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1-Alkyl-3-methyl Imidazolium Bromide Ionic Liquids in the Ionothermal Synthesis of Aluminium Phosphate Molecular Sieves

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The systematic increase in alkyl chain length from 2 to 5 carbons in 1-alkyl-3-methyl imidazolium bromide ionic liquids is investigated in the ionothermal synthesis of aluminophosphate (AlPO) zeolite materials in sealed autoclaves. The effect of alkyl chain branching and the use of an imidazolium dication ionic liquid are also investigated. On addition of HF to the reaction mixture, a small amount of 1,3-dimethylimidazolium cation is formed in all cases (except when the alkyl chain length is 2), which acts as the structure directing agent (SDA) in the formation of AlPO molecular sieves with the CHA framework (SIZ-10). For 1-ethyl-3-methyl imidazolium bromide ionic liquids, the cation is incorporated intact into the SIZ-4 structure. The resulting materials are characterized by single-crystal X-ray diffraction and ^{13}C MAS NMR.

Introduction

Ionothermal synthesis is the use of an ionic liquid[1] or eutectic mixture[2] as the reaction solvent and, in many cases, structure directing agent (SDA) in the synthesis of materials.[3−10] The negligible vapor pressure produced from the ionic liquids when heated results in the ionothermal synthesis taking place at near ambient pressure.[3] This eliminates the safety concerns associated with high pressures and allows for the ionothermal synthesis of microporous materials in glass vessels on the lab bench[3,11] and the use of low-pressure microwave heating.[7,8] The different chemistry of the ionothermal solvent system compared to that of the traditionally used hydrothermal and solvothermal systems produces conditions under which novel structure types appear to be accessible. In recent years, we have prepared novel structures including SIZ-1 (**S**t Andrews **I**onothermal **Z**eolite-**1**), the first material reported using the ionothermal method, which displays some unusual hanging P−O bonds and contains aluminum in both 4- and 5-coordination;[3] SIZ-6, a layered material displaying aluminum with 4-, 5-, and 6-coordination;[4] and SIZ-7, a novel Co-AlPO zeolite framework.[5] In addition, a number of materials with known topologies can be prepared. Figure 1 demonstrates the versatility of the 1-ethyl-3-methylimidazolium bromide (EMIBr) ionic liquid as solvent and SDA in the previously reported synthesis of SIZ-1, SIZ-3 (which has the AEL topology), SIZ-4 (the CHA topology), and SIZ-6.[3,4]

To date, much of the work on ionothermal synthesis has concentrated predominantly on the use of the ionic liquid EMIBr, with the exception of a couple of reported studies using 1-butyl-3-methylimidazolium bromide (BMIBr)[7,11] and 1-hexyl-3-methylimidazolium bromide (HMIBr).[12] Here, we report the findings from systematically increasing the ionic liquid alkyl chain length from 2 to 5 carbons, introducing branching on the alkyl chain and the effects of using an imidazolium dication ionic liquid in the synthesis of AlPOs under conventional oven heating methods in sealed autoclaves.

The properties of an ionic liquid, including viscosity, solvating ability, and melting point, can be altered dramatically by varying the cation.[13] Recent studies have shown that, in general, increasing the alkyl chain length initially reduces the melting point of the ionic liquid, with a tendency toward glass formation for alkyl chain lengths of 4−8 carbons.[14] On the alkyl chain length being further increased to >8 carbons, the melting points of the salts start to increase again with increasing chain length. These changes in melting point

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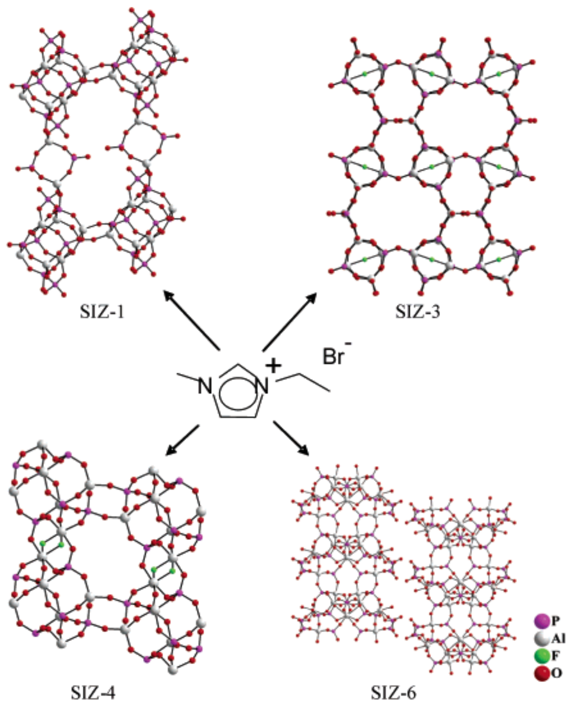

Figure 1. Aluminophosphate materials previously synthesized ionothermally from EMIBr.

are due to the changes in the efficiency of ion packing.[15] Increasing the alkyl chain branching at the imidazolium ring 3-position has been found to increase the melting point[16,17] due to the changes in efficiency of the crystal packing as free-rotation volume decreases and atom density increases.[18]

One of the advantages of ionothermal synthesis is the precise control we have over the nature and amount of mineralizers used. Mineralizers, such as fluoride or hydroxide ions, added to the reaction mixtures in the correct quantities are often vital for crystallization of the desired molecular sieve products. Fluoride in particular has recently been an extremely useful mineralizer for aluminophosphate[19] and silicate[20−23] synthesis. In addition to helping solubilize the starting materials under the reaction conditions, there is evidence that fluoride itself can play a structure directing role[24−27] and is intimately involved in SDA ordering in certain materials.[28,29] In ionothermal synthesis, the addition of fluoride also seems to be important in determining the phase selectivity of the reaction.[3]

Here, we describe the synthesis of an aluminophosphate material with the CHA framework topology starting from several different imidazolium-based ionic liquids. When fluoride is added as a mineralizer, all the resulting products contain the same cation as SDA, 1,3-dimethyl imidazolium, regardless of the starting ionic liquid. The only exception to this is in the case of 1-ethyl-3-methyl imidazolium bromide, in which the ionic liquid cation is occluded intact into the zeolite.

Experimental Section

Synthesis of 1-Ethyl-3-methylimidazolium Bromide (EMIBr), Mp = 81−83 °C: Under inert atmosphere conditions, degassed ethylbromide (86.04 g, 0.790 mol, Avocado) was added to the redistilled *N*-methyl imidazole (49.86 g, 0.607 mol, Aldrich) with constant stirring. This was refluxed at 40 °C for 3 h and then allowed to cool to room temperature. Ethyl acetate was added, and the product crashed out of solution. This was filtered, washed with ethyl acetate, and dried under a vacuum at 25 °C for 10 h to give 1-ethyl-3-methylimidazolium bromide as a white solid. The product was stored under an inert atmosphere. Yield: 94%. ^{1}H NMR (D_2O): δ 1.41 (t, 3H, CH_3, $J = 7.3$ Hz), 3.81 (s, 3H, NCH_3), 4.15 (q, 2H, NCH_2, $J = 7.3$ Hz), 7.38 (d, 2H, NC(*H*)C(*H*)N, $J = 21.0$ Hz), 8.66 (s, 1H, NC(*H*)N). ^{13}C NMR (D_2O): δ 14.68 (s, *C*H_3), 35.85 (s, N*C*H_3), 44.88 (s, N*C*H_2), 121.94, 123.52 (2 × s, N*CC*N), 135.63 (s, N*C*N). NMR comparable with literature values.[30]

Synthesis of 1-Propyl-3-methylimidazolium Bromide (PrMIBr): The same synthesis procedure as that used for EMIBr was carried out using degassed propylbromide (114 g, 0.927 mol, Avocado) and redistilled *N*-methyl imidazole (56.3 g, 0.686 mol, Aldrich). The mixture was refluxed at 45 °C for 3 h and then allowed to cool to room temperature. The oily product was washed three times with ethyl acetate and dried under vacuum at 50 °C for 10 h to give PrMIBr as a colorless oil. The product was stored under an inert atmosphere. Yield: 83%. ^{1}H NMR (D_2O): δ 0.87 (t, 3H, CH_3, $J = 7.4$ Hz), 1.78−1.91 (m, 2H, CH_2CH_3) 3.86 (s, 3H, NCH_3), 4.13 (t, 2H, NCH_2, $J = 7.0$ Hz), 7.42 (d, 2H, NC(*H*)C(*H*)N, $J = 12.0$ Hz), 10.14 (s, 1H, NC(*H*)N). ^{13}C NMR (D_2O): δ 9.75 (s, *C*H_3), 22.29 (s, *C*H_2), 35.56 (s, N*C*H_3), 52.03 (s, N*C*H_2), 122.14, 123.42 (2 × s, N*CC*N), 135.83 (s, N*C*N). NMR comparable with literature values.[31]

Synthesis of 1-Isopropyl-3-methylimidazolium Bromide (iPrMIBr), Mp = 56−59 °C: The same synthesis procedure as that used for EMIBr was carried out using degassed isopropylbromide (102 g, 0.829 mol, Aldrich) and redistilled *N*-methyl imidazole (47.4 g, 0.577 mol, Aldrich). The mixture was refluxed at 50 °C for 4 h. A white solid was produced. Yield: 81%. ^{1}H NMR ($CDCl_3$): δ 1.41 (d, 6H, CH(CH_3)$_2$, $J = 6.7$ Hz), 3.61 (s, 3H, NCH_3), 4.56−4.72 (m, 1H, NC*H*), 7.50 (d, 2H, NC(*H*)C(*H*)N, $J = 9.5$ Hz), 10.12 (s, 1H, NC(*H*)N). ^{13}C NMR (D_2O): δ 24.21 (s, CH(*C*H_3)$_2$), 35.50 (s, N*C*H_3), 54.04 (s, N*C*H), 122.16, 123.39 (2 × s, N*CC*N), 135.78 (s, N*C*N). NMR comparable with literature values.[32]

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Table 1. Synthesis Details and Conditions for the Preparation of Materials Using Various Imidazolium-Based Ionic Liquids

		mass of reagents added (g) (molar ratio of reagents)						
product	IL	Al(O*i*Pr)$_3$	H_3PO_4	HF	H_2O	IL	*T* (°**C)**	*t* (h)
SIZ-4	EMIBr	0.1054 (1.0)	0.1772 (3.0)	0.015 (0.70)	(0.0)	3.82 (39)	150	68
SIZ-6	EMIBr	0.1000 (1.0)	0.1730 (3.1)	0.00 (0.0)	(0.0)	4.25 (45)	200	96
SIZ-10a	PrMIBr	0.1018 (1.0)	0.1742 (3.0)	0.015 (0.72)	(3.8)[a]	5.90 (58)	150	72
SIZ-10b	BMIBr	0.1040 (1.0)	0.1740 (3.0)	0.015 (0.71)	(3.7)[a]	4.10 (37)	200	96
SIZ-10c	PeMIBr	0.1009 (1.0)	0.1700 (3.0)	0.015 (0.73)	(3.7)[a]	4.58 (40)	170	240
SIZ-10d	dication	0.1017 (1.0)	0.1757 (3.1)	0.015 (0.72)	(3.81)[a]	4.01 (25)	170	45
SIZ-10e	*i*PrMIBr	0.1048 (1.0)	0.1756 (3.0)	0.015 (0.70)	(3.69)[a]	4.04 (38)	150	96
SIZ-11	*i*PrMIBr	0.1080 (1.0)	0.1748 (2.9)	0.00 (0.0)	(2.9)[a]	4.06 (37)	150	96

[a] Small amounts of water present come from the aqueous HF and H_3PO_4 solutions.

Synthesis of 1-Butyl-3-methylimidazolium Bromide (BMIBr): The same synthesis procedure as that used for PrMIBr was carried out using degassed butylbromide (29 g, 0.212 mol, Aldrich) and redistilled *N*-methyl imidazole (11.3 g, 0.138 mol, Aldrich). The mixture was refluxed at 50 °C for 5 h and then allowed to cool to room temperature. A pale yellow oil was produced. Yield: 79%. ^{1}H NMR (D_2O): δ 0.89 (t, 3H, CH_3, $J = 7.3$ Hz), 1.22−1.33 (m, 2H, CH_2), 1.76−1.88 (m, 2H, CH_2), 3.86 (s, 3H, NCH_3), 4.17 (t, 2H, NCH_3, $J = 7.2$ Hz), 7.43 (d, 2H, NC(*H*)C(*H*)N, $J = 15.4$ Hz), 8.69 (s, 1H, NC(*H*)N). ^{13}C NMR ($CDCl_3$): δ 13.68 (s, CH_3), 20.01, 32.59 (2 × s, CH_2), 36.91 (s, NCH_3), 50.62 (s, NCH_2), 123.17, 124.49 (2 × s, N*CC*N), 136.44 (s, N*C*N). NMR data comparable with literature values.[16]

Synthesis of 1-Pentyl-3-methylimidazolium Bromide (PeMIBr): The same synthesis procedure as that used for PrMIBr was carried out using degassed pentylbromide (108.9 g, 0.721 mol, Aldrich) and redistilled *N*-methyl imidazole (41.1 g, 0.501 mol, Aldrich). The mixture was refluxed at 60 °C for 5 h. A pale brown oil was produced. Yield: 80%. ^{1}H NMR (D_2O): δ 1.41 (t, 3H, CH_3, $J = 7.3$ Hz), 1.17−1.37 (m, 4H, CH_2CH_2), 1.78−1.89 (m, 2H, CH_2), 3.86 (s, 3H, NCH_3), 4.16 (t, 2H, NCH_2, $J = 7.2$ Hz), 7.38 (d, 2H, NC(*H*)C(*H*)N, $J = 14.85$ Hz), 8.68 (s, 1H, NC(*H*)N). ^{13}C NMR (D_2O): δ 13.05 (s, CH_3), 21.34, 27.47, 28.86 (3 × s, CH_2), 35.57 (s, NCH_3), 49.50 (s, NCH_2), 122.14, 123.40 (2 × s, N*CC*N), 135.78 (s, N*C*N). NMR data comparable with literature values.[33]

1,1′-Dimethyl-3,3′hexamethylene-diimidazolium Dibromide, Mp = 112−116 °C: The same synthesis procedure as that used for EMIBr was carried out using degassed 1,6-dibromohexane (40.36 g, 0.165 mol, Aldrich) and redistilled *N*-methyl imidazole (31.24 g, 0.380 mol, Aldrich). The mixture was refluxed at room temperature for 5 h. A slightly off white solid was produced. Yield: 97.5%. ^{1}H NMR (D_2O): δ 1.23 (m, 4H, 2 × CH_2CH_2), 1.76 (m, 4H, 2 × CH_2CH_2), 3.78 (s, 6H, 2 × NCH_3), 4.08 (t, 4H, 2 × NCH_2, $J = 7.17$ Hz), 7.34 (m, 4H, 2 × NC(*H*)C(*H*)N), 8.61 (s, 2H, 2 × NC(*H*)N). ^{13}C NMR (D_2O): δ 24.80, 29.00 (2 × s, CH_2), 35.57 (s, NCH_3), 49.32 (s, NCH_2), 122.10, 123.47 (2 × s, N*CC*N), 135.78 (s, N*C*N). NMR data comparable with literature values.[34]

Synthesis of Zeolite Analogues in Sealed Autoclaves: A typical synthesis procedure was as follows: a Teflon-lined autoclave (volume 23 mL) was charged with the ionic liquid, $Al[OCH(CH_3)_2]_3$ (Aldrich) and H_3PO_4 (85 wt % in H_2O, Aldrich). HF (48 wt % in H_2O, Aldrich) was added if required. The stainless steel autoclave was then heated in an oven to the required temperature. The reagent masses, temperatures, and length of time left in oven needed to produce the optimum purity are as detailed in Table 1. These conditions were optimized by changing the reaction compositions slightly and ascertaining the product composition after each reaction. SIZ-4 and SIZ-6 were synthesized as previously reported.[3,4] Water was removed by heating the $Al[OCH(CH_3)_2]_3$, H_3PO_4 and HF before adding the ionic liquid.

Structural Characterization Using X-ray Diffraction: Single-crystal X-ray diffraction data for SIZ-10 were collected on Station 9.8 at the Synchrotron Radiation Source (SRS), Daresbury Laboratories, Cheshire, U.K. The structure was solved using standard direct methods and refined using the least-squares minimization techniques against F^2. The CIF file is available in the Supporting Information. Framework phase identification was accomplished for SIZ-11 using powder X-ray diffraction (Stoe STADIP diffractometer, Cu Kα radiation).

^{13}C, ^{31}P, ^{27}Al, and ^{19}F MAS NMR spectra. ^{13}C, ^{31}P, and ^{27}Al data were collected at the EPSRC solid-state NMR service facility at the University of Durham, U.K., on a 300 MHz Varian UNITY*Inova* with a 7.05 T Oxford Instruments magnet. ^{19}F data were collected on an Infinity plus 500 MHz spectrometer. The frequencies for data collection were 75.368 MHz (^{13}C), 121.371 MHz (^{31}P), 78.125 MHz (^{27}Al), and 125.666 MHz (^{19}F). Proton decoupled ^{13}C NMR spectra were collected with the samples spun at the magic angle at 5 kHz, a contact time of 1 ms and a recycle time of 30 s. The chemical shift reference was $(CH_3)_4Si$. ^{31}P NMR spectra were collected with proton decoupling using a recycle time of 120 s and a 20 ms acquisition time. Spectra were referenced to 85% H_3PO_4 at 0 ppm. ^{27}Al NMR spectra were collected without ^{1}H decoupling using a 10 ms acquisition time and a recycle time of 0.5 s. The spectra were referenced to 1 M $AlCl_3$ at 0 ppm. ^{19}F MAS NMR spectra were collected with a 10 ms acquisition time and a recycle time of 60 s. The chemical shift reference was $CFCl_3$ and there was no decoupling used.

A Jeol JSM-5600 SEM was used to collect the scanning electron micrographs of all the materials prepared.

Results

In the case of 1-ethyl-3-methyl imidazolium bromide ionic liquids (i.e., alkyl chain length is 2), the synthesis produced either the SIZ-4 or SIZ-6 materials depending on the conditions as described in our previous papers.[3,4] Increasing the alkyl chain length in the 1-alkyl-3-methylimidazolium bromide ionic liquid to 3, 4, and 5 carbons and adding no HF to the zeolite analogue reactions resulted in no AlPO framework forming. However, on addition of HF, materials with the same framework topology as previously reported for SIZ-4 were prepared. Phase recognition was achieved by comparison of X-ray powder diffraction data with those recorded for SIZ-4. The same results were reported for the dication 1,1′-dimethyl-3,3′hexamethylene-diimidazolium dibromide. Materials with this topology were designated SIZ-10a−e to differentiate them from SIZ-4 on the basis of the

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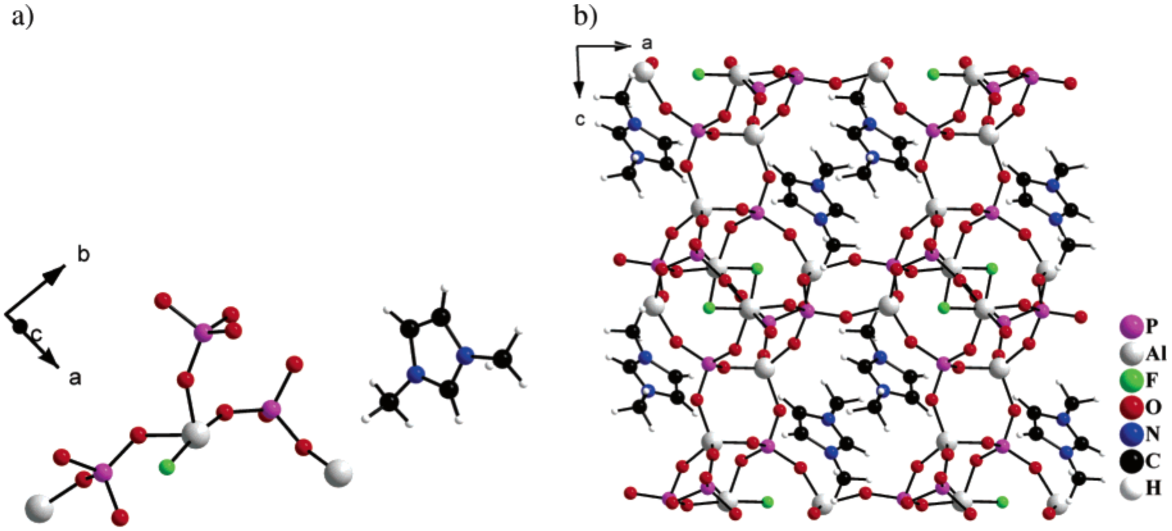

Figure 2. (a) Asymmetric unit of SIZ-10c. (b) Ball and stick diagram down the *b*-axis of SIZ-10c.

ionic liquid used (Table 1).

Single-crystal data were collected for a SIZ-10c crystal formed using PeMIBr as the solvent and SDA provider. The SDA was completely resolved (including the location of the hydrogen atoms; see Figure 2) and revealed to be the 1,3-dimethylimidazolium cation. Crystal data and structure refinement details for SIZ-10c are given in the Supporting Information. Data were also collected for a SIZ-10d crystal formed using 1,1′-dimethyl-3,3′hexamethylene-diimidazolium dibromide as the solvent and SDA provider. Again, the SDA was completely resolved, revealing the 1,3-dimethylimidazolium cation. Solid-state NMR experiments (below) confirm that all SIZ-10 structures contain the same SDA as SIZ-10c.

The asymmetric unit of SIZ-10c (Figure 2a) consists of three aluminum, three phosphorus, 12 oxygen, and one fluorine atom with one molecule of 1,3-dimethylimidazolium. The framework is negatively charged because of the presence of the fluorine atom, and the nitrogen atoms of the imidazolium cation are positioned at 3.31 and 4.86 Å from the nearest fluorine atom. The SIZ-10 CHA framework consists of double six-membered rings (D6Rs) of alternating aluminum and phosphorus tetrahedra. These are linked through four-membered rings to produce a three-dimensional pore structure with eight-membered ring windows (Figure 2b). Each six-membered ring of the D6Rs contains one octahedral aluminum that connects to another octahedral aluminum of another D6R through two bridging fluorines. This framework structure is the triclinic variation of the CHA topology, which on removal of the SDA and fluoride ion on calcination leaves a porous AlPO$_4$ CHA framework. This is, however, the first time this framework has been characterized with a 1,3-dimethylimidazolium SDA.

^{31}P, ^{27}Al, and ^{19}F MAS NMR were collected for the various SIZ-10 samples a−e made with the different ionic liquids. The results were comparable to those collected for SIZ-4 CHA, consistent with the single-crystal X-ray diffraction results that the topologies of the framework are equivalent. ^{13}C MAS NMR data were collected for the different SIZ-10 samples a−e to confirm the presence of the 1,3-dimethylimidazolium cation (Figure 3). From this data, it is possible to see that all the SIZ-10 samples have one intense peak in the region of 40 ppm from the methyl carbons, confirming the presence of the 1,3-dimethylimidazolium cation. This can be compared to SIZ-4 sample containing the 1-ethyl-3-methylimidazolium cation, which has three peaks in this region of the spectrum, one from the methyl carbon and two from the ethyl carbons. The peaks at about 130 ppm are from the imidazolium carbons and are present in all the spectra (these peaks are relatively weak in the SIZ10c (PeMIBr) material because of a small quantity of sample.

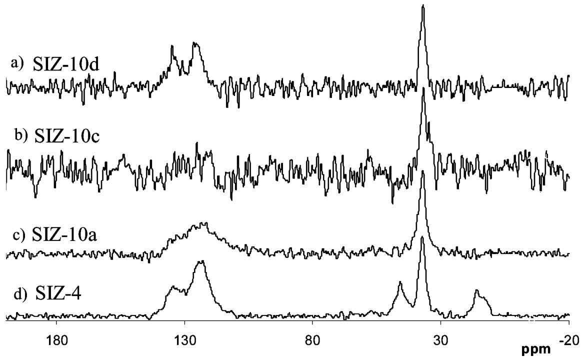

Figure 3. ^{13}C Solid-state NMR data for SIZ-10 and SIZ-4 samples synthesized using various imidazolium-based ionic liquids.

To investigate whether the bulk solvent ionic liquid was breaking up under the reaction conditions to form the 1,3-dimethylimidazolium cation, we repeated the AlPO syntheses and recovered the remaining solvent from the reaction mixture, and tested it by ^{1}H solution state NMR. Integration of the ^{1}H NMR signals for the dication ionic liquid and ionic liquids with alkyl chain lengths of 3, 4, and 5 carbons showed the bulk of the solvent to have stayed intact, indicating that the 1,3-dimethylimidazolium cation of the ionic liquid is only present in very small amounts.

1-isopropyl 3-methyl imidazolium bromide (*i*PrMIBr) was used to investigate the effect of ionic liquid alkyl chain branching on the AlPO structures formed. Without the addition of HF, SIZ-11 was formed, a material with the same topology as the material SIZ-6 prepared using EMIMBr. On addition of HF, the SIZ-10 AlPO-CHA framework was

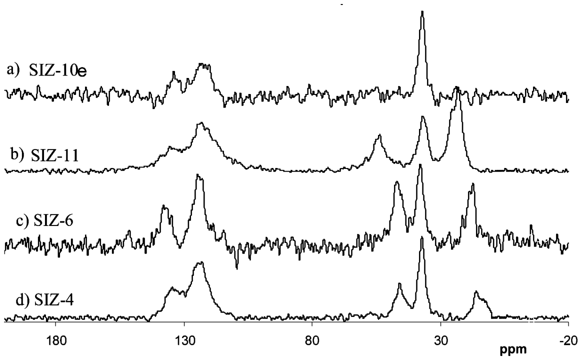

Figure 4. ^{13}C Solid-state NMR data for SIZ-10e and SIZ-11 synthesized using *i*PrMIBr and SIZ-4 and SIZ-6 using EMIBr.

formed. Phase recognition was achieved by comparing X-ray powder diffraction data with that recorded for SIZ-6 and SIZ-10.

In order to unambiguously identify the SDA, we collected ^{13}C MAS NMR data for the samples made with and without HF using the ionic liquid *i*PrMIBr. From Figure 4, it can clearly be seen that there are three peaks in the 15−50 ppm region for SIZ-4 and SIZ-6, which have previously been identified as the methyl and ethyl carbons from the 1-methyl-3-ethylimidazolium cation.[3,4] For the structure formed using *i*PrMIBr and no HF (SIZ-11), there are also three peaks, but these are consistent with the SDA being the 1-isopropyl 3-methyl imidazolium cation. With the addition of HF, there is only one peak in the 15−50 ppm region. This is the same ^{13}C MAS NMR spectra as that for the SIZ-10 materials, indicating that the ionic liquid solvent has again broken down on the addition of HF to form the 1,3-dimethylimidazolium cation. (The peaks at about 130 ppm are from the imidazolium carbons and are present in all the spectra.)

Figure 5 shows representative scanning electron micrographs for SIZ-10b, SIZ-10c, and SIZ-4. In general, the morphology of all the materials is similar, with rhomboid crystallite shapes often intergrown to form clusters of microcrystals. The one major difference between SIZ-4 (prepared using 1-ethyl-3-methyl imidazolium bromide) and SIZ-10 is that the latter tend to be rather larger, with maximum crystal dimensions in excess of 200 μm for SIZ-10b, compared to only 40−50 μm for SIZ-4. This may be a consequence of fewer nucleation sites and slower crystal growth when the SDA is formed slowly via the decomposition reactions, as opposed to the SIZ-4 case, in which the SDA is also the solvent and always in large excess.

Discussion

It is clear from both the single-crystal XRD and NMR results that the SDAs occluded in the SIZ-10 materials are not the original cations from the ionic liquid, but 1,3-dimethylimidazolium cation formed at some point in situ during the reaction process. It also appears that the addition of fluoride as a mineralizer seems to aid in the formation of this cation compared to reactions containing no fluoride, where either no materials are formed or materials (e.g., SIZ-11) are formed that occlude the original ionic liquid cation. The stability of ionic liquids is currently of great interest as it impacts their potential applications greatly. The thermal stability of imidazolium-based ionic liquids has recently been studied by Chowdhury and Thynell[35] using IR and ToF (time-of-flight) studies. They show that thermolysis leads to breakage of the *N*-alkyl bonds in these materials and that this reaction is susceptible to catalytic enhancement. It seems likely that in the presence of fluoride, some of the *N*-alkyl bonds in the imidazolium cations are also broken and reformed under ionothermal synthesis conditions, and that the 1,3-dimethylimidazolium cations are formed via a transalkylation of the alkyl groups. It may be that the cages in the CHA topology are too small to accommodate cations larger than the 1-ethyl-3-methyl imidazolium cations and that the formation of this framework is favorable only in the presence of either the 1,3-dimethylimdazolium or the 1-ethyl-3-methyl imidazolium cations. This would explain why the SIZ-10 and SIZ-4 structures are the only phases to be formed in the presence of fluoride.

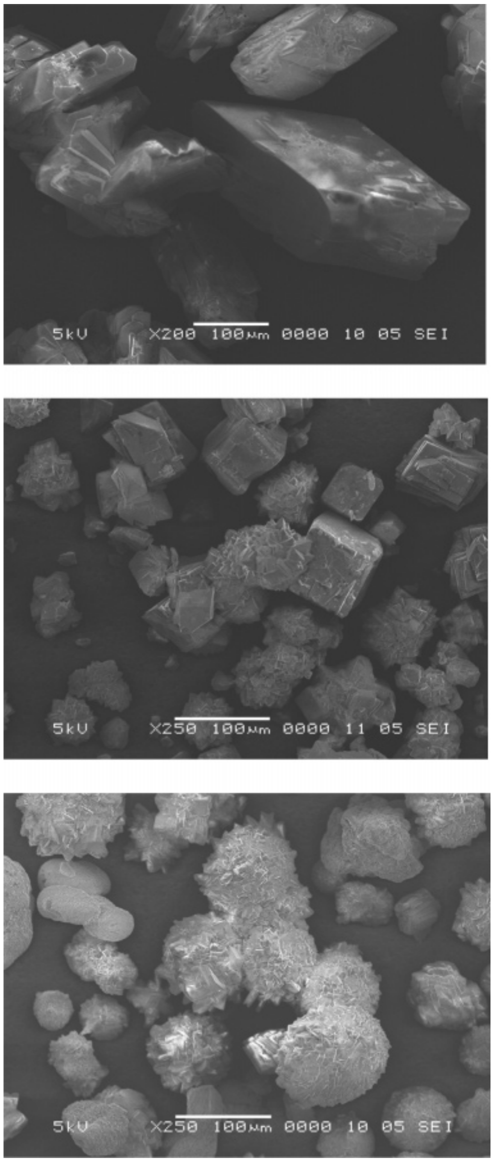

Figure 5. Representative SEM micrographs for SIZ-10b (top), SIZ-10c, and SIZ-4. Scale bars are 100 μm in all three cases.

A recent publication by Xu et al. reports the use of BMIBr as solvent and template in the microwave-enhanced synthesis

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(35) Chowdhury, A.; Thynell, S. T. *Thermochim. Acta* **2006**, *443*, 159.

of a mixture of AlPO-5 (AFI) and AlPO-11 (AEL) at ambient pressure.[7] These results have also been produced on the bench top in a round-bottom flask using an oil bath to heat the reaction.[11] The template in both structures is confirmed by ^{13}C MAS NMR to be the 1-butyl-3-methyl imidazolium cation. These reactions are carried out at generally higher temperatures (190−280 °C) for much shorter lengths of time (0.5−4 h) than we have used in our experiments. The appearance of larger pore frameworks such as AFI rather than CHA seems to be consistent with our thoughts that the 1-butyl-3-methyl imidazolium cation is too large to act as an SDA for the CHA framework.

AEL and AFI ALPO structures are, however, possible to form using BMIBr in an autoclave if reactions are carried out for shorter periods of time (4 h). On longer heating (4 days), the product formed was the SIZ-10 CHA. Experiments carried out to see the affects of heating the reactions in glass beakers for up to 4 days resulted in the synthesis of only AEL and AFI ALPO topologies. Most likely, this is due to the transalkylation reaction not being possible in an open vessel because any methyl bromide (boiling point = 4 °C) or butyl bromide (boiling point = 102 °C) produced on breaking of the *N*-alkyl bonds in the ionic liquid would escape from the reaction mixture through evaporation, making the production of the 1,3-methylimidazolium cation unlikely. However, in a sealed system, the 1,3-methylimidazolium cation is more likely to form.

It is apparent that despite the large number of ionic liquids available, they will not all necessarily produce new zeotype structures. The synthesis of zeolites is, in general, very sensitive to the various reaction conditions, including the type of reaction vessel used and the nature of the heat source. The framework topology CHA appears to be a default structure in the autoclave work, possibly due to a seeding effect occurring because of the porous nature of the Teflon liners. The fact that the SIZ-4 and SIZ-10 CHA frameworks have different templates points to the organic acting more as a space-filler than a structure directing agent according to the definition by Davis and Lobo.[36] The same is true of SIZ-6 and SIZ-11, for which the organic cation is 1-methyl-3-ethylimidazolium and 1-isopropyl-3-methylimidazolium, respectively. This work, however, does show some interesting findings about the effect of HF on ionothermal synthesis and extends the possibilities of the ionothermal synthesis method by adding further reaction variables such as quantity of HF added, type of reaction vessel, and choice of heating method.

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Supporting Information Available: Crystallographic information file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM0615929

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(36) Davis, M. E.; Lobo, R. F. *Chem. Mater.* **1992**, *4*, 756.