0 A1 : 1.0 P		diquat-5	D		
18	1.0 A1 : 1.0 P	0.3	diquat-5	$AFX + ERI^d$		
19	0.1 Mg : 0.9 Al : 1.0 P		diquat-5	AFX		
20	0.15 Mg : 0.85 Al : 1.0 P		diquat-5	AFX	Mg _{0.17} Al _{0.83} PO ₄	$Mg_{0.21}Al_{0.79}PO_4$
21	0.2 Mg : 0.8 Al : 1.0 P		diquat-5	AFX	Mg _{0.30} Al _{0.70} PO ₄	
22	0.25 Mg : 0.75 Al : 1.0 P		diquat-5	AFX	Mg _{0.39} Al _{0.61} PO ₄	$Mg_{0.45}Al_{0.55}PO_4$
23	0.5 Mg : 0.5 Al : 1.0 P		diquat-5	AFX + E	-	-
24	0.1 Co : 0.9 A1 : 1.0 P		diquat-5	AFX + F		
25	0.1 Si : 1.0 Al : 0.9 P		diquat-5	$AFX + ERI^d$		
26	0.2 Si : 1.0 Al : 0.8 P		diquat-5	AFX + F		

^{*a*} Templates were added as concentrated aqueous hydroxide solutions at a mole ratio of 0.6, to give an initial gel pH of *ca.* 7; diquat-3 = 1,3-bis(*N*-methylpyrrolidinium)propane; diquat-4 = 1,4-bis(*N*-methylpyrrolidinium)butane; diquat-5 = 1,5-bis(*N*-methylpyrrolidinium)pentane. ^{*b*} Unidentified impurity phases are labelled A–F. ^{*c*} Poorly crystalline. ^{*d*} Approximately 50 : 50 mixture.

The crystal morphology in selected samples was examined by scanning electron microscopy. Samples were mounted on carbon stubs and gold coated before being examined on a Zeiss Evo 50 SEM. Infrared spectra were recorded on a Mattson Genesis II FT-IR system equipped with an ATR accessory (32 scans at 1 cm⁻¹ resolution).

The inorganic composition of selected materials was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES). Samples were dissolved in nitric acid (Aristar) and analysed with a Spectro Ciros CCD spectrometer. The amount of included organic and water was determined by thermogravimetric analysis (TGA) on a Mettler Toledo TG 50 thermobalance. Finely ground samples were heated in flowing air (200 cm³ min⁻¹) to 900 °C at 10 °C min⁻¹.

To determine whether the template molecules had been incorporated intact within the materials' pores, ¹³C solid state NMR spectroscopy was performed. Data were collected at ambient temperature on a Varian UNITY Inova spectrometer equipped with a 7.05 T Oxford Instruments magnet. ¹H-¹³C CP MAS NMR spectra were recorded at 75.40 MHz with an acquisition time of 30 ms, relaxation delay of 1 s and contact time of 1 ms (the 1 H 90.0° pulse was 4.5 µs). The samples were spun at 5 kHz and referenced to TMS. Similarly ²⁷Al and ³¹P NMR data were obtained, for selected materials, to examine the local structure of the inorganic framework. DP MAS NMR spectra were recorded for ²⁷Al at 78.12 MHz with a 1 μ s (20.0°) pulse, an acquisition time of 30 ms and relaxation delay of 0.2 s, and for ³¹P at 121.37 MHz with a $4.5 \,\mu\text{s}$ (90.0°) pulse, an acquisition time of 20.2 ms and relaxation delay of 60 s. Samples were spun at 14 kHz and referenced to 1 M AlCl₃ or 85% H₃PO₄, for Al and P, respectively. A ¹H-²⁹Si CP MAS NMR spectrum was recorded at 59.56 MHz with an acquisition time of 30 ms, relaxation delay of 1 s and contact time of 3 ms (the ¹H 90.0° pulse was 5 μ s). The sample was spun at 5 kHz and referenced to TMS. All relaxation delays were optimised.

Results and discussion

Synthesis

Materials were prepared with diquaternary templating cations, the length of the methylene chain being varied systematically to investigate the effect on product formation. Attempts were made to introduce elements (Mg^{2+} , Si^{4+} , Co^{2+}) into the AlPO₄ framework, the level being adjusted (in selected cases) to try to obtain phase pure materials. It is expected that the presence of these cations will modify the catalytic behaviour of the solids formed. The results of representative hydrothermal syntheses are given in Table 1, including synthesis gel compositions, identified phases and inorganic elemental analysis of selected samples.

Microporous materials having the framework-type code **ERI** (AlPO₄-17) were formed as hexagonal prismatic crystals from gels containing the 1,3-bis(*N*-methylpyrrolidinium)propane (diquat-3) template. Aluminophosphates crystallise with or without the inclusion of F^- in the gel, although a trace amount of an unidentified impurity is always present (denoted phase A, with the longest *d*-spacing at *ca* 10.4 Å). The MgAPO, SAPO and CoAPO may also be prepared, although in the case of the Mg- and Si-containing materials an additional impurity is observed (denoted phase B, with longest *d*-spacing at *ca* 9.3 Å). Increasing the Si

content of the gel, or switching from fumed to colloidal silica, did not change the products formed. The CoAPO is obtained pure, as a blue solid, which indicates the presence of tetrahedral Co^{2+} included within the aluminophosphate framework.

Preparations using the 1,4-bis(N-methylpyrrolidinium)butane (diquat-4) cation also yield materials of the ERI frameworktype. The crystals possess a hexagonal prismatic morphology, however, they are of poor quality being composed of blades. Aluminophosphates may be synthesised in the presence or absence of F⁻, phase pure material being obtained with a gel F/P ratio of 0.8 (Fig. 2a-2b). The MgAPO, SAPO and CoAPO ERItype materials are prepared phase pure from gels containing 10 mol% Mg, Si or Co, respectively. Increasing the Si content above 15 mol%, using either fumed or colloidal silica sources, reduces the crystallinity of the resultant material. This is presumably due either to the accumulation of amorphous material, or to the presence of faulting, as has been observed in other SAPO materials in the ABC-6 family.^{17,18} Notwithstanding this, the general reduction in impurity phases seen in these products of reaction (compared to those prepared with diquat-3) is probably due to there being a closer match between the size of the template and the ERI cavity.



Fig. 2 XRD patterns of as-prepared solids templated with diquat-4, (a) AlPO₄–**ERI** + trace A, (b) AlPO₄(F)–**ERI**, (c) Mg_{0.1}–**ERI**, (d) Mg_{0.15}–**ERI**, (e) Mg_{0.2}–**ERI**, (f) Mg_{0.25}–**ERI**, (g) Mg_{0.5}–**ERI** + C. Asterisks mark reflections from impurity phases. The average refined unit cell was found to be hexagonal with a = 13.23(3) Å, c = 14.76(9) Å, which is similar to literature values.²

To determine the range of gel compositions from which materials could be obtained further Mg-containing gels were prepared (Table 1). Solids were obtained apparently pure (by XRD) with Mg/P of 0.1–0.25. The XRD patterns (Fig. 2c–2f) change subtly, particularly in the 2θ region 23–25°, as the Mg/P ratio in the gel increases; this will be discussed further below. A gel with Mg/P of 0.5 yields an impure sample containing materials with both the **ERI** and an unidentified structure-type (Fig. 2g).

When syntheses were carried out with 1,5-bis(*N*-methylpyrrolidinium)pentane (diquat-5) cations microporous solids were again formed. SEM revealed twinned crystals, of a hexagonal rosette-like appearance. From purely aluminophosphate gels, in the absence of fluoride ions, an unidentified phase crystallised (Fig. 3a). If F^- was included in an identical gel, at an F/diquat-5 ratio of 0.5, a mixed phase product comprising **ERI** and **AFX**type aluminophosphates (Fig. 3b) was obtained. In a further attempt to prepare pure AlPO₄(F)-56 the F/diquat-5 ratio was adjusted systematically. At ratios other than 0.5 AlPO₄(F)-56 was not obtained, instead a poorly crystalline material formed. A mixed phase product, containing equal quantities of **AFX** and **ERI** crystals, was formed if Si was included at a Si/Al ratio of 0.1.

Fig. 3 XRD patterns of as-prepared solids templated with diquat-5, (a) phase D, (b) AlPO₄(F)–**AFX** and AlPO₄(F)–**ERI**, (c) Mg_{0.1}–**AFX**, (d) Mg_{0.15}–**AFX**, (e) Mg_{0.2}–**AFX**, (f) Mg_{0.25}–**AFX**, (g) Mg_{0.5}–**AFX** + E. Asterisks mark reflections from impurity phases. The average refined unit cell was found to be trigonal with a = 13.78(2) Å, c = 19.93(9) Å, which is similar to literature values.²

Doubling the Si ratio gave **AFX**, in the absence of **ERI**, but with a small amount of an impurity phase present. This mixture (**AFX** + F) formed again from the Co-containing gels. Including Mg in the aluminophosphate gel led to the production of phase pure **AFX**-type materials over the Mg/P range 0.1–0.25 (Fig. 3c–3f). Only when Mg/P reaches 0.5 does an impure sample form, containing materials with both the **AFX** and an unidentified framework-type (Fig. 3g).

Framework characterisation

To characterise further the MgAPO materials synthesised from gels with increasing Mg-loading, a spectroscopic analysis was performed. FT-IR spectra, in the structural region, are given in the ESI† for as-prepared materials synthesised with diquat-4 and -5, respectively. The most important changes in the spectra to note occur when Mg is included in the aluminophosphate gels. There is significant broadening and a small red shift in the T–O–T asymmetric stretching region (*ca* 1055 cm⁻¹) of the MgAPO spectra when compared to the AlPO₄ spectra, indicating that Mg is substituting into the aluminophosphate lattice.

Further characterisation was carried out on magnesioaluminophosphates prepared from gels with Mg/P = 0.15 and 0.25, these being chosen to be representative samples. The mixed phase formed with diquat-4 at Mg/P = 0.5 was also studied. The ²⁷Al MAS NMR spectra of as-prepared $Mg_{0.15}$ -ERI, $Mg_{0.25}$ -ERI and Mg_{0.5}-ERI (the subscript representing the Mg/P ratio in the synthesis gel) all show a resonance at ca 35 ppm (Fig. 4a-4c) which is attributed to Al in tetrahedral coordination. The sample Mg_{0.15}-ERI has an additional signal at 14.5 ppm which may be attributed to a pentacoordinated species in which a water molecule is additionally coordinated to the framework Al.¹⁹ The presence of 5-coordinate Al leads to distortion of the framework structure, which was indicated by changes in the powder XRD patterns discussed above (cf. Fig. 2d with 2f-g in the 2θ region 23-25°). Mg_{0.15}-AFX and Mg_{0.25}-AFX both show two resonances in their ²⁷Al spectrum (Fig. 4d–4e). The signal at *ca* 36 ppm is assigned to Al in tetrahedral coordination, while the signal at 7.0 ppm is attributed to pentacoordinated Al, as before.

The ³¹P MAS NMR spectra (Fig. 5) of these samples comprise a cluster of poorly resolved resonances between -5 and -32 ppm. Additional signals (at ca 0.2 and -1.8 ppm) with narrow linewidths, are seen in the samples Mg_{0.25}-ERI and Mg_{0.5}-ERI, and these are ascribed to the unidentified phase C. It should be noted that by XRD Mg_{0.25}-ERI appears phase pure, however the greater sensitivity of NMR has revealed the trace impurity. The relative intensities of the other signals in each of the ³¹P spectra vary between the samples and may be deconvoluted to yield four or five resonances (see ESI[†]). If the changes in ³¹P chemical shifts in the spectra are due primarily to changes in the next nearest neighbour (i.e. Mg substitution), rather than differences in crystallographic site, as several authors have stated,²⁰ then the most negative chemical shift may be assigned to a phosphorus with four aluminium next-nearest neighbours, P(4Al), the next to P(3Al, Mg), then P(2Al, 2Mg), then P(Al, 3Mg) and finally to P(4Mg) species. Table 2 gives the relative contribution of each signal to the spectrum, and also the expected contribution (calculated from the binomial theorem²¹) if the Mg distribution is random. It can be seen in all cases there is a discrepancy between the observed and





Fig. 4 ²⁷Al MAS NMR of as-prepared (a) $Mg_{0.15}$ -ERI (diquat-4), (b) $Mg_{0.25}$ -ERI (diquat-4), (c) $Mg_{0.5}$ -ERI (diquat-4), (d) $Mg_{0.15}$ -AFX (diquat-5), and (e) $Mg_{0.25}$ -AFX (diquat-5).

calculated populations which suggests there is some ordering of the Mg within the aluminophosphate lattice. Such ordering has previously been noted in MgAPO-11, MAPO-36¹⁸ and MgAPO-20.²¹ In the spectra of Mg_{0.15}–**ERI**, Mg_{0.25}–**ERI**, Mg_{0.5}–**ERI** and Mg_{0.15}–**AFX** the population of P(3Al, Mg) is greater than that calculated for random distribution, but for Mg_{0.25}–**AFX** is lower. The lower level implies the presence of regions of high Mg content which are predicted to be similar to the M–O–P–O– M units reported in CoAPO-50.²² The presence of such ordering is attributed to the positive charge on the dumb-bell shaped organic SDAs being concentrated towards each end of each molecule (see Fig. 1), which may direct Mg-substitution towards the ends of the large cavity in which the SDA resides.



Fig. 5 ³¹P MAS NMR of as-prepared (a) $Mg_{0.15}$ -ERI (diquat-4), (b) $Mg_{0.25}$ -ERI (diquat-4), (c) $Mg_{0.5}$ -ERI (diquat-4), (d) $Mg_{0.15}$ -AFX (diquat-5), and (e) $Mg_{0.25}$ -AFX (diquat-5).

To test whether the assignment of ³¹P resonances to P atoms with differing numbers of Al next nearest neighbours is reasonable, the framework composition many be calculated from the NMR data and compared to that obtained by chemical analysis. Calculations were performed using the equations of Barrie and Klinowski,²¹ and the results given in Table 1. The overall inorganic framework composition determined by NMR and ICP-OES compare reasonably well, with the closeness in match being poorer for the **ERI** materials. This is clearly, in the case of the material crystallised from the gel of Mg/P = 0.5, due to the impurity C phase, which is presumably Mg-rich. Thus the solid state NMR results distinguish between the composition of the **ERI** material and the impurity, whereas the ICP-OES gives the total bulk composition.

 Table 2
 Comparison of ³¹P MAS NMR peak areas obtained by deconvolution of the spectra with those expected for materials with a random Mg distribution within the framework (calculated from the binomial theorem)

		³¹ P MAS NMR (%)				Binomial theorem (%)					
Run no.	Mol. sieve	P(4Al)	P(3Al)	P(2Al)	P(1Al)	P(0Al)	P(4Al)	P(3Al)	P(2Al)	P(1Al)	P(0Al)
10	ERI	6.8	64.9	18.8	9.5	_	20.5	39.8	29.1	6.4	1.2
12	ERI	6.3	71.6	14.5	7.7		22.8	40.8	27.3	5.6	0.9
13	ERI	26.3	60.4	13.4			37.4	41.7	17.4	2.5	0.2
20	AFX	27.7	63.5	5.4	3.5		38.6	41.5	16.7	2.4	0.2
22	AFX	16.4	22.5	37.5	12.1	11.3	9.3	30.1	36.7	11.0	4.0

To investigate the mode of Si substitution in the silicoaluminophosphate Si_{0.1}-ERI MAS NMR spectra were measured. Two possible modes of substitution are known in SAPO materials: Si may substitute for P (Si \rightarrow P, designated mechanism I) or two Si may substitute for one Al and P (2Si \rightarrow Al + P, designated mechanism II). The ²⁹Si NMR spectrum (Fig. 6) shows two signals at -90.5 and -93.2 ppm. The first is assigned to isolated Si which has substituted directly for P and so is surrounded by four Al atoms as next-nearest neighbours (Si(4Al), mechanism I). The resonance at -93.2 ppm is assigned to Si(3Al, Si), which results from substitution by mechanism II. The absence of signals at lower chemical shifts indicates that large silica 'islands' are not present in this sample, as have been observed in, for example, SAPO-18.23 Brønsted acidity will therefore be present once the organic SDA is removed by calcination because of the requirement to maintain charge neutrality.



Fig. 6 ²⁹Si MAS NMR of as-prepared Si_{0.1}–ERI (diquat-4).

Template characterisation

The **ERI** and **AFX** framework types may be considered to be constructed entirely of planar 6-rings (as rings composed of six tetrahedral and six oxygen atoms are known). The rings may have their centres at either the (0,0), (2/3, 1/3) or (1/3, 2/3) positions (A, B or C, respectively) in the hexagonal *ab* plane, and may link to other rings above and below them in the *c* direction. Although materials containing randomly stacked 6-rings have been synthesised,²⁴ in **ERI** and **AFX** they are arranged in the ordered stacking sequences AABAAC and AABBC-CBB, respectively. The reason for this non-random arrangement is necessarily due to the controlling presence of the organic SDA.

The diquat-4 and -5 template molecules were included intact within the materials' principal cavities, as evidenced by the 1 H– 13 C CP MAS NMR spectra (Fig. 7). Carbons not adjacent to a nitrogen atom exhibit a resonance at *ca* 23 ppm, but are not resolved, which leads to similar spectra for both templates. The methyl carbons in diquat-4 appear as a single signal (51 ppm), which indicates that both ends of the template are likely to be in the same average environment. This contrasts the case of diquat-4 in the **STI** zeolite channels¹³ in which the resonance of the methyl



Fig. 7 ¹³C MAS NMR of as-prepared (a) $Mg_{0.15}$ -ERI (diquat-4), (b) $Mg_{0.25}$ -ERI (diquat-4), (c) $Mg_{0.5}$ -ERI (diquat-4), (d) $Mg_{0.15}$ -AFX (diquat-5), and (e) $Mg_{0.25}$ -AFX (diquat-5) showing, in all cases, that the template is included intact (see text for further details).

carbons is split into two due to differences in interaction between each end of the template and the framework. The resonance at 65 ppm is assigned to methylene carbons adjacent to the quaternary nitrogens. In the MgAPO-56 materials additional signals are present in the ¹³C MAS NMR spectra (Fig. 7d– 7e) which are likely to arise from fragments of SDA becoming included in the smaller gmelinite-type cavity also present in the framework.

Attempts to locate the SDA molecule within the large cavity of $Mg_{0.15}$ -ERI and $Mg_{0.15}$ -AFX by Rietveld refinement of powder XRD data collected on Station 2.3 of the Daresbury synchrotron (not shown) have so far proved unsuccessful.

To determine the amount of included structure-directing agent and water, TGA was performed. For $\text{Co}_{0.1}$ –**ERI** templated with diquat-3 there is a small (1.8 wt%) loss below 175 °C, followed by a larger two-stage loss (of 17.1 wt%) between 325 and 645 °C. The former is attributed to water, while the latter corresponds to the template. Similarly, all preparations yielding pure **ERI**-type solids with diquat-4 show an analogous pattern: 1.3 wt% loss below 115 °C, attributed to water, followed by a 2.2 wt% loss between 365 and 450 °C, and a 16.0 wt% loss between 450 and 665 °C. These latter two losses are more resolved and may be attributed either to the removal of template molecules weakly bound to the outer surface of the crystallites followed by those within the cavity, or to a two stage breakdown of the template included within the cavity.²⁵ No satisfactory explanation for the presence of a pentacoordinate Al in Mg_{0.15}–**ERI** and not in Mg_{0.25}–**ERI** was obtained from the TGA. In all MgAPO **AFX** samples TGA showed a weight loss of *ca* 5.4 wt% below 180 °C which is attributed to loosely bound water. The magnitude of the template mass loss corresponds well with the expected change in mass with increasing methylene chain length. The template (15.25 wt%) is removed in a two-stage loss between 430 and 645 °C. These are insufficiently resolved, however, to permit calculation of the proportion of the template being removed at each stage.

Combining the results of chemical and thermal analysis with crystallographic data allows the calculation of the unit cell contents. So, for example, the magnesioaluminophosphate prepared from a gel containing Mg/P = 0.25 and diquat-4 (Mg_{0.25}–**ERI**) may be formulated as $|(H_2O)_2(C_{14}H_{30}N_2)_{2.2}|[Mg_3Al_{15}P_{18}O_{72}]$. The mass loss of 16 wt% observed by TGA equates to 1.93 diquat-4 molecules per cell. This suggests that the cavities are likely to be completely occupied, the excess observed being adsorbed onto outer surface sites. The analogous sample prepared with diquat-5 (Mg_{0.25}–**AFX**) has the overall unit cell contents $|(H_2O)_{11}(C_{15}H_{32}N_2)_{2.3}|[Mg_9Al_{15}P_{24}O_{96}]$. The template excess may be rationalised by the presence of organic fragments included within the gmelinite-type cavity, as suggested by the ¹³C MAS NMR spectra.

Conclusion

A novel family of α, ω -bis(N-methylpyrrolidinium)alkane structure directing agents have been synthesised. When added to aluminophosphate-based synthesis gels these were found to direct the crystallisation of materials possessing either the ERI or AFX framework types. Control of the phase which crystallised was achieved by varying the methylene chain length in the SDA. A close relationship between this and the length of the cavity rationalises the observed templating effect. Moreover the use of these SDAs was found to improve upon those previously applied to prepare these solids by allowing a greater level of control of the level of metal substitution into the aluminophosphate framework. This will allow the level of active catalytic sites in the materials to be readily changed, whilst still retaining a high degree of phase purity. As expected divalent Mg and Co were found to substitute for Al, but ³¹P solid state NMR showed unexpectedly that these may be distributed non-randomly throughout the framework. Si was found to substitute by two different mechanisms (Si \rightarrow P and $2Si \rightarrow Al + P$ in the **ERI**-type solid, which is expected to modify the acidity of the resultant SAPO-17 material to produce a catalyst complimentary to the related solid acids SAPO-18 and SAPO-34.

Acknowledgements

We are grateful to the Leverhulme Trust for funding and the CCLRC for providing access to synchrotron radiation. We thank Dr David Apperley (EPSRC Solid State NMR Service, University of Durham) for collecting and deconvoluting the NMR spectra and Mrs Diane Spencer (University of Wolverhampton) for the ICP-OES analyses.

Notes and References

- 1 S. T. Wilson, B. M. Lok, C. A. Messina, T. T. Cannan and E. M. Flanigen, *J. Am. Chem. Soc.*, 1982, **104**, 1146.
- 2 Ch. Baerlocher, W. M. Meier and D. H. Olson, *Atlas of Zeolite Framework Types*, 5th edn, 2001, Elsevier, Amsterdam, also available at http://www.iza-structure.org/databases/.
- 3 R. F. Lobo, S. I. Zones and M. E. Davis, J. Inclusion Phenom. Mol. Recognit. Chem., 1995, 21, 47.
- 4 R. F. Lobo, S. I. Zones and R. C. Medrud, Chem. Mater., 1996, 8, 2409.
- 5 G. W. Noble, P. A. Wright and Å. Kvick, J. Chem. Soc., Dalton Trans., 1997, 4485.
- 6 J. L. Casci, B. M. Lowe and T. V. Whittam, US Pat. 4,537,754, 1985.
- 7 P. A. Wright, C. Sayag, F. Rey, D. W. Lewis, J. D. Gale, S. Natarajan and J. M. Thomas, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 3537.
- 8 M. Hartmann and L. Kevan, Chem. Rev., 1999, 99, 635.
- 9 A. Corma, Chem. Rev., 1995, 95, 559.
- 10 J. M. Thomas, R. Raja, G. Sankar and R. G. Bell, *Nature (London)*, 1999, **398**, 227.
- 11 P. A. Wright, M. J. Maple, A. M. Z. Slawin, V. Patinec, R. A. Aitken, S. Welsh and P. A. Cox, J. Chem. Soc., Dalton Trans., 2000, 1243.
- 12 F. Gramm, Ch. Baerlocher, L. B. McCusker, S. J. Warrender, P. A. Wright, B. Han, S. B. Hong, Z. Liu, T. Ohsuna and O. Terasaki, *Nature (London)*, 2006, 444, 79.
- 13 S. B. Hong, E. G. Lear, P. A. Wright, W. Z. Zhou, P. A. Cox, C. H. Shin, J. H. Park and I. S. Nam, J. Am. Chem. Soc., 2004, 126, 5817.
- 14 A. Tuel, C. Lorentz, V. Gramlich and Ch. Baerlocher, C. R. Chim., 2005, 8, 531; U. Lohse, E. Löffler, K. Kosche, J. Jänchen and B. Parltiz, Zeolites, 1993, 13, 549.
- 15 S. T. Wilson, R. W. Broach, C. S. Blackwell, C. A. Bateman, N. K. McGuire and R. M. Kirchner, *Microporous Mesoporous Mater.*, 1999, 28, 125; P. Feng, X. Bu and C.-S. Yang, *Microporous Mesoporous Mater.*, 2001, 50, 145.
- 16 J. March, Advanced Organic Chemistry: Reactions, Mechanisms and Structure, 4th edn, 1992, Wiley: New York, p. 411.
- 17 N. K. McGuire, C. A. Bateman, C. S. Blackwell, S. T. Wilson and R. M. Kirchner, *Zeolites*, 1995, 15, 460.
- 18 S. T. Wilson, R. W. Broach, C. S. Blackwell, C. A. Bateman, N. K. McGuire and R. M. Kirchner, *Microporous Mesoporous Mater.*, 1999, 28, 125.
- 19 C. S. Blackwell and R. L. Patton, J. Phys. Chem., 1984, 88, 6135.
- 20 S. Prasad and J. F. Haw, *Chem. Mater.*, 1996, **8**, 861–864; D. B. Akolekar and R. F. Howe, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, 3263.
- 21 P. J. Barrie and J. Klinowski, J. Phys. Chem., 1989, 93, 5972
- 22 J. M. Bennett and B. K. Marcus, *Stud. Surf. Sci. Catal.*, 1988, **37**, 269. 23 J. Chen, P. A. Wright, J. M. Thomas, S. Natarajan, L. Marchese, S. M.
- Bradley, G. Sankar, C. R. A. Catlow, P. L. Gai-Boyes, R. P. Townsend and C. M. Lok, *J. Phys. Chem.*, 1994, 98, 10216.
 24 B. Szostak and K. P. Lillerud, *J. Chem. Soc. Chem. Commun.* 1994.
- 24 R. Szostak and K. P. Lillerud, J. Chem. Soc., Chem. Commun., 1994, 2357.
- 25 E. Bourgeat-Lami, F. Di Renzo, F. Fajula, P. H. Mutin and T. Des Courieres, J. Phys. Chem., 1992, 96, 3807.