

Mixed template effect adjusted by amine concentration in ionothermal synthesis of molecular sieves†

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Cationic templating of imidazolium adjusted by the amine concentration in an ionothermal system results in products with larger channels or cage-like structures by reassembling the inorganic hosts around the changed organic guests.

Molecular sieves are solid crystals with ordered pores, usually synthesized through the assembling of host inorganic frameworks by guest organic species. Novel pore structures and the appropriate channel size for catalysis are the main pursuits in their synthesis field. To achieve these aims, researchers have focused much attention on guest species, such as designing the size and geometry of the template,¹ using mixed templates to interact with frameworks² or using supramolecular assembling of organic structure directing agents (SDA).^{3–5} These methods have inspired us to develop a simpler route to control the synthesis of molecular sieves.

Ionothermal synthesis⁶ using an ionic liquid⁷ as both the solvent and template to prepare molecular sieves, is a promising method in terms of synthesis^{8–9} and mechanistic studies.¹⁰ Its unique solvent property could be suitable for many new applications, such as, microwave assisted ionothermal synthesis.^{11–12} Our previous work studied the structure directing role of various organic amines in an ionothermal system.^{13–14} The focus of this current study is to investigate the tuning effect of the organic amine's concentration on the geometric size of the mixed templates of the amine and the cations of the ionic liquids, as well as on the structure of the molecular sieve products. We obtained products of a less framework density (FD) structure when increasing the amount of amine added through reassembling of the host materials around the amine-adjusted guests.

Experiments were carried out in an open system with stirring.† Detailed crystallization information in 1-butyl-3-methyl imidazolium bromide ([BMIm]Br) is listed in Table 1. The effect of *n*-DPA concentration (molar ratio to IL) on the crystal products is illustrated in Fig. 1, and XRD patterns are compared with ref. 15. In the absence of amine, the product of the initial gel is AlPO₄-11 (AEL, 10 MR, FD is 19.1 T/1000 Å³, 6.5 × 4.0 Å in size), whereas, the addition of amine will change the crystal product. AlPO₄-5 (AFI, 12 MR, FD is 17.3 T/1000 Å³, 7.3 × 7.3 Å) is formed when the amount of *n*-DPA reaches 0.033 (molar ratio to [BMIm]Br,

Table 1 Detailed synthesis information using organic amine to adjust the cationic templating of imidazolium^a

Experiment	Organic additives	Molar ratio to IL	Products	<i>t</i> /h	<i>T</i> /°C
B-1	None	0	AEL	4	160
B-2	<i>n</i> -DPA	0.022	AFI, AEL	4	160
B-3	<i>n</i> -DPA	0.033	AFI	4	160
B-4	<i>n</i> -DPA	0.053	LTA, AFI	4	160
B-5	<i>n</i> -DPA	0.086	LTA	4	160
B-6	<i>n</i> -BA	0.145	LTA	12	160
B-7	TriBA	0.056	LTA	4	160
B-8	DEA	0.075	LTA	8	160
B-9	CHA	0.059	LTA	4	160
B-10	HMTA	0.052	LTA	16	160
B-11	Imidazole	0.075	LTA	4	160
B-12	Pyridine	0.054	LTA	4	160

^a Gel composition (7.37 IL : 1.01 H₃PO₄ : Al(O₂Pr)₃ : 1.07 HF); *n*-DPA, *n*-dipropyl amine; *n*-BA, *n*-butylamine; TriBA, tributylamine; DEA, diethyl amine; CHA, cyclohexanamine; HMTA, hexamethylenetetraamine.

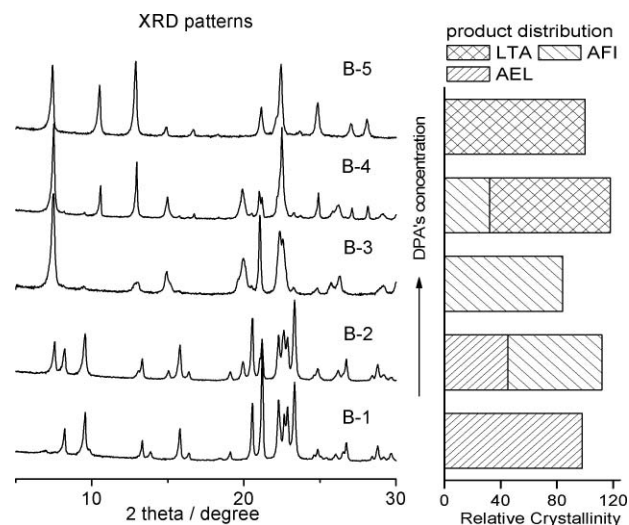


Fig. 1 XRD patterns of products and their relative crystallinity (RC) versus concentration of *n*-DPA in [BMIm]Br system (RC on the right is calculated by the area of their main peaks area in XRD patterns).

the same below); furthermore, AlPO₄-42 (LTA, 8 MR, FD is 12.9 T/1000 Å³, 4.1 × 4.1 Å) with *lta* cage is well crystallized when the amount of *n*-DPA is increased to 0.086. The transit of products above occurs gradually. For instance, AFI exists simultaneously with AEL in B-2 (*n*-DPA is 0.022) and a mixture of LTA and AFI is the product of B-4 (*n*-DPA is 0.053).

From 10 MR AEL to 12 MR channel AFI, and then to LTA with α cages, the products change when the concentration of

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n-DPA is increased. The mass loss caused by decomposition increases gradually according to their TG analysis in air (see ESI,† S4), which quantitatively shows that the amount of organic compounds occluded in three pure products increases. This indicates that the amine makes the frameworks more open and less dense. Compounds occluded in the pores are imidazolium cations together with the amine, which can be concluded by FT-IR and ¹³C NMR spectra. For example, imidazole or pyridine exist together with imidazolium cations in the pores of LTA sample B-11 and B-12 (see spectra with marked symbol in Fig. 2; IR and NMR spectra of *n*-DPA overlaps with that of the imidazolium cation). Other amines introduced to the system can also result in the formation of LTA structure despite the different size, type or shape (see Table 1 and ESI S3†), which implies the cooperative structure direction of the amine is closely related to the aggregated state of the mixed template.

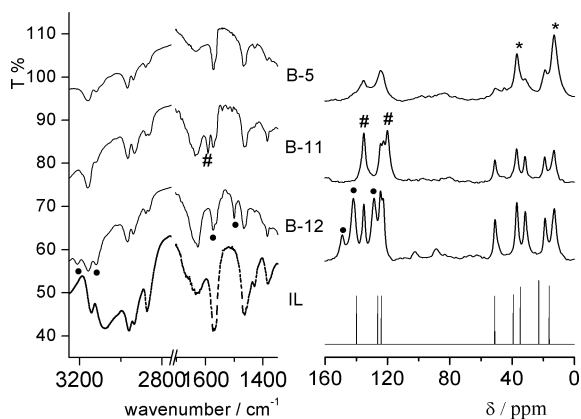


Fig. 2 FTIR and ¹³C CP MAS NMR spectra of as-synthesized LTA samples and neat [BMIm]Br ionic liquids (peaks marked with *, # and • are caused by *n*-DPA, imidazole and pyridine respectively).

Protonated organic amines often act as guest species in either hydrothermal¹⁶ or solvothermal synthesis.¹⁷ Lobo *et al.* have elucidated the effect of guest materials as space fillers, true templates and/or structure directing agents,¹⁸⁻¹⁹ whereas in an ionothermal system, hydrogen bond interactions between the amine and imidazolium is vital to the structure directing of certain frameworks.¹³⁻¹⁴ Lin *et al.* also reported that the hydrogen bond direction of organic amines and ligands in ionic liquids could control and construct metal coordination polymers.²⁰ Therefore, the geometric size of the mixed template could be adjusted by

changing the concentration of amine. Subsequently, inorganic frameworks reassemble around these aggregated guest species, and then products with different topologies are formed, as depicted in Fig. 3.

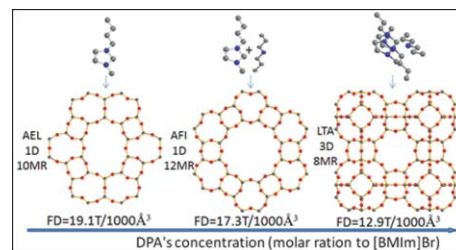


Fig. 3 Product change illustration of a mixed template adjusted by amine concentration in the ionothermal synthesis of molecular sieves (FD of AEL, AFI and LTA is 19.1, 17.3 and 12.9, respectively).

When a small quantity of *n*-DPA is introduced in an ionothermal system, the hybrids of the amine and imidazolium cation promote the nucleation of the products with a larger channel, and AFI with a straight channel of 12 MR crystallizes. The π - π stacking of aromatic ring cations,²¹⁻²² or the zigzag chain-like connecting mode of the imidazolium cations²³ may be the main reason leading to products with one dimension cylindrical structures. Therefore the stick-like samples are easy to obtain in this system (see Fig. 4(A) and (B)).

Whereas ionic liquids with concentrated *n*-DPA would rearrange its internal order to accommodate introduced molecules, the hydrogen bond interactions between the amine and imidazolium cations will facilitate the forming of an aggregated larger cationic complex as a supramolecular inclusion complex or as liquid clathrates as described in ref. 23 and 24. The AlPO₄-LTA structure was directed by macro-ring molecules (kryptofix 222) hydrothermally in the presence of fluoride;²⁵⁻²⁶ and supramolecular self-assembling of a quinolinium derivative led to pure silica LTA ITQ-29.³ In this case, it is rational to generate cage-like structures due to the existence of both aggregated organic complexes. Also, the fluoride synthesis media will facilitate the formation of a ring-like unit, because F⁻ ions tend to reside inside small cages.²⁷⁻²⁸ The occurrence of a peak at -19 ppm in ³¹P NMR spectra of B-5 can prove the interaction of P with F⁻ ions in D4R unit (see ESI,† Fig. S5). These units will be organized to form *sod* cages or *lta* cages around the aggregated cationic complex. This is a typical example of adjusting inorganic species to form cages and fit the

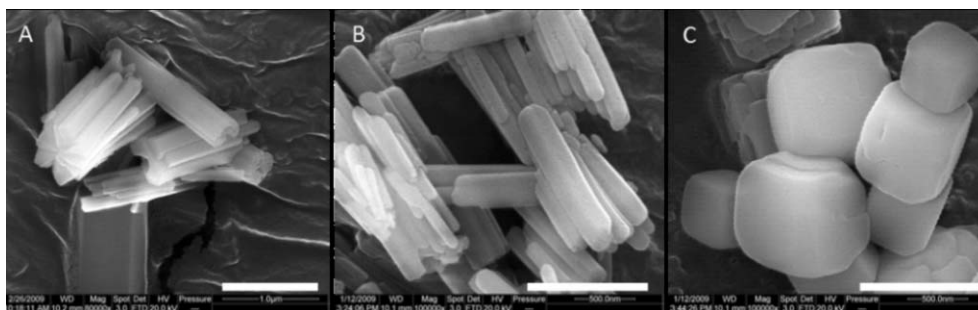


Fig. 4 SEM images of products crystallized using a mixed template adjusted by amine in a [BMIm]Br system (A, B and C: AEL, AFI and LTA sample (B-1, B-3 and B-5), respectively). White scale bar is 1.0 µm.

geometry of the template as mentioned in ref. 29. SEM images show that the LTA sample grains are cubic instead of stick-like AEL or AFI (see Fig. 4(C)).

The structural transition from AFI to LTA is not abrupt from the crystallographic point of view. They have equal maximal interplanar spacing, containing the same link unit such as 6R and 4R, only with different space configuration. A folded link unit forms a cage-like structure due to the adaptation to the aggregated supramolecular complex. The structure directing adjusted by amine concentration enriches the topology of the final product possibly formed ionothermally.

In summary, as an additional synthesis variable, the concentration of amine can change the aggregated state and the geometric dimension of the mixed template. Inorganic materials reassemble and adapt to the adjustable guest species, resulting in an enlargement of straight channel or a conversion to cage-like structure in the crystal product. An ionic liquid is a designable solvent, and many eutectic mixtures have similar properties to it. We hope that novel frameworks can be obtained based on amine adjusted templating in other ionothermal systems containing various cations.

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Notes and references

‡ Typical synthesis procedure: a 100 mL beaker was charged with [BMIm]Br (30 g, 137 mmol), then the following were added under vigorous stirring: H₃PO₄ (2.15 g, 18.6 mmol, 85 wt% in water), Al[OCH(CH₃)₂]₃ (3.80 g, 18.6 mmol), and hydrofluoric acid (0.5 g, 20.0 mol, 40 wt% in water). Organic amine was added if required according to a certain ratio. The beaker was then moved into an oil bath for crystallization at the target temperature. The crystallization was ceased at different times, and cooled to room temperature. The products were washed thoroughly with distilled water and acetone, then dried at 110 °C for further characterization. Ionic liquid used as solvent was prepared from *N*-methylimidazole and butyl bromide or propyl bromide as described in ref. 7.

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