Microporous and Mesoporous Materials 193 (2014) 1–6

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Ionothermal synthesis of phase pure $AlPO_4$-5 using a series of tri-substituted imidazolium bromides

Yawei Shi, Guozhu Liu *, Li Wang, Xiangwen Zhang

Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, People's Republic of China

ARTICLE INFO

Article history:
Received 10 December 2013
Received in revised form 13 February 2014
Accepted 6 March 2014
Available online 15 March 2014

Keywords:
Ionothermal synthesis
$AlPO_4$-5
Aluminophosphate
Ionic liquid
Hexagonal

ABSTRACT

The ionothermal synthesis of phase pure $AlPO_4$-5 was achieved using a series of tri-substituted imidazolium bromides (1-ethyl-, 1-butyl- and 1-hexyl-2,3-dimethylimidazolium bromides [EMMIMBr, BMMIMBr and HMMIMBr]). ^{13}C nuclear magnetic resonance (NMR) measurements revealed that the cations of the ionic liquids were incorporated into the final structures. It was also found that the morphologies of the samples varied with the types of IL used. The possible reason for the different morphologies was that the decreasing charge density gradually weakened the interaction between the $AlPO_4$–AFI framework and the IL cation, with an increase in the alkyl chain length.

© 2014 Elsevier Inc. All rights reserved.

1. Introduction

Zeolites and aluminophosphates molecular sieves are crystalline materials with uniform micropores [1–3]. They are widely used as catalysts, adsorbents and ion-exchangers in a variety of chemical processes [2,4]. Normally, these materials are prepared under hydrothermal conditions, with water in a sealed autoclave under autogenous pressure [2]. Some other methods were also proposed, including solvothermal synthesis [5], dry-gel conversion [6], microwave-assisted synthesis [7], solvent-free synthesis [8,9], etc. In all the methods mentioned above, a closed vessel must be used to avoid the escape of water or other solvents.

Morris et al. [10] reported a new ionothermal approach, in which ionic liquids (ILs) were employed as both the solvent and the structure directing agent (SDA). The ILs, composed of only ions, have negligible vapor pressure, making it possible to prepare aluminophosphates molecular sieves in open vessels, thus reducing the safety concerns associated with closed ones [10–13]. Meanwhile, as the ILs play two roles, the competition between template–framework and solvent–framework interaction is removed, making it convenient to address some fundamental questions that are hard to study in conventional methods [14]. After then, plenty of ionic liquids have been used in the ionothermal approach [10,15–25]. The addition of a SDA brought even more possibilities [19,26–28].

To date, a series of aluminophosphate molecular sieves have been synthesized [10,15,18–24,26–29], among which $AlPO_4$-5 with AFI topology has attracted extensive attention due to its advantages such as large micropores and excellent thermal stabilities [30–32]. $AlPO_4$-5 has been synthesized in the ionothermal way using a variety of ILs with or without an amine or a quaternary ammonium cation as a second SDA [14,19,20,24–27]. For the synthesis without a second SDA, the cation of the IL was usually larger than that of 1-ethyl-3-methylimidazolium bromide (EMIMBr) [14,19,20,24]. As reported previously, the pore sizes of all the $AlPO_4$ products synthesized ionothermally in EMIMBr were no larger than 10-MR, while a mixture of $AlPO_4$-11 and $AlPO_4$-5 was obtained using 1-butyl-3-methylimidazolium bromide (BMIMBr) without a second SDA or microwave heating [26]. This indicates that the cation size of either EMIMBr or BMIMBr is not suitable for $AlPO_4$-5. 1-Ethyl-2,3-dimethylimidazolium bromide (EMMIMBr) and 1-butyl-2,3-dimethylimidazolium bromide (BMMIMBr), each with three alkyl substituents, have cations slightly larger than that of EMIMBr and BMIMBr, respectively. Thus the tri-substituted imidazolium bromides may be proper for $AlPO_4$-5. However, there are few reports on the use of tri-substituted imidazolium bromides in the ionothermal synthesis [22–25]. Multiple variables, for example, choice of heating method [33], kind of heteroatom [34], addition of second SDAs or mineralizers [14,26], have great impacts on the final structure. Thus, the application of a series of tri-substituted imidazolium bromides may further extent the possibilities of ionothermal synthesis.

---

* Corresponding author. Tel./fax: +86 22 27892340.
E-mail address: gliu@tju.edu.cn (G. Liu).

http://dx.doi.org/10.1016/j.micromeso.2014.03.009
1387-1811/© 2014 Elsevier Inc. All rights reserved.

In the present work, the ionothermal synthesis of AlPO$_4$-5 using a series of tri-substituted imidazolium bromides is investigated. We demonstrated that phase pure AlPO$_4$-5 with different morphologies could be obtained in several hours. The as-synthesized aluminophosphates were in the orthorhombic form and transferred to the hexagonal form upon calcination. The effect of side chain length and the role of F-anion were also discussed.

2. Experimental section

2.1. Materials

EMIMBr, EMMIMBr, BMMIMBr and HMMIMBr were purchased from Lanzhou Institute of Chemical Physics (Lanzhou, China). Phosphoric acid (H$_3$PO$_4$, 85 wt.% in water), aluminium isopropoxide (Al[OPr$_i$]$_3$), hydrofluoric acid (HF, 40 wt.% in water) and ethanol (CH$_3$CH$_2$OH, AR) were purchased from Tianjin Guangfu Chemical Industry (Tianjin, China). All the reagents were used without further purification. Distilled water was used in all the experiments.

2.2. Ionothermal synthesis

The synthesis experiment was carried out in a 50 mL round bottom flask with a magnetic stirrer. In a typical synthesis, 8.14 g EMMIMBr was put into the flask and heated to 130 °C. Then the following materials were added under stirring: 0.2026 g Al(OPr$_i$)$_3$, 0.3431 g H$_3$PO$_4$ and 27 μL HF. The gel had a composition of 40IL:1.0Al:3.0P:0.6F. The initial mixtures were aged at 130 °C for about 1 h. The gels then were heated to 170 °C and kept for 2 h for crystallization. The product was suspended in water, filtered by suction and washed for several times with water and ethanol, then dried at 120° overnight. Calcination was performed at 550 °C for 5 h with a heating rate of 1 °C/min. Synthesis details are summarized in Table 1. The samples are named with the IL used.

2.3. Characterizations

The morphologies of the samples were characterized by scanning electron microscopy (SEM, FEI, Nanosem 430 field emission gun scanning electron microscope). Powder X-ray diffraction (XRD) patterns were collected on a Rigaku D/MAX-3B powder X-ray diffractometer using the Cu Kα radiation (λ = 0.154 nm).

Thermal analysis was conducted on a RIGAKU standard-type spectrometer (Rigaku Corporation) using dynamic dry air, with a flow rate of 25 mL/min. The selected heating rate was 10 °C/min and the temperature range was 30–750 °C.

^{13}C CP/MAS NMR measurements were performed on a Varian Infinity plus-300 spectrometer recorded at 75.4 MHz with spinning rate of 10 kHz, 1880 scans, 3 ms contact time, and 5 s recycle delay. The chemical shifts were referenced to hexamethybenzene at 17.3 ppm.

Liquid-state ^{13}C NMR measurements were recorded at 500 MHz on a Varian Inova-500 spectrometer, in D$_2$O with Me$_4$Si as standard.

Table 1
Synthesis conditions employed.[a]

Sample	IL	Phase[c]
EMM	EMMIMBr	AFI
BMM	BMMIMBr	AFI
HMM	HMMIMBr	AFI
EM	EMIMBr	AEL
Mix-1	EMIMBr:EMMIMBr = 0.5:1[b]	AFI
Mix-2	EMIMBr:EMMIMBr = 1:1[b]	AFI
Mix-3	EMIMBr:EMMIMBr = 2:1[b]	AFI + AEL
Mix-4	EMIMBr:HMMIMBr = 1:1[b]	AEL

[a] Gel composition (IL:Al:P:F = 40:1:3:0.6 molar ratio); 170 °C, 2 h.
[b] Molar ratio.
[c] Determined by XRD.

3. Results and discussion

3.1. Phase determination and the hexagonal-orthorhombic phase transformation of AlPO$_4$-5

The ionothermal synthesis of AlPO$_4$-5 was performed using three kinds of tri-substituted imidazolium bromides, the structures of which are very similar, with a slight difference in one of their substitute. In all three cases, the obtained samples were white solids. Fig. 1 displays the XRD patterns of the as-synthesized and calcined samples. As can been seen in Fig. 1, the XRD patterns of all the calcined samples were almost identical. All diffraction peaks were assigned to the AFI structure of AlPO$_4$-5 (JCPDS 41-0044) with P6mm symmetry.

For the as-synthesized samples, the splitting of some peaks are clearly seen, which indicates that the symmetry of the unit cell is lower than the hexagonal one [35]. These samples were assigned to orthorhombic form AlPO$_4$-5 [14,19,25–27,36]. However, in a very recent report, the sample obtained using EMMIMBr with a similar XRD pattern was marked as a mixture of AFI and AEL [25]. AlPO$_4$-11(AEL), with a higher framework density, is energetically more stable than AlPO$_4$-5 [33], thus the transformation from AlPO$_4$-11 to AlPO$_4$-5 is not likely to take place.

3.2. Structure directing effect and thermal stability

The ^{13}C CP/MAS NMR spectra of the solid samples and the ^{13}C liquid NMR spectra of the corresponding ILs are shown in Fig. 2. Although lines are considerably broadened and some peaks are not well-resolved, most of the peaks possess approximately the same chemical shift value. In all cases, two lines around 121 and 122 ppm corresponding to the two adjacent carbon atoms of the imidazolium ring overlap into one broadened peak of the solid state NMR spectra. Also, the two lines at 29.2 and 30.7 ppm

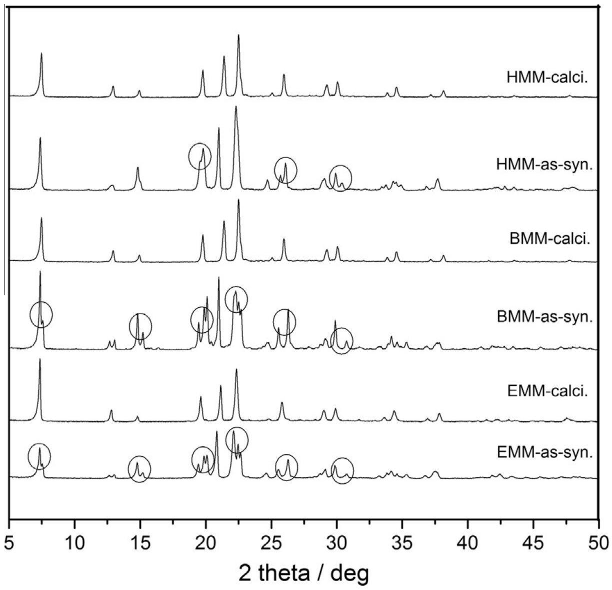

Fig. 1. XRD patterns of as-synthesized and calcined AlPO$_4$-5 samples (as-syn.: as-synthesized, calci.: calcined; splitting of some peaks are marked with circles).

Download English Version:

https://daneshyari.com/en/article/73032

Download Persian Version:

https://daneshyari.com/article/73032

Daneshyari.com