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Ionothermal approach for synthesizing AlPO-5 with hexagonal thin-plate morphology influenced by various parameters at ambient pressure

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ABSTRACT

Pure and crystalline AlPO-5 with hexagonal thin-plate morphology was synthesized ionothermally in 1-ethyl-2,3-dimethylimidazolium bromide ([edmim]Br) ionic liquid as both the solvent and structure-directing agent (SDA). The resulting microcrystalline solids were characterized using various techniques. Further studies on the influence of chemical compositions and synthesis conditions in the crystallization process of AlPO-5 were also investigated. The results showed that AlPO-5 crystals with hexagonal thin-plate morphology were obtained when [edmim]Br ionic liquid was used in ionothermal treatment. The crystallinity, size and morphology of the AlPO-5 materials were also found to be strongly influenced by two major factors, chemical composition of the gel mixture and the heating time of the gel mixture.

1. Introduction

In recent years, the study of microporous aluminophosphates (AlPO-*n*) materials has opened up remarkable routes in designing new materials for adsorption, catalysis, membrane, sensor, etc. [1–3]. These materials were first reported by Wilson et al., in 1982 and since then extensive researches had been carried out leading to the synthesis of various AlPO-*n* type materials with interesting topologies and properties [4–6]. This initiative was made possible using a variety of organic structure-directing agent (SDA) such as dialkylamines, trialkylamines and quaternary ammonium salts (e.g. TMAOH, TEAOH and TPAOH) [7–10]. In this new family of microporous materials, the AlPO-5 molecular sieve with AFI topology has been most extensively studied due to its large pore (7.3 Å) and cylindrical hexagonal structure [11]. The framework of AlPO-5 crystals are hexagonal symmetry and consist of one-dimensional 12-membered ring channels packed parallel to the *c*-axis with alternate AlO_4 and PO_4 tetrahedral forming a neutral framework [5,12].

The most common route used to synthesize AlPO-5 microcrystalline solid is the hydrothermal method. This method involves the mixing of the reagents in water which was then heated in a sealed autoclave at autogeneous pressure [13]. The use of water as a solvent in hydrothermal method, however, causes interference with the templating effect of the structure-directing agent and concurrently, creates high vapor pressure which results in safety issues [14,15].

In 2004, a new method referred to as ionothermal synthesis has been reported, which has opened up an alternative route for the synthesis of the AlPO-*n* molecular sieves [16]. In this approach, ionic liquids are employed as both the solvent and the structure-directing agent (SDA). From the environmental and safety aspects, ionic liquid which replaces the use water, presenting significant practical advantages over the conventional hydrothermal method [16,17].

Unlike molecular water and conventional organic solvents, ionic liquid is a liquid consists of only ions and therefore exhibits ionic character [18]. It has excellent solvating behaviors for a wide range of organic, inorganic and polymeric materials [19]. In addition, its very low vapor pressure and high thermal stability properties allow the synthesis to be performed at ambient pressure, alleviating safety concerns caused by hydrothermal pressure risks [20]. The ionic liquids after ionothermal synthesis can also be purified, recycled and reused in subsequent cycles of synthesis, preventing and reducing wastage of chemical reagents [18]. Thus, the use of

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ionic liquid in ionothermal synthesis presents significant practical advantages over the conventional hydrothermal approach [21].

Recent studies show that 1-ethyl-3-methylimidazolium bromide ([emim]Br), 1-butyl-3-methylimidazolium bromide ([bmim]Br), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF$_4$) and 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF$_6$) ionic liquids have been employed in the preparation of AlPO-5 molecular sieves [9,15,22,23]. It is interesting to mention here that these ionic liquids produce AlPO-5 crystals with different morphologies which are hardly achieved with hydrothermal technique. The different morphology and crystal shape of AlPO-5 molecular sieve strongly depend on the synthesis conditions, hydrophobicity/hydrophilicity and environment of the ionic liquids used [24]. For instance, the AlPO-5 materials with barrel, hexagonal prism, rod, column, needle-like and spheroidal shapes have been reported using the ionothermal pathway [9,25–28]. Thus, any insight in exploring AlPO-5 with new and interesting morphology is highly appreciated.

Herein we reported the use of self-prepared 1-ethyl-2,3-dimethylimidazolium bromide ([edmim]Br) as the SDA and solvent for the synthesis of AlPO-5 molecular sieves with unique morphologies and different sizes under different synthesis conditions. Previously, we also reported the use of similar [edmim]Br ionic molten salt to synthesize nanoscale MnAlPO-5 with uniform round shape and different chemical composition [27,29]. The nanoparticles had monomodal particle size distribution with a size between 50 and 100 nm, and negligible agglomeration and coalescence of nanoparticles were observed. Similarly, the [edmim]$^+$ cation has a cationic size of 7.0 Å × 5.1 Å, thus is expected to fit well in the crystals channels of AlPO-5 with a pore diameter of 7.3 Å × 7.3 Å [28]. Further to that, the reaction conditions affecting the crystallization kinetics, crystalline phase, morphology and crystal size were also investigated and discussed.

2. Experimental details

2.1. Synthesis of 1-ethyl-2,3-dimethylimidazolium bromide, [edmim]Br ionic molten salt

All the chemicals and solvents used for the synthesis were of reagent grade and were obtained commercially. The [edmim]Br ionic molten salt was prepared as follows: 1,2-dimethylimidazole (47.10 g, 96%, Merck) was added to the bromoethane (80.08 g, 99%, Merck) in a round bottom flask with a ratio of 1:1.5 under stirring. The mixture was refluxed at 50 °C for 2 h and then was allowed to cool down to room temperature when an emulsion formed turned into a yellow viscous solution (Scheme 1). The yellow viscous compound was dissolved in acetonitrile (350 mL) before cooling in an ice bath to allow recrystallization. The resulting white crystals with needle shape were purified, washed with diethyl ether and finally dried at 50 °C under vacuum condition. The pure ionic molten salt was kept in a tight propylene bottle and stored in a desiccator. Product yield 92.1%. ^{1}H NMR (400 MHz, D$_2$O): $\delta = 1.30$ (3H, *t*, $J = 9$ Hz, imidazole N3−CH$_2$−C*H*$_3$), 2.47 (3H, s, N1−C(C*H*$_3$)−N3), 3.64 (3H, s, imidazole N1−CH$_3$), 4.02 (2H, m, imidazole N3−C*H*$_2$−CH$_3$), 7.19 (1H, d, $J = 3$ Hz, N3−C*H*═CH−N1), 7.24 (1H, d, $J = 3$ Hz, N3−CH═C*H*−N1). ^{13}C NMR (400 MHz, D$_2$O): $\delta = 10.0$ (N3−C(*C*H$_3$)−N1), 14.0 (N3−CH$_2$−*C*H$_3$), 35.2 (N1−*C*H$_3$), 44.0 (N3−*C*H$_2$−CH$_3$), 120.4 (N3−*C*H═CH), 129.9 (N3−CH═*C*H), 144.8 (N3−*C*2(CH$_3$)−N1) (Please see Supplementary information). FT-IR (KBr disk) cm^{-1}: 1019 (imidazolium C−N), 1423 and 1613 (aromatic C═C), 1535 (imidazolium C═N), 3446 (broad O−H stretching). Anal. Cacld. for C$_7$H$_{13}$N$_2$Br: C, 40.99%; H, 6.39%; N, 38.96%; Br, 13.66%; found: C, 41.30%; H, 6.26%; N, 37.93%; Br, 14.51%.

Table 1
Effect of heating time on the phase of products.

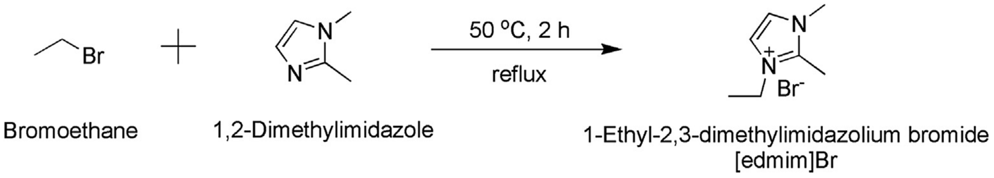
Entry	Molar ratio				Time (h)	Temperature (°C)	Phase(s)
	Al$_2$O$_3$	P$_2$O$_5$	[edmim]Br	H$_2$O			
IT-1	1	1.8	75	3.5	20	150	Amorphous
IT-2	1	1.8	75	3.5	44	150	Amorphous > AFI
IT-3	1	1.8	75	3.5	90	150	AFI
IT-4	1	1.8	75	3.5	120	150	AFI and dense
IT-5	1	1.8	75	3.5	140	150	Dense

2.2. Ionothermal synthesis of AlPO-5 molecular sieve

Typically, aluminum isopropoxide (1.30 g, Al[OCH(CH$_3$)$_2$]$_3$, 98%, Aldrich) and [edmim]Br ionic molten salt (4.96 g) were introduced into a 50 ml round bottom flask. Phosphoric acid (1.33 g, H$_3$PO$_4$, 85%, Mallinckrodt) was subsequently added in dropwise to give a final chemical composition of Al$_2$O$_3$: 1.8P$_2$O$_5$: 75[edmim]Br: 3.5H$_2$O. The round bottom flask was then heated in an oven at 150 °C for 20, 44, 90, 120 and 140 h. The sample was cooled to room temperature and the solid product was washed thoroughly with distilled water and acetone before drying at 100 °C for 5 h. In order to study the influence of reaction conditions and chemical compositions on final solid products, similar procedure was applied by using various mixture compositions and synthesis conditions as shown in Tables 1–4. *Note: No additional water was introduced in the gels unless stated in the tables.*

2.3. Characterization techniques

Liquid ^{1}H NMR spectrum was recorded on a Bruker Ultrashield 400 spectrometer with tetramethylsilane as a reference and D$_2$O as a solvent. Heteronuclear multiple bond correlation (^{13}C HMBC) spectroscopy was conducted to delineate long-range proton-carbon bonded interactions, using a polarization transfer time corresponding to $^3J_{CH} = 10$ Hz. The HMBC data were typically acquired with spectral widths of 7.2 kHz for ^{1}H and 36.2 kHz for ^{13}C, a relaxation delay of 1.0 s between transients, and an array of 2K × 256 points, zero-filled to 2K × 1K points. Chemical analyses were also performed on a Perkin Elmer 2400 Series II CHNS/O analyzer to determine the constituent of elements in [edmim]Br. The crystalline phase of the samples was determined by a Siemens D5000 Kristalloflex diffractometer (step size 0.02°, CuK$_\alpha$ radiation). The morphology of the solid particles was inspected by a Leo Supra 50VP field emission scanning electron microscope operating at



Scheme 1. Synthesis route of [edmim]Br ionic liquid.