Zeolites

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A Rational Approach to the Ionothermal Synthesis of an $AlPO_4$ Molecular Sieve with an LTA-Type Framework[**]

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Dedicated to Yves Chauvin

The ionothermal synthesis of a zeolite in an ionic liquid (IL) presents significant practical advantages over the hydrothermal method as ILs have a negligible vapor pressure and high thermal stability.[1,2] Alkyl imidazolium ILs have already been successfully used to synthesize phosphate-based zeolites with framework types including AFI, AEL, CHA, LTA, and -CLO.[2–7] Herein we report a novel ionothermal route for the crystallization of phosphate-based LTA-type zeolite using 1-benzyl-3-methylimidazolium chloride ([BenzMIM]Cl). A rational synthesis protocol that exploits templates for the sodalite and α cages and takes charge balancing into account is presented. This approach is shown to confer stability to the crystallized LTA framework, which is then amenable to controlled calcination and evacuation of the micropores without deterioration of the structure.

Aluminosilicate zeolites and their aluminophosphate[8] and silicoaluminophosphate[9] analogues are highly efficient in molecular separation and heterogeneous catalysis. Accordingly, considerable efforts have been made to synthesize new framework types and to prepare known phases by alternative more convenient synthesis routes. The conventional hydrothermal method still is the major strategy for the synthesis of zeolites, and large majority of known zeolites have been prepared by using this technique.[10a,11] Amines and quaternary ammonium compounds act as structure-directing agents (SDAs) in hydrothermal crystallization to favor the formation of the desired zeolite.[12] In 2004, Cooper et al. reported pioneering work on the crystallization of zeolites in ILs with a technique termed "ionothermal synthesis".[2] The organic cations of the IL have been demonstrated to be efficient SDAs that often reside in the cavities of the synthesized zeolite.[3] The introduction of additional SDAs into the IL also was proven to be effective.[13]

The use of 1-ethyl-3-methylimidazolium bromide ([EMIM]Br) and 1-butyl-3-methylimidazolium bromide ([BMIM]Br) ionic liquids has been investigated in the area of zeolite synthesis. The synthesis of AEL and CHA phases was particularly successful when [EMIM]Br was used, while the use of [BMIM]Br favored the formation of AFI phases.[4] LTA-type $GaPO_4$ zeolite were first synthesized ionothermally using a deep eutectic mixture.[6] Recently, Han et al. reported a ionothermal synthesis protocol for LTA-type $AlPO_4$ and $GaPO_4$ zeolites in which [EMIM]Br serves as solvent as well as SDA.[5] [C_nMIM]Br ($n = 2$–6) ILs have also been used to crystallize ionothermally $GaPO_4$ molecular sieves with LTA and -CLO framework structures.[6] The LTA framework can be viewed as being composed of sodalite cages that are interconnected with D4R units to form large α cages. The formation and stabilization of cages must be a goal in the development of a suitable synthesis protocol. Such a strategy was successfully adopted in the original hydrothermal synthesis of $AlPO_4$-LTA materials where diethanolamine was found to be a template for the α cages of the structure.[14] Later efforts mainly employed crown ethers, especially Kryptofix 222 (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8.8.8]hexacosane), to direct the formation of α cages in LTA zeolite materials.[15–18]

Herein we report the use of [BenzMIM]Cl as an IL medium for the ionothermal synthesis of $AlPO_4$-LTA phases. [BenzMIM]Cl has excellent thermal stability under the applied reaction conditions (Table 1).[19] All reagents were readily soluble in [BenzMIM]Cl and a clear solution was obtained after a few minutes of mixing. [BenzMIM]Cl molecule also potentially presents attractive SDA properties. Molecular modeling studies (see the Supporting Information) suggested that the LTA structure can accommodate two $BenzMIM^+$ ions per α cage.

Table 1: Ionothermal synthesis studies.

Sample[a]	IL[b]/TMA/Al/P/F	Time [h]	Phase
IL-1	40:0:1:3:0.7	10	LTA
IL-2	40:0:1:3:0.7	15	LTA + AFI
IL-3	40:0:1:3:0.7	24	AFI
IL-4	40:0:1:3:0.0	10	Amorphous
IL-5	40:0.0833:1:1:0.7	10	LTA
IL-6	40:0.0833:1:1:0.7	24	LTA

[a] Crystallization at 160 °C in an open round-bottom flask. [b] [BenzMIM]Cl.

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The crystallization of a phase-pure $AlPO_4$-LTA was completed within 10 h (Table 1, IL-1). Upon further heating, the LTA phase was gradually converted into the AFI phase (Table 1, IL-2, IL-3). Successive transformation of zeolite phases in an order of increasing framework density (FD) and thermodynamic stability is a well-known phenomenon.[20] In previously reported ionothermal syntheses, transformation of $AlPO_4$-AFI phases into denser AEL phases was observed.[13] Here we observed the progressive conversion of the LTA phase (FD = 12.9 T/1000 Å^3)[21] into the more stable AFI phase (FD = 17.3 T/1000 Å^3).[21]

The typical faceted octahedral habit of LTA crystals was shown by scanning electron microscopy (SEM; see the Supporting Information). In SEM pictures of IL-2, the AFI crystals appeared as bundles of needles (see the Supporting Information). After 24 h, the transformation from LTA to AFI was completed (Table 1, IL-3). The important mineralizing and co-templating role of F^- ions has been already recognized in early efforts toward the preparation of $AlPO_4$-LTA phases.[14,15] The importance of F^- ions was also evident in this work: in the absence of fluoride ions (Table 1, IL-4), the product was amorphous.

The incorporation of $BenzMIM^+$ ions into the $AlPO_4$-LTA crystals of IL-1 was confirmed with ^{13}C MAS NMR spectroscopy (see the Supporting Information). Rietveld refinement of the XRD pattern (see the Supporting Information) confirmed the presence of approximately two $BenzMIM^+$ ions per α cage.[22] The $BenzMIM^+$ ion was refined as a freely moving rigid body, with the option to rotate rings along central bonds. The remaining electron density in the vicinity of the imidazolium ring was assigned to charge-compensating Cl^- ions. Refinement of the occupation of this site resulted in the same number of Cl^- ions as the $BenzMIM^+$ ions per unit cell. Rietveld refinement also indicated electron density in the sodalite cages, which could be interpreted as octahedra with bond lengths around 2 Å.

^{27}Al MAS NMR spectroscopy (Figure 1) revealed the presence of tetracoordinated Al ($\delta = 32.5$ ppm) as well as pentacoordinated Al ($\delta = 21$ ppm) and hexacoordinated Al ($\delta = -13$ ppm). The signal at 32.5 ppm was assigned to tetrahedrally coordinated framework $\{Al(PO)_4\}$ environments. The pentacoordination corresponds to framework Al atoms with a fifth ligand, which is most probably F^- ions. This coordination assignment is in agreement with the Rietveld refinement, where each D4R in the structure was found to be occupied by fluoride ions in proximity to a tetrahedral framework atom that was assumed to be Al. Hexacoordinated Al species in $AlPO_4$ give rise to broad signals around −13 ppm in the ^{27}Al MAS NMR spectrum.[14,15,23] Based on the Rietveld refinement this NMR signal was tentatively assigned to water coordinated Al octahedra as species occupying the sodalite units. The positive charge corresponding to the refined number of the Al^{3+} ions matched exactly the negative charge of the F^- ions present in the D4Rs. We believe that apart from charge compensation, the hexaaquo aluminum cations also contributed to the stabilization of the sodalite cages thus serving as an SDA.

Inspired by the hypothesis that an SDA specific for sodalite cages might be needed, we introduced tetramethylammonium (TMA) ions, which are known for their great affinity for sodalite cages, into the synthesis medium.[14,15,24] TMA^+ ions were added in a proportion of 1 TMA^+ ion per 12 Al atoms, thus corresponding to 1 TMA^+ ion per sodalite cage. TMABr was dissolved in [BenzMIM]Cl prior to the addition of the oxides and fluoride ions (Table 1, IL-5) and phase-pure $AlPO_4$-LTA was obtained. In the presence of TMA^+ ions, there was no successive transformation of the LTA into AFI phase as observed in absence of TMA^+ ions (Table 1, IL-6).

^{13}C Echo-MAS NMR spectroscopy (Figure 2) confirmed the presence of both TMA^+ and $BenzMIM^+$ ions in the sample IL-5. The multiplet centered at about 130 ppm corresponds to unsaturated aromatic carbon atoms on the benzene ring of BenzMIM as well as the unsaturated carbon atoms of the imidazolium structure. The triplet around 56 ppm corresponds to the CH_2 bridge between the imidazolium and benzene moieties, and the quadruplet around 37 ppm corresponds to the carbon atom of the methyl chain on the imidazolium ring. The quadruplet around 59 ppm was assigned to the CH_3 group of the TMA^+ ion. Quantification of both species based on the integration of their respective NMR signals (see the Supporting Information) revealed a molar ratio of approximately 2:1, which is consistent with the

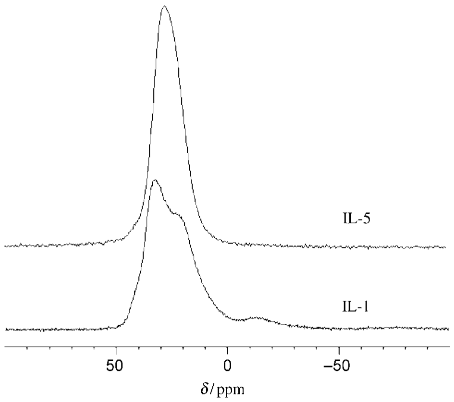

Figure 1. ^{27}Al MAS NMR spectrum (relative to $Al(NO_3)_3$) of AlPO4-LTA crystallized in [BenzMIM]Cl in the absence (IL-1) or presence (IL-5) of TMA^+ ions.

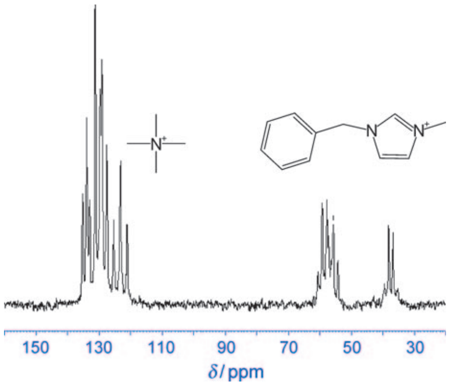

Figure 2. ^{13}C Echo-MAS NMR (relative to tetramethylsilane, TMS) of as-synthesized AlPO4-LTA crystallized in the presence of TMA (IL-5).

presence of two BenzMIM$^+$ ions per α cage and one TMA$^+$ ion per sodalite cage.

The single signal observed around 30 ppm in the ^{27}Al MAS NMR in IL-5 (Figure 1) showed that all the Al atoms were tetrahedrally coordinated. This result was consistent with our expectations that TMA replaced the hexacoordinated aluminum cations in the sodalite cages. Rietveld refinement of the XRD pattern revealed that electron density in the D4R units was no longer located close to the framework but rather in the middle of the D4R.[25] When this electron density was assigned to the F$^-$ ion, a site occupation of approximately 88 %, that is, 21 of the 24 available D4Rs in the unit cell, was calculated. The BenzMIM$^+$ ion occupation refined to 15.4 molecules per unit cell (comprising 8 α cages). The charge difference of −3, which resulted from the presence of 8 TMA$^+$, approximately 16 [BenzMIM]$^+$, and 21 F$^-$ ions was most probably compensated by Cl$^-$ ions in the α cages, but could not be refined. The observed, calculated, and difference profiles for the AlPO$_4$-LTA material IL-5 are shown in Figure 3 (see the inset of Figure 3 for the positions of the BenzMIM$^+$ and TMA$^+$ ions, and of the F$^-$ ions in the LTA structure). Only two of the many symmetry-equivalent positions of the BenzMIM$^+$ ions are shown. Chemical analysis revealed Al and P to be present in a an atomic ratio close to 1:1. C and N represented 13.72 wt % and 3.11 wt %, respectively of the dried LTA sample. Based on these values, as well as on the Rietveld refinement and NMR data, the idealized chemical formula of the AlPO$_4$-LTA material crystallized in [BenzMIM]Cl in the presence of TMA$^+$ and F$^-$ ions corresponded to $[(\mathrm{BenzMIM})_{16}\mathrm{TMA}_8\mathrm{F}_{24}\{\mathrm{Al}_{12}\mathrm{P}_{12}\mathrm{O}_{48}\}_8]$.

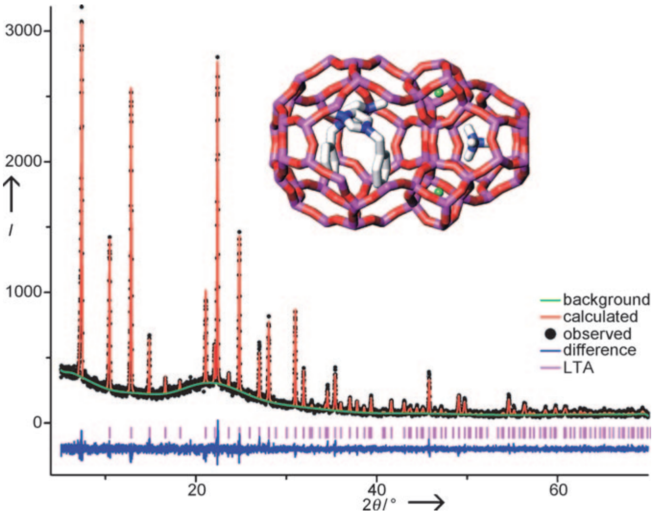

Figure 3. Observed, calculated, and difference XRD profiles of AlPO4-LTA synthesized in [BenzMIM]Cl in the presence of TMA$^+$ ions. The inset shows the refined positions of the [BenzMIM]$^+$ ions in the α cage, TMA$^+$ ions in the sodalite cage, and F$^-$ ions in D4R. C gray, N blue, O red, Al and P purple, F green.

Samples of AlPO$_4$-LTA have previously been reported to be unstable upon calcination, which removes organic molecules.[15] Calcination of IL-1 and IL-5 at 550 °C similarly resulted in partial amorphization, and ^{27}Al MAS NMR spectroscopy revealed severe framework deformation caused by coordinative bonding of adsorbed water molecules.[26] Thermogravimetric analysis (TGA) of AlPO$_4$-LTA sample crystallized ionothermally in presence of TMA$^+$ ions revealed that BenzMIM$^+$ ions can be removed prior to the removal of TMA$^+$ ions (see the Supporting Information). Sample IL-6, which contained BenzMIM$^+$ and TMA$^+$ ions, was calcined at 400 °C for 12 h to produce a stable TMA$^+$-containing LTA structure. The type I nitrogen adsorption isotherm of IL-6 was typical for a microporous material (Figure 4); the large micropore volume (0.23 mL g^{-1}) and high BET specific surface area (510 m^{2}g^{-1}) demonstrate the effective evacuation of the α cages. To the best of our knowledge, this is the first report of how micropores can be evacuated in an AlPO$_4$-LTA molecular sieve without damaging the structure. The aluminosilicate counterparts of AlPO$_4$-LTA, known as zeolite 3A, 4A, and 5A, are very important adsorbents and molecular sieves applied, for example, in drying operations and in separation of branched from straight-chain alkanes.[27] Likewise, the stable AlPO$_4$-LTA is expected to be useful in molecular sieve applications.

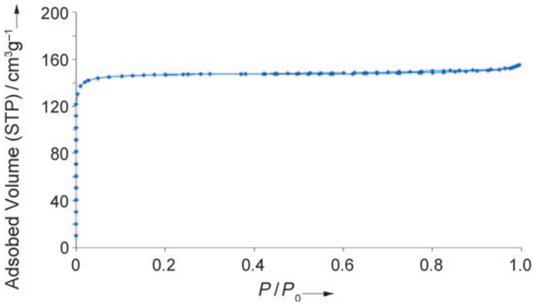

Figure 4. Nitrogen adsorption isotherm of AlPO$_4$-LTA zeolite IL-6 stabilized through TMA$^+$ ions in sodalite cages.

In conclusion, we have reported a novel ionothermal method for synthesizing AlPO$_4$-LTA zeolite in [BenzMIM]Cl. It has been shown that BenzMIM$^+$ ions reside in pairs in the α cage of the zeolite. The concept of a rational selection of a co-SDA for assisting the formation of the sodalite cages of the LTA structure was demonstrated. According to our hypotheses, a filling of α cages, sodalite cages, and D4R units with the BenzMIM$^+$, TMA$^+$, and F$^-$, respectively, was achieved. This work demonstrates how powerful the concepts of a co-SDA and charge balancing can be in the area of ionothermal AlPO$_4$ zeolite synthesis, and that the α-cages of AlPO$_4$-LTA framework could be evacuated while maintaining structural integrity.

Experimental Section

Inorganic oxides were obtained from commercial sources and used without purification. 1-benzyl-3-methylimidazolium chloride (Iolitec, 98 %, mp = 70 °C) was introduced into a 250 mL round-bottom flask and maintained at 100 °C. Al(O*i*Pr)$_3$ (98.28 %, Aldrich) was added to the IL melt at 100 °C, which was stirred for 10 min before addition of

H_3PO_4 (85 % in water, SDS) followed by HF (40 % in water, Carlo–Erba). The crystallization was interrupted by cooling the slurry to room temperature. The crystals were filtered on a Buchner funnel, and washed thoroughly with deionized water followed by acetone. The products were dried overnight at 100 °C.

Powder XRD patterns were collected on a Bruker D4 X-ray diffractometer with CuKα radiation at 40 kV and 40 mA and fitted with an energy discriminating detector. 2θ angles were scanned from 2° to 60° at a rate of $0.02^\circ\,s^{-1}$. XRD in transmission mode for Rietveld refinement was conducted on samples in 0.3 mm capillaries. The XRD patterns were collected on a PANalytical X-ray diffractometer equipped with a $Cu_{K\alpha1}$ source and position sensitive detector. The X-ray optics consisted of a parabolic mirror followed by a double-crystal monochromator. 2θ angles were scanned from 5° to 80° at a rate of 0.008°/step and 500 s/step. Rietveld refinement was performed using the GSAS software package based on the starting framework parameters provided by international zeolite association.[22,25,28,29] The ILs were introduced in the large cages using rigid bodies with freely rotating aromatic rings. Thermal parameters of the guest molecules were constrained.

^{13}C MAS and ^{27}Al MAS NMR spectra were recorded on a Bruker 400 MHz Avance instrument (9.4 T). The samples were loaded in 4 mm rotors and spun at the magic angle at 8 kHz for ^{13}C and 12 kHz for ^{27}Al. ^{13}C Echo MAS spectra were recorded with 2000 scans using a $\pi/2$ flip angle and a recycle delay of 30 s. ^{27}Al MAS spectra were collected with 4000 scans under selective and quantitative conditions using a $\pi/12$ flip angle and a recycle delay of 0.5 s.

Thermogravimetric analysis was performed on a TGA 851 Mettler thermobalance under a flow of air ($25\,mL\,min^{-1}$) up to 800 °C at $10\,°C\,min^{-1}$. Nitogen adsorption at −196 °C was performed on a Micrometrics ASAP 2000 analyzer. The samples were degassed under vacuum for 12 h at room temperature.

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