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Ionothermal synthesis of $AlPO_4$ molecular sieves in the presence of quaternary ammonium cation

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ABSTRACT

Several aluminophosphate molecular sieves were synthesized ionothermally, in ionic liquid 1-butyl-3-methyl imidazolium bromide ([BMIm]Br) with adding various quaternary ammonium cation (quats, including tetramethyl ammonium (TMA^+), choline, tetraethyl ammonium (TEA^+), tetrapropyl ammonium (TPA^+) and tetrabutyl ammonium (TBA^+)). These products were characterized by X-ray diffraction (XRD), ^{13}C nuclear magnetic resonance (NMR) and scanning electron microscope (SEM). The result indicates that the crystallization pathway is changed by adding these quats. $AlPO_4$-42 (IZA code LTA) crystallizes when TMA^+ is added in the system, $AlPO_4$-5 (AFI) crystallizes when choline or TEA^+ is added, and the $AlPO_4$-11 (AEL) crystallizes when TPA^+ or TBA^+ is added. ^{13}C NMR analysis indicates that these introduced quats may either replace the $[BMIm]^+$ to act as template alone, or direct structures cooperatively with the $[BMIm]^+$, or in some cases they cannot change the original structure directing effect of $[BMIm]^+$.

1. Introduction

Molecular sieves are attractive materials due to their wide applications [1]. The synthesis of such materials with desirable architecture is becoming increasingly important [2]. Ionothermal synthesis [3], using an ionic liquid as both solvent and template to synthesize molecular sieves, has been gaining great interest in terms of preparing novel materials [4–6] and studying the crystallization mechanism [7].

Quaternary ammonium cation (quats) is a kind of good structure directing agent because of their positive charge and suitable dimensional size [8]. They could influence the arrangement of oxide tetrahedra around themselves so as to make certain host frameworks form easily [9]. But the understanding of the structure direction of cationic template is not very clear, nor are the factors affecting them, since the disturbance of solvent in traditional synthesis system is not conducive to study these issues. Notably, the synthesis carried out in ionothermal system can eliminate the solvent disturbance [10], which makes it easy to evaluate the factors affecting the structure directing effect of the cationic template. Moreover, in ionothermal system, the introduced amine plays a cooperative structure directing role together with the cation of ionic liquid [11–14]. In the work, we synthesized molecular sieves ionothermally in [BMIm]Br ionic liquid with the presence of several quats as a second cationic template, so as to compare their influences on the structure directing effect of the original system. The factors affecting the crystallization is discussed on the basis of the characterization of the crystal products synthesized using these quats.

2. Experimental

2.1. Ionic liquid

1-butyl-3-methyl imidazolium bromide ([BMIm]Br), was prepared by neutralization of redistilled N-methyl imidazole (99.9%, Kaile Chemical Factory, Zhejiang China) and butyl bromide (AR, Sinopharm Chemical Reagent Co., Ltd.) according to the procedure reported in Ref. [15].

2.2. Synthesis

All commercially available reagents (AR) were used without further purification. The synthesis experiment was carried out in an open 50 ml beaker charged with 30 g [BMIm]Br as solvent. Then the following materials were added under vigorous stirring: phosphoric acid (H_3PO_4, 85 wt.% in water), aluminium isopropoxide ($Al[OCH(CH_3)_2]_3$), hydrofluoride acid (HF, 40 wt.% in water) and various quats, detailed synthesis information and the reactant ratios were listed in Table 1. Quats additives include TMAOH (tetramethyl ammonium hydroxide), ChCl (choline chloride), TEAC (tetraethyl ammonium chloride), TPAB (tetrapropyl ammonium bromide) and TBAB (tetrabutyl ammonium bromide). Then the beaker was moved into an oil bath at 160 °C for crystallization. The reaction was ceased by quench to room temperature after crystallization. The crystal product

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Table 1
Crystallization information for molecular sieves synthesis in [BMIm]Br ionic liquid.

Entry	Batch composition[a]	IL	Secondary template	Molar ratio to Al	Time/h
IL-0	7.35:1.00:1.00:1.08	[BMIm]Br	–	–	4
IL-1	7.35:1.00:1.00:1.08	[BMIm]Br	TMA^+	0.63	2
IL-2	7.35:1.00:1.00:1.08	[BMIm]Br	$Choline^+$	1.07	10
IL-3	7.35:1.00:1.00:1.08	[BMIm]Br	TEA^+	0.41	2
IL-4[b]	7.35:1.00:1.00:1.08	[BMIm]Br	*n*-DPA	0.24	4
IL-5	7.35:1.00:1.00:1.08	[BMIm]Br	TPA^+	0.41	8
IL-6	7.35:1.00:1.00:1.08	[BMIm]Br	TBA^+	0.41	8

[a] IL: Al: P: F(molar ratio).

[b] Same gel to prepare AFI as Ref. [13].

was washed thoroughly with distilled water and acetone, respectively, then dried at 110 °C for other characterization.

2.3. Characterizations

Powder X-ray diffractions analysis of the as-synthesized samples were performed on a PANalytical X′Pert PRO diffractometer fitted with Cu Kα radiation ($\lambda = 1.5418$ Å) operating at 40 mA and 40 kV. The FT-IR spectra were recorded on a Perkin Elmer spectrum GX spectrometer by 10 mm potassium bromide pellet. Number of scan was 64 and interval is 1 cm^{-1}. The thermal behavior was investigated with Perkin Elmer Pyris 1 TGA instrument, using dynamic dry air, with a flow rate of 20 ml min^{-1}. The selected heating rate was 20 °C min^{-1} and temperature range was 30 to 850 °C. ^{13}C CP/MAS NMR measurements were performed on a Varian Infinity plus-400 spectrometer. Scanning electron microscopy (SEM) was carried out on Hitachi S4800 field-emission scanning electron microscopes or Phenom scanning electron microscope (FEI Electron Optics).

3. Results and discussion

The XRD patterns of as-synthesized products in [BMIm]Br system with adding various quats are shown in Fig. 1. As can be seen, $AlPO_4$-42 (LTA) with sodalite cage crystallizes when TMA^+ is added, and AlPO4-11 (AEL) crystallizes when TPA^+ or TBA^+ is added into the system. In fact, $AlPO_4$-11 (AEL) can be generated in the system without any organic additives [13], i.e., TPA^+ or TBA^+ does not change the original product. In addition, $AlPO_4$-5 (AFI) crystallizes when $choline^+$ or TEA^+ is added in the system. This topology was also obtained when using *n*-DPA as additives [11,13]. We denote these products as AFI–TEA, AFI–choline and AFI–DPA on behalf of the additive used for synthesis. Although they have the same topology, these products are different in their diffraction patterns, and the peaks thereof are split for the case of AFI–DPA, especially at 2θ angles of 13.2, 20.0, 22.5, and 26.0° versus that of AFI–TEA. Moreover, the case of AFI–choline is similar to AFI–DPA except some AEL impurity. Actually, AFI–TEA is hexagonal phase whereas AFI–choline and AFI–DPA are orthorhombic, hence the discrepancy of lattice symmetry leads to these splits. Possibly, the organic molecules occluded in their pores could be able to explain the problem.

The ^{13}C CP MAS NMR spectra of $AlPO_4$-42 (TMA^+ as additive) and $AlPO_4$-5 (AFI–choline, AFI–TEA and AFI–DPA) are shown in Fig. 2, which can give accurate information about the occluded molecules in the pores. As can be seen, the orthorhombic AFI (AFI–choline and AFI–DPA) and LTA sample occlude mainly $[BMIm]^+$ (see Fig. 3A, B and D). In these cases, the peaks at 140 and 126 ppm are attributed to carbon atoms on rings (two adjacent carbons are overlapped). Meanwhile, the other five peaks of the substituted chain can also be recognized clearly. As for the hexagonal AFI sample, its ^{13}C NMR spectra clearly shows that it is TEA^+ in the pore, with two equal peaks attributed to the ethyl group. The differences in the C-H vibration bands in infrared spectra of TEA^+ from that of $[BMIm]^+$ in the channel could also

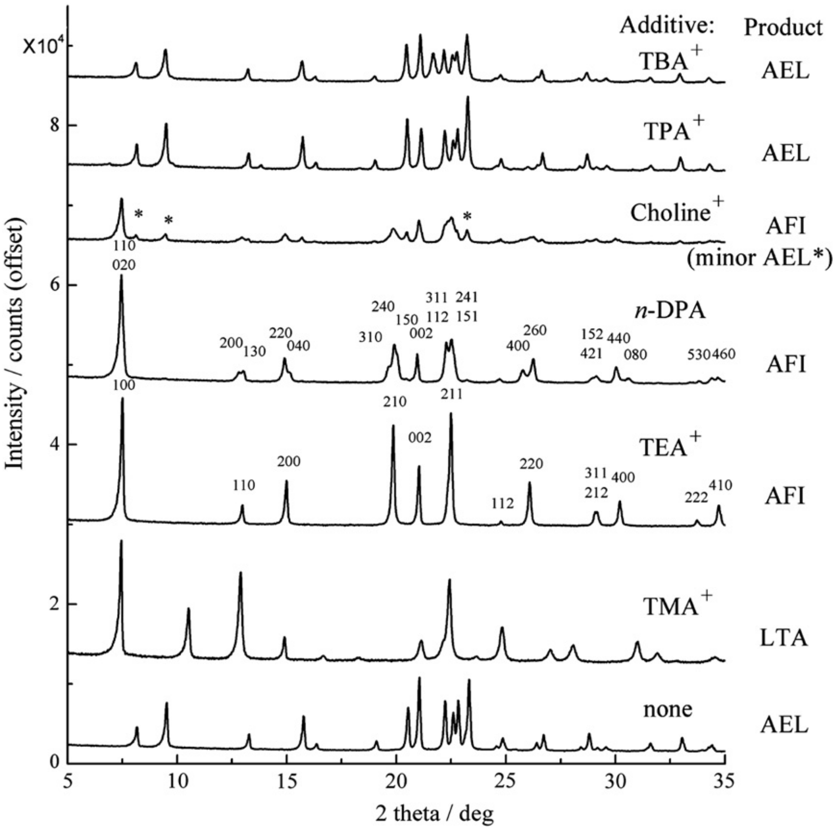

Fig. 1. XRD patterns of as-synthesized products in [BMIm]Br system in the presence of various quats cation as additives.