

Cooperative structure-directing effect in the synthesis of aluminophosphate molecular sieves in ionic liquids†

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In situ two-dimensional NMR and fluorescence emission spectroscopy were employed to investigate the cooperative structure-direction effect of organic amine such as morpholine in the synthesis of aluminophosphate molecular sieves in ionic liquids. *In situ* rotating frame nuclear Overhauser effect spectra (ROESY) together with fluorescence measurements demonstrate that the aggregates between imidazolium cations and morpholines through intermolecular hydrogen bonds can be formed in the gel during the crystallization of molecular sieves. Combining with the characterizations of the solid products by solid-state NMR, it is verified that different aggregates of organic amines with imidazolium cations, which is similar to self-assembled supramolecular analogues, could act as the structure-directing agents for selective tuning of the framework topologies such as AEL, AFI and LTA in the final solid products.

Introduction

The design and synthesis of new molecular sieves is still one of the major activities in materials science due to a wide range of practical applications such as catalysis and gas separation, *etc.*^{1,2} These materials can usually be made under hydrothermal or solvothermal conditions in which the organic amines are added as the structure-directing agents (SDAs).^{3–11} In some cases, two or more organic amines are needed in the synthesis of the desired structures.^{9–11} Despite a large number of organic amines with different sizes and shapes having been utilized, the choice as the structure-directing agents has almost invariably considered the features of single molecular units. Recently, a new concept in the use of self-assembled molecules as the structure-directing agents has been reported in the synthesis of molecular sieves by Corma *et al.*⁵ and Gómez-Hortigüela *et al.*^{7,8} Although some “*in situ*” spectroscopic studies have been reported,^{12–15} The mechanism of the structure-directing effect of organic amines during crystallization of molecular sieves has not been fully understood up to now. In recent years, Morris *et al.* developed a novel preparation method, termed as ionothermal synthesis, in which ionic liquids (ILs) or eutectic mixtures were used as both solvent and template.^{16,17} Unlike the conventional synthesis, ionothermal synthesis can be performed at ambient pressure due to the very weak vapor pressure of ILs, and is currently attracting great interest. To date, ionothermal synthesis has been used to prepare molecular

sieves, zeolite analogues, zeolite films, *etc.*^{16,18–31} Many of these structures are new, demonstrating the potential of this approach in the discovery of novel materials. In our previous studies, it was found that the addition of organic amines into ILs can alter the crystallization process of molecular sieves and result in better phase selectivity.^{27,31} This provides opportunities for addressing fundamental questions like the structure-directing mechanism of amines in the zeolite synthesis by *in situ* NMR spectroscopy and other techniques. In the present work, morpholine (Morp) organic amines with different contents have been added to imidazolium ionic liquids during the gel formation stage to understand the cooperative role of IL–organic amine hybrid in the selective synthesis of molecular sieves with different phases. *In situ* rotating frame nuclear Overhauser effect spectroscopy (ROESY) and fluorescence emission spectroscopy have been applied to investigate the intermolecular interactions between the 1-butyl-3-methyl-imidazolium bromide ([bmim]Br) IL and Morp during the crystallization of aluminophosphate molecular sieves. Combining with the characterizations of the final solid products by XRD and solid-state MAS NMR, the nature of the cooperative structure-directing effect has been revealed. Different hybrids of Morp with imidazolium cations connected through the hydrogen bond, which are similar to self-assembled supramolecular analogues, could act as the structure-directing agents for the formation of molecular sieves with different framework topologies.

Experimental

Sample preparation

The ionothermal synthesis of molecular sieves in ionic liquids was carried out in a close system according to our previous procedures.^{27,31} In general, AlPO₄-11(AEL structure), AlPO₄-5 (AFI structure) and AlPO₄-LTA (LTA structure) molecular

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† Electronic supplementary information (ESI) available: MAS NMR spectra of the pure phased AEL, AFI and LTA structures ²⁷Al MAS NMR spectra (Fig. S1); ³¹P MAS NMR spectra of the pure phased AEL, AFI and LTA structures (Fig. S2). See DOI: 10.1039/b920232n

sieves were prepared from the gel with a composition of 40[Bmim]Br : 1.0Al₂O₃ : 3.0P₂O₅ : 0.5HF : xMorp. Al(OPr_i)₃ (triisopropylate aluminium) and H₃PO₄ (85 wt%) were used as the sources of aluminium and phosphorus, respectively. Crystallization was performed at 423 K in an oil bath for 0.5–22 h. After cooling to room temperature, the products were washed with distilled water and ethanol, and dried at 393 K overnight. All samples were characterized by powder X-ray diffraction on a Rigaku D/Max-2500 diffractometer using Cu-K α radiation.

Solution and solid-state NMR spectroscopy measurements

All the solution NMR experiments were performed on a Bruker DRX-400 spectrometer using a DMSO capillary for the lock. ¹H NMR spectra were acquired at 400.13 MHz. The chemical shifts were referenced to tetramethyl silane (TMS). AlPO₄-11(AEL structure), AlPO₄-5 (AFI structure) and AlPO₄-LTA (LTA structure) zeolites with templates were dissolved in a 36% HCl solution at room temperature. When the solid samples were fully dissolved, the solution was collected and analyzed by liquid-state ¹³C NMR. Two-dimensional ROESY experiments were performed *in situ* on AIPO-AEL, AFI and LTA gels at 423 K for about 3.5 h in the TPPI phase-sensitive mode with 1 s recycle delay, 600 ms mixing time, 128 increments in *f*₁ field, and 96 scans per increment. The *in situ* ROESY NMR experiments collect a history of the AlPO₄ gel evolution, and mainly the species in solution could be detected.

The solid-state MAS NMR measurements were performed on the Varian Infinityplus-400 spectrometer equipped with a 4 mm MAS probe. ¹H → ¹³C CP/MAS NMR spectra were recorded at a spinning rate of 10 kHz with a contact time of 4 ms, a recycle delay of 4 s, and 2000 scans. The chemical shifts were referenced to adamantane with the upfield methine peak at 29.5 ppm. ²⁷Al MAS NMR spectra were collected at 104.2 MHz with a spinning rate of 10 kHz, 200 scans, and 2 s recycle delay. The chemical shifts were referenced to 1% Al(NO₃)₃ aqueous solution. ³¹P MAS NMR experiments with high power proton decoupling were conducted at 161.8 MHz with a spinning rate of 10 kHz and 4 s recycle delay. The chemical shifts were referenced to 85% H₃PO₄.

Fluorescence emission spectroscopy measurements

The AlPO₄ gels of molecular sieves were prepared at 423 K for 3 h, and then cooled down to room temperature for the fluorescence spectroscopy measurements. The fluorescence spectra were recorded on a Hitachi model F-4500 FL spectrophotometer with a xenon lamp as the excitation source. Both the excitation and emission slit width were 5.0 nm. The photomultiplier voltage was 700 V.

Results

In situ ROESY NMR and fluorescence spectra of the gel during crystallization

In our study, morpholine (Morp) was added as organic amine into the gel with ionic liquid [bmim]Br (Fig. 1) at 423 K. The imidazolium cation–cation interaction and cation–organic

amine interaction of the AlPO₄ gels with different molar ratios were studied by homonuclear Overhauser effect (NOE) in the rotating frame. According to our previous study,³¹ there is an obvious intermolecular interaction of imidazolium protons with organic amines in the mixtures of [bmim]Br and Morp. However, the *in situ* ¹H–¹H ROESY spectrum in Fig. 1a shows that neither the intermolecular cross peaks of imidazolium protons with Morp nor imidazolium cations–cations could be observed at 423 K for the AlPO₄ gel with 1Morp:60ILs. It seems that there are strong interactions of H₃PO₄ acid to protonate Morp amines at 423 K. The absence of cross peaks may be due to the charge repulsions between protonated amines and imidazolium cation at high temperature.³¹ Moreover, the excessive H₃PO₄ can also destroy the intermolecular interaction of imidazolium cations at 423 K. Under the same conditions but with higher Morp concentration, both Fig. 1b and 1c show significant intermolecular cross peaks of Morp protons (H-b and H-c) with imidazolium protons (H-6, H-7, H-8, H-9 and H-10). Meanwhile, the intermolecular interactions of imidazolium cations can also be observed. This may be due to the high concentration of Morp, one part may interact with H₃PO₄, the others may interact with imidazolium cations. The presence of cross peaks demonstrates the intermolecular distance between Morp and imidazolium cation is less than 4 Å in terms of the NOE principles.³² As for the ILs system, the presence of cross peaks in the ROESY spectra means a hydrogen bond formed.^{33,34} As a potential electron-pair donor, Morp may form a hydrogen bond with the imidazolium ring of ILs.²³ The specific hydrogen atom (H-2) of the imidazolium cation can be shared by the oxygen or nitrogen atom of Morp through the hydrogen bond because imidazolium ionic liquids are polymeric supramolecules, in which the strongest hydrogen bond involves the most acidic H-2 of the imidazolium cation.³⁵ Therefore, a hybrid structure of [bmim] cation with organic amine molecules connected through the intermolecular H-bond interactions is formed during crystallization with higher Morp contents, which is similar to the self-assembled supramolecular analogue.

The AlPO₄ gels obtained at 423 K for 3 h with different ratios of Morp to ILs were also studied by fluorescence emission spectroscopy. Fig. 2a, b and c exhibit the emission maximum shifting toward red with the variation of the excitation wavelength from 290 to 470 nm, these three AlPO₄ gels exhibit notably different fluorescence behaviors. This excitation-dependent emission behavior in ILs systems can be ascribed to the presence of various aggregates that are energetically different.^{36,37} As the excitation wavelength is increased, aggregates with different sizes and shapes may be excited.^{8,38–41} When the molar ratio of Morp to ILs is 1:60, it can be seen that the fluorescence emission maximum is at 411 nm with the excitation of 350 nm, and the fluorescence intensity decreases dramatically with the increase of excitation wavelength. Increasing the Morp/ILs ratio to 1:23, the emission maximum shifts to 421 nm which is independent of the excitation when λ_{ex} is lower than 350 nm. Further increasing the Morp/ILs ratio to 1:7, the emission maximum appears at 457 nm with excitation of 390 nm. Moreover, it should be noted that the relative

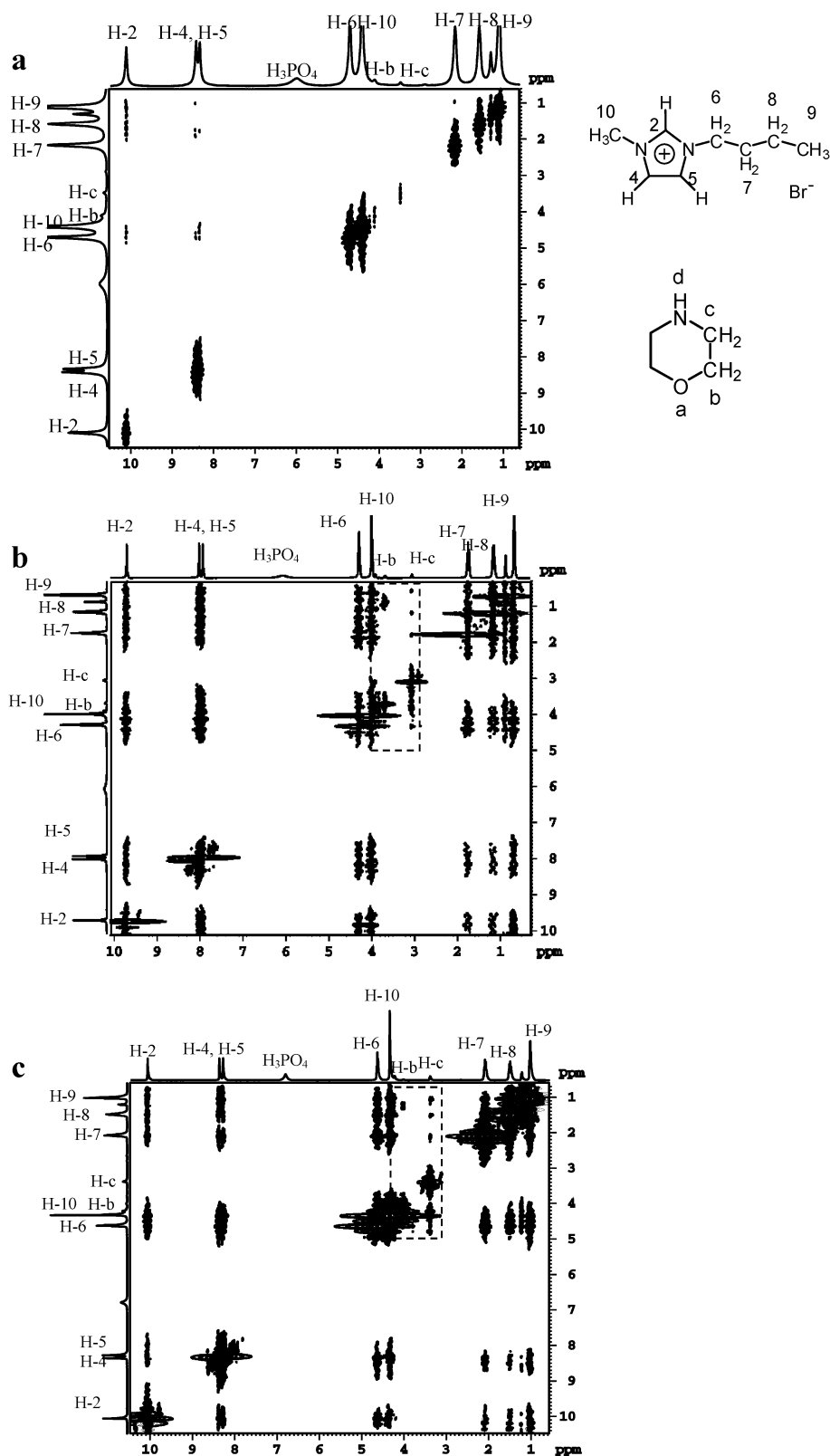


Fig. 1 *In situ* ^1H - ^1H NMR ROESY spectra of the AlPO_4 gel with the molar ratio of Morp to [bmim]Br (a) 1 : 60, (b) 1 : 23 and (c) 1 : 7. Each spectrum was acquired at 423 K with a mixing time of 600 ms. The C and H positions of morpholine and IL are marked.

fluorescence intensity increases at longer wavelength. So aggregation state changes with increasing Morp contents,

and larger aggregates may be formed in the AlPO_4 gels during crystallization.

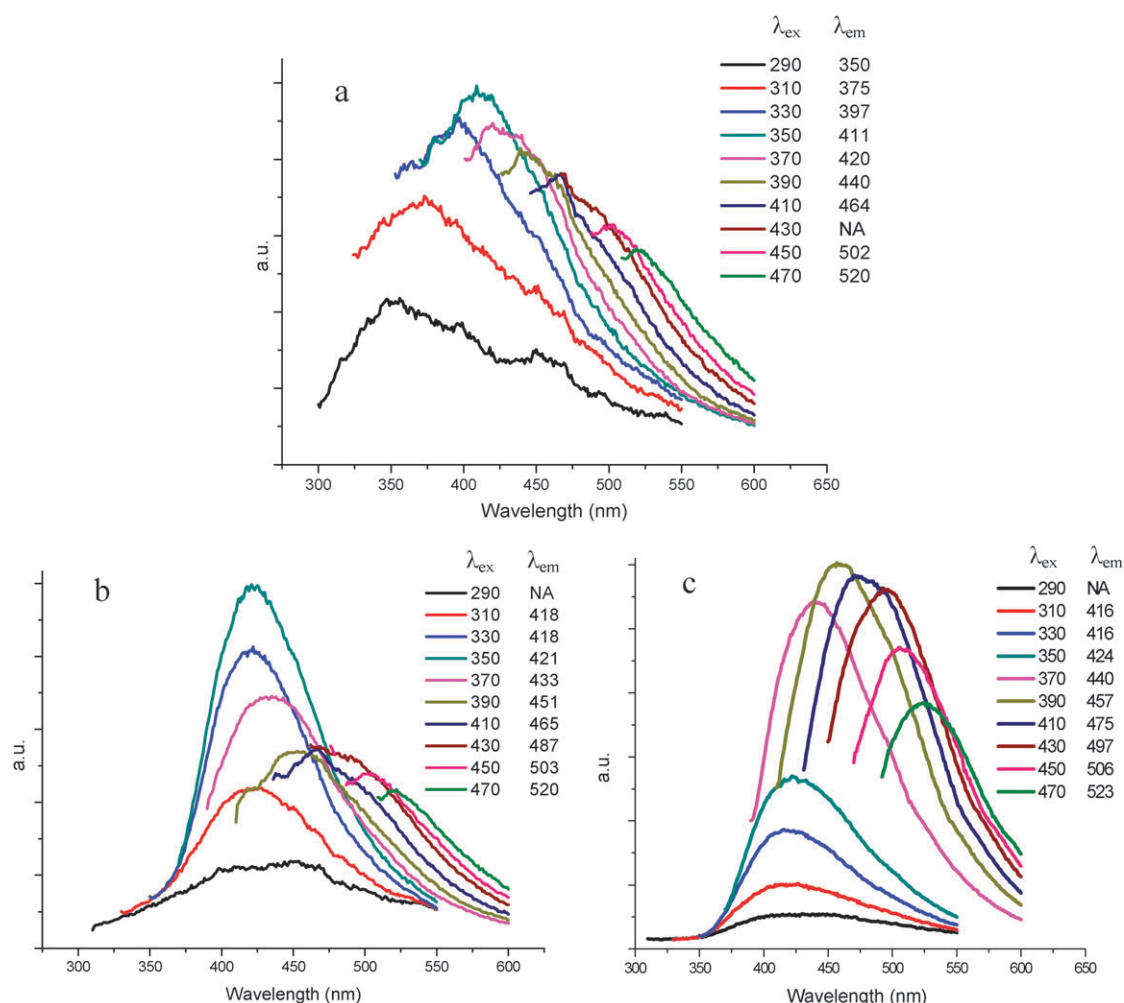


Fig. 2 Fluorescence emission spectra of the AlPO_4 gel with the molar ratio of Morp to $[\text{bmim}]\text{Br}$ at 423 K (a) 1 : 60, (b) 1 : 23 and (c) 1 : 7. Each spectrum was acquired with varied excitation wavelength (λ_{ex}) at 298 K.

Characterizations of the final solid products

Fig. 3 shows the XRD patterns of the final solid products synthesized with various contents of Morp to $[\text{bmim}]\text{Br}$. It is found that the framework topology changes with the increase of Morp amount. When the molar ratio of Morp to $[\text{bmim}]\text{Br}$ is 1 : 60, a pure phased AEL structure which contains a unidimensional channel system with 10-membered ring noncircular pores can be obtained.⁴² With increase of the molar ratio of Morp/ $[\text{bmim}]$ to 1 : 30, a major AEL structure with a minor AFI structure (12-membered ring) is obtained. With further increase of the molar ratio of Morp/ILs to 1 : 23, a pure phased AFI structure appears. When the Morp/ILs ratio reaches 1 : 7, a pure AlPO-LTA structure containing a 1.14 nm cavity is obtained. So, a controlled phase tuned by organic amine can be achieved with the change of Morp/ILs ratios. It is worth to note that the increase of the Morp content in ILs benefits the formation of molecular sieves with larger channels or cavities. The local structures of the resultant samples are also characterized by solid-state MAS NMR (ESI, Fig. S1–S2).† As for the pure phased AEL, AFI and LTA solids, nearly all the Al and P atoms are positioned in the zeolitic framework.

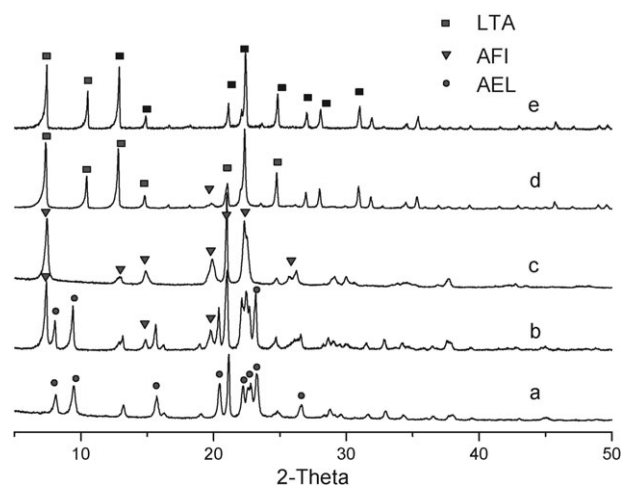


Fig. 3 XRD patterns of solid samples synthesized with different molar ratios of Morp to $[\text{bmim}]\text{Br}$, (a) 1 : 60, (b) 1 : 30, (c) 1 : 23, (d) 1 : 7.5 (e) 1 : 7. The crystallization time is 6 h at 423 K.

The state of the structure-directing agent inside the channels or cavities of the resultant molecular sieves can be detected by $^1\text{H} \rightarrow ^{13}\text{C}$ CP/MAS NMR spectra. In our study, the samples

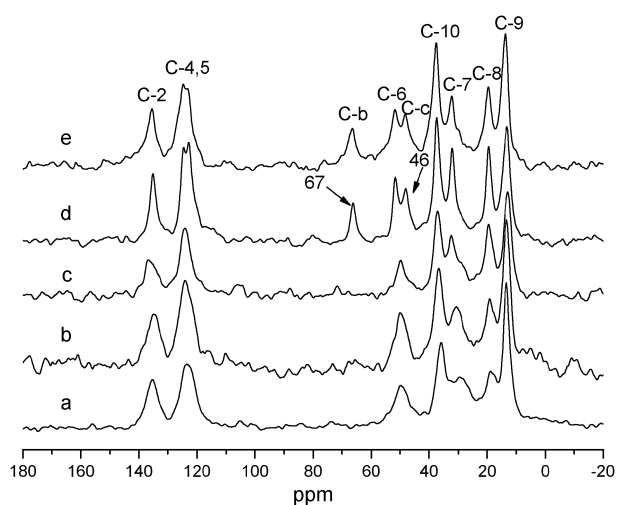


Fig. 4 $^1\text{H} \rightarrow ^{13}\text{C}$ CP/MAS NMR spectra of the solid samples with different Morp/[bmim]Br ratios (a) 1 : 60, (b) 1 : 30, (c) 1 : 23, (d) 1 : 7.5, (e) 1 : 7. The crystallization time is 6 h at 423 K.

were washed thoroughly with deionized water before drying to avoid the remaining ILs on the external surfaces. Fig. 4 shows the room-temperature $^1\text{H} \rightarrow ^{13}\text{C}$ CP/MAS NMR spectra of the solid products synthesized with different Morp/ILs ratios. As for the samples with AEL and/or AFI structure, each spectrum has almost the same feature, *i.e.* there is no new signal except for $[\text{bmim}]^+$. Two new signals at 46 and 67 ppm, which can be assigned to the Morp, are observed with the appearance of AlPO-LTA structure. In order to ascertain the occlusion of organic amines in the products, the resultant solid samples were dissolved with a concentrated HCl solution, and characterized by solution ^{13}C NMR techniques (Fig. 5). No new signal except for $[\text{bmim}]^+$ is observed for AEL samples. As for AFI and LTA samples, both Morp and imidazolium can be observed. So, the ^{13}C NMR results indicate that both $[\text{bmim}]$ cations and Morp are occluded in the channels of AFI and cavities of LTA molecular sieves while only ILs are restricted in the channels of AEL phase.

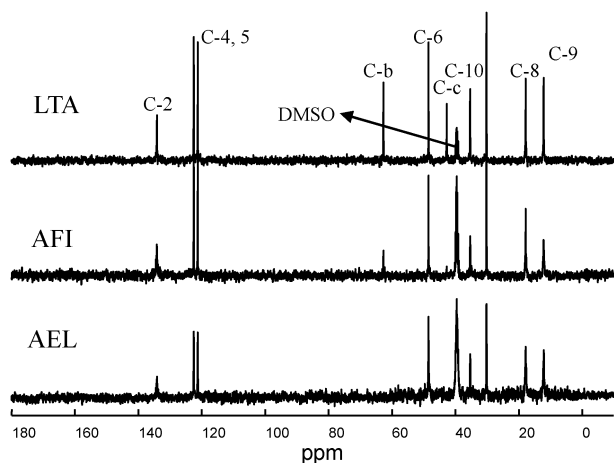


Fig. 5 Solution ^{13}C NMR spectra of solid AEL, AFI and LTA products dissolved in concentrated HCl solution, which was synthesized with different $[\text{bmim}]\text{Br}/\text{Morp}$ molar ratios.

In order to further reveal the cooperative structure-directing effect of organic amine, the typical crystallization process of AlPO-LTA zeolite is also studied. Fig. 6 exhibits the XRD patterns at different synthesis stages. With the preparation time up to 3.0 h the solid product shows the reflections identical to the LTA structure but less crystallinity. With further increasing the crystallization time, the diffraction intensity increases remarkably. Heating the gel for 22 h leads to complete AlPO_4 -LTA crystallines. The state of the structure-directing agent inside the LTA cavity can also be followed by $^1\text{H} \rightarrow ^{13}\text{C}$ CP/MAS NMR at different crystallization stages. As shown in Fig. 7, neither imidazolium cations nor Morp can be observed for the 0.5 h sample because of no zeolite product. As for the 3, 8, 16 and 22 h samples, all spectra have almost the same feature *i.e.* there are the signals of both Morp and $[\text{bmim}]^+$. This demonstrates that both $[\text{bmim}]^+$ cations and Morp are occluded in the cavity spaces of LTA zeolites. Therefore, combining the above *in situ* ROESY and $^1\text{H} \rightarrow ^{13}\text{C}$ CP/MAS NMR results may suggest that the hybrid of Morp with imidazolium cations intercalates into the gel as a structure-directing agent at the beginning of the crystallization process.

Discussion

From the above it is clear that in the ionothermal synthesis of aluminophosphate molecular sieves, the addition of morpholine in the $[\text{bmim}]\text{Br}$ ionic liquids has a great effect on the final framework topologies. With minor Morp, a pure phased AEL structure with 10-membered ring can be obtained. *In situ* $^1\text{H}-^1\text{H}$ ROESY spectrum shows that there are no intermolecular interactions of imidazolium protons with Morp at 423 K. It seems that a small amount of Morp may react with excessive H_3PO_4 during crystallization. Combining with the characterizations of the solid products by MAS NMR, it can be concluded that only the ionic liquids play the role of structure directing agents. With increasing the Morp/ILs ratio to 1 : 23, a pure phased AFI structure

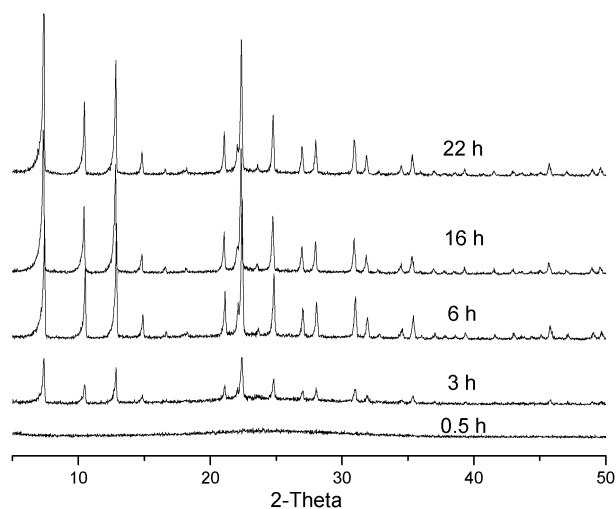


Fig. 6 XRD patterns of samples synthesized from a gel with a molar ratio of 1Morp:7[bmim]Br after a different crystallization time at 423 K.

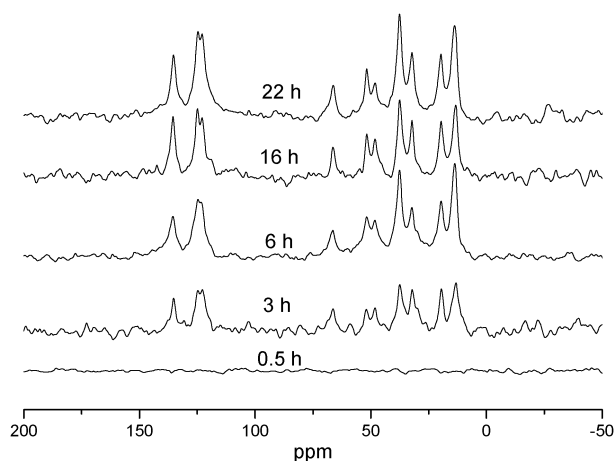


Fig. 7 $^1\text{H} \rightarrow ^{13}\text{C}$ CP/MAS NMR spectra of the samples synthesized from a gel with a molar ratio of 1Morp:7[bmim]Br after a different crystallization time at 423 K.

(12-membered ring, large-pore) is obtained. In this case a hybrid of an imidazolium cation with Morp is formed through the intermolecular H-bond during crystallization, as shown by an *in situ* $^1\text{H}-^1\text{H}$ ROESY experiment. However, there are no signals of Morp in the ^{13}C solid-state NMR spectrum. This may be due to the low content and/or the mobility of organic amines in the solids, while the solution ^{13}C NMR spectrum further confirms that there are minor Morp in the channel of AFI. A possible mechanism for the synthesis of the AFI structure is that a small amount of hybrid of imidazolium with morpholine as SDA provides the initial nucleation selectivity, then large imidazolium cations as the pore-filling agents for the crystal growth.³¹ With further increasing the Morp levels, a pure phased AIPO-LTA structure (large cage, 1.14 nm) is obtained. In general, as for the synthesis of pure-silica zeolite A and AIPO-LTA, it is necessary to utilize bulky organic structure-directing agents which can fit within the large cavity of LTA molecular sieves.^{5,43} In our case, the *in situ* ROESY NMR spectrum clearly indicates that a hybrid of an imidazolium cation with Morp is formed in the gel through the intermolecular H-bond during the crystallization process. For the solid products, both morpholine and imidazolium can be observed in the $^1\text{H}-^{13}\text{C}$ CP/MAS NMR spectra. So our results demonstrate that the hybrid of Morp with imidazolium through a hydrogen bond may act as the structure-directing agent for the AIPO-LTA molecular sieve. It has been reported that the size and shape of the organic guest molecules have an impact on the zeolite structure.⁴⁴ In our study, although the intermolecular interactions of Morp with imidazolium cations can be observed during the process of crystallization for the synthesis of AFI or LTA molecular sieves, the hybrid structures of imidazolium with Morp may be different. In comparison with the synthesis of AFI, we assume that a larger hybrid between the imidazolium cations and Morp could be formed during the crystallization with increasing the molar ratios of Morp to ILs, and the hybrid appears to direct the LTA structure. This is in general agreement with the fluorescence emission results, which demonstrate that larger aggregates are formed with increasing the Morp content in the

reaction mixtures. So, our findings provide evidence of the importance of SDAs in nucleation with regard to phase selectivity. Different aggregates of Morp with imidazolium cations similar to self-assembled supramolecular analogues formed in the gel could be employed as the cooperative structure-directing agents for selective tuning of the phase in the final solid products.

Conclusions

In summary, the effect of organic amine such as morpholine on the phase selectivity in the ionothermal synthesis of molecular sieves is discussed in detail. *In situ* two-dimensional ROESY NMR and fluorescence emission spectra show that different hybrids of morpholine with an imidazolium cation can be formed through the intermolecular hydrogen bond during the crystallization of aluminophosphate molecular sieves. $^1\text{H} \rightarrow ^{13}\text{C}$ CP/MAS NMR results clearly demonstrate that more morpholine was occluded with ILs in the channels or cavities of the final solid products when increasing its amount at the initial stage. Our findings show that the hybrids between morpholine and the imidazolium cation with different aggregates in the gel can act as the cooperative structure-directing agents for different framework topologies such as AEL, AFI and LTA in the final solids. This approach allows us to selectively tune the product phase through a rational control of the size of structure-directing agent in the AIPO₄ gel.

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