

Microporous Materials

DOI: 10.1002/anie.200600054

Microwave-Enhanced Ionothermal Synthesis of Aluminophosphate Molecular Sieves**

Yun-Peng Xu, Zhi-Jian Tian, Shao-Jun Wang, Yue Hu, Lei Wang, Bing-Chun Wang, Ying-Chong Ma, Lei Hou, Jia-You Yu, and Li-Wu Lin*

Molecular sieves are crystalline or amorphous materials with uniform micropores or mesopores.^[1-3] They are effective separation materials and are the most important catalysts in industry because of their special structures and acidities.^[3,4]

[*] Dr. Y.-P. Xu, Prof. Z.-J. Tian, L. Wang, B.-C. Wang
Laboratory of Natural Gas Utilization and Application Catalysis
Dalian Institute of Chemical Physics
Chinese Academy of Sciences
Dalian 116023 (P.R. China)
Fax: (+86) 411-843-79151
E-mail: xuy@dicp.ac.cn

Prof. S.-J. Wang, Y. Hu, Y.-C. Ma, L. Hou, Prof. J.-Y. Yu
Department of Chemical Engineering
Dalian Institute of Light Industry
Dalian 116034 (P.R. China)

Prof. Z.-J. Tian, Prof. L.-W. Lin
State Key Laboratory of Catalysis
Dalian Institute of Chemical Physics
Chinese Academy of Sciences
Dalian 116023 (P.R. China)

[**] Financial support from PetroChina Company Ltd. (Grant Nos. W050508-03-03 to Y.-P.X. and Z.-J.T.) and State Key Projects for Basic Research & Development, China (Grant No. 2003CB615805 to S.-J.W.) is gratefully acknowledged. We thank Prof. Mark Schlossman, University of Illinois, for useful discussions.



Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

The synthesis of molecular sieves is usually conducted in water or other polar solvents in a sealed container under hydrothermal or solvothermal conditions.^[2,3] Many effective methods have been developed for the synthesis of molecular sieves during the last century,^[2,3] with one of them being microwave dielectric heating synthesis.^[5] Microwaves are a form of electromagnetic energy, and microwave dielectric heating is known popularly as a domestic cooking method, but it is also widely used in organic synthesis, analytical chemistry, polymer curing, and inorganic synthesis.^[6] In contrast to conventional heating, the heating effect of microwaves is caused by dielectric loss from the irradiated sample.^[5] Microwave heating has been used in the hydrothermal synthesis of molecular sieves,^[7,8] and highlighted the advantages of fast crystal growth and high selectivity obtained relative to conventional heating.^[5] However, hydrothermal synthesis under microwave heating has safety concerns because of the high temperatures required (>100°C) and autogenous pressure. Moreover, organic templates used in the synthesis of molecular sieves tend to decompose under microwave irradiation at high temperatures, which impairs the structure-directing function of the templates.^[5] These drawbacks limit the utilization of microwaves in the hydrothermal synthesis of molecular sieves.

Recently, Morris and co-workers reported a novel method for the synthesis of molecular sieves known as ionothermal synthesis,^[9] which has attracted the interest of other researchers.^[10–12] In ionothermal synthesis, molecular sieves are synthesized in an ionic liquid, which is different from hydrothermal and solvothermal synthesis which employs a molecular liquid.^[9] The predominant advantages of the ionothermal synthesis of molecular sieves are that a separate organic template is not required and the synthesis can be carried out at ambient pressure. Ionic liquids are special molten salts typically containing organic cations and inorganic anions.^[13,14] They have a low melting point (<100°C), relatively low viscosity, high electric and thermal stability, are good solvents for a wide range of organic and inorganic materials, and, importantly, have negligible vapor pressure.^[13,14] These characteristics enable ionic liquids to be widely used as a “green” solvent, functional solvent, or catalyst in organic synthesis,^[15,16] inorganic preparation,^[17,18] electrochemistry,^[19,20] as well as other areas.^[21,22] Ionic liquids have been proven to be good media for absorbing microwaves,^[23,24] so there is a possibility to combine the “green” solvent aspect of ionic liquids with the “green” chemistry aspect of microwave irradiation to yield a new synthesis method. Very recently Zhu et al. reported a new microwave-assisted ionic liquid method (MAIL) for the fast, controlled synthesis of nonporous nanomaterials.^[25] This is a good example of combining microwaves and ionic liquids for inorganic synthesis.

Here we report the ionothermal synthesis of molecular sieves under microwave heating—namely, the microwave-enhanced ionothermal synthesis of molecular sieves—which combines the advantages of both microwave heating and ionothermal synthesis. The synthesis of a series of aluminophosphate molecular sieves by this process demonstrates the advantages of a rapid crystal growth rate, high product selectivity, and low pressure. The method overcomes the

drawbacks of the hydrothermal synthesis of molecular sieves by microwave heating, including safety concerns, and provides a new way to synthesize molecular sieves.

The microwave-enhanced ionothermal synthesis was carried out in a microwave reaction system, and the crystallization reaction was conducted in an open round-bottom glass flask under microwave irradiation. The effects of different heating methods (conventional and microwave dielectric) on the ionothermal synthesis of molecular sieves were investigated.

In contrast to microwave-heating hydrothermal synthesis of molecular sieves, the use of ionic liquids allows the synthesis with microwave heating to be conducted under low pressure and safe conditions. The crystallization of the molecular sieves during the ionothermal synthesis is carried out in an open flask at 150°C. Under the conditions of hydrothermal synthesis, the pressure can reach 476 KPa at this temperature. Therefore, a pressure-resistant vessel such as a metal autoclave would be needed in hydrothermal synthesis, but this is not suitable for microwave dielectric heating. Teflon and other microwave-transparent polymers are widely used to make autoclaves for microwave heating, but they become flexible at high temperatures and cannot withstand the high pressure. This may lead to a serious safety concern, which limits the utilization of microwave dielectric heating at high pressures. The use of an ionic liquid such as 1-ethyl-3-methylimidazolium bromide ([emim]Br) addresses this problem, since it has negligible vapor pressure and high stability at 150°C or even higher temperatures.^[14] In addition, ionic liquids have high polarity and electric conductivity. Both dipolar polarization losses and conduction losses occur^[23] when ionic liquids are irradiated by microwaves which generate heat. Ionic liquids readily absorb microwaves and can be heated rapidly;^[23] therefore, ionic liquids are the ideal solvent for the safe synthesis of molecular sieves by microwave irradiation.

Ionothermal synthesis has been shown to be an effective method for the preparation of aluminophosphate molecular sieves.^[9] AEL-type aluminophosphate molecular sieves (AlPO₄-11 and SAPO-11) were successfully synthesized in [emim]Br under ionothermal conditions.^[9,26] The microwave-enhanced ionothermal synthesis in the same ionic liquid produced the same type of aluminophosphate molecular sieve (AEL, PDF-410556), nevertheless the crystallization time was much shorter than that with conventional heating. The X-ray diffraction (XRD) patterns of AEL-type aluminophosphate molecular sieves prepared with microwave heating and conventional heating ionothermal processes are shown in Figure 1. The effect of crystallization time on the growth of the AEL molecular sieves under microwave and conventional heating is shown in Figure 2. Complete crystallization required several hours under conventional heating as shown in Figure 2b, while the yield of solid product decreased with increasing time (Table 1). However, the crystallization of the molecular sieve under microwave heating was completed within tens of minutes (Figure 2a) and the yield of solid product increased within the crystallization time investigated (Table 1). We can conclude from these results that microwave heating led to a more rapid growth of crystalline molecular

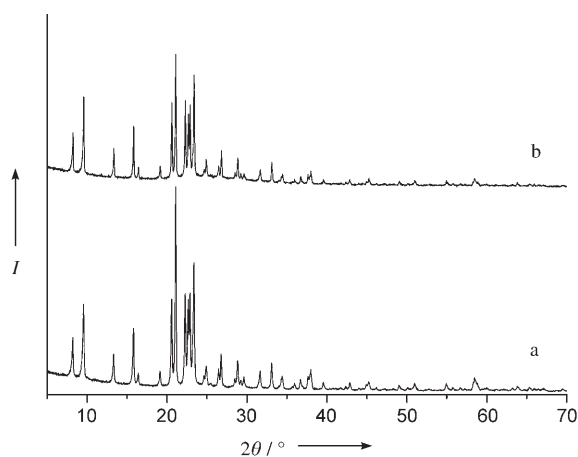


Figure 1. XRD patterns of the aluminophosphate molecular sieves (AEL type) prepared by ionothermal synthesis: a) with 24 h of conventional heating and b) with 20 minutes of microwave heating. Synthesis conditions: 150 °C, ambient pressure, ionic liquid: [emim]Br.

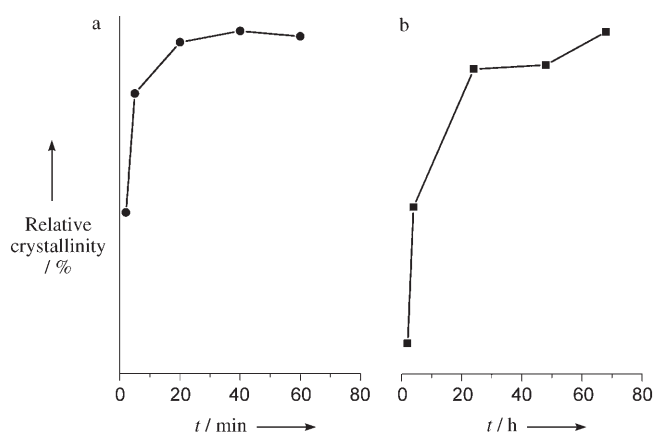


Figure 2. Relative crystallinities of aluminophosphate molecular sieves (AEL type) prepared by ionothermal synthesis as a function of time: a) with microwave heating and b) with conventional heating. Synthesis conditions: 150 °C, ambient pressure, ionic liquid: [emim]Br.

Table 1: Crystallinities and yields of molecular sieve (AEL-type) samples synthesized by ionothermal processes.^[a]

Sample	IL ^[b] :P:Al:F:Si	Heating mode	t [min]	Relative crystallinity [%]	Solid product yield [%]
CH-1	40:3:1:0.8:0	conventional	240	48.8	103
CH-2	40:3:1:0.8:0	conventional	1440	89.1	75.3
CH-3	40:3:1:0.8:0	conventional	4080	100	62.9
MW-1	40:3:1:0.8:0	microwave	2	47.0	26.3
MW-2	40:3:1:0.8:0	microwave	20	96.7	47.1
MW-3	40:3:1:0.8:0	microwave	60	98.4	62.7
MW-4	40:3:1:1.6:0	microwave	20	144.3	10.9
MWS-1	40:3:1:0.8:0.25	microwave	60	25.1	74.0
MWS-2	40:3:1:1.6:0.25	microwave	60	100	17.2

[a] Synthesis conditions: 150 °C, ambient pressure, ionic liquid [emim]Br.
[b] Ionic liquid [emim]Br.

sieve compared with that by conventional heating during ionothermal synthesis. The rapid crystallization under microwave heating also produced a different morphology of the

AEL molecular sieve crystallines (Figure 3). Samples obtained by conventional heating have needlelike features; however, samples synthesized by microwave heating consist primarily of cuboidlike crystallites. In ionothermal synthesis,

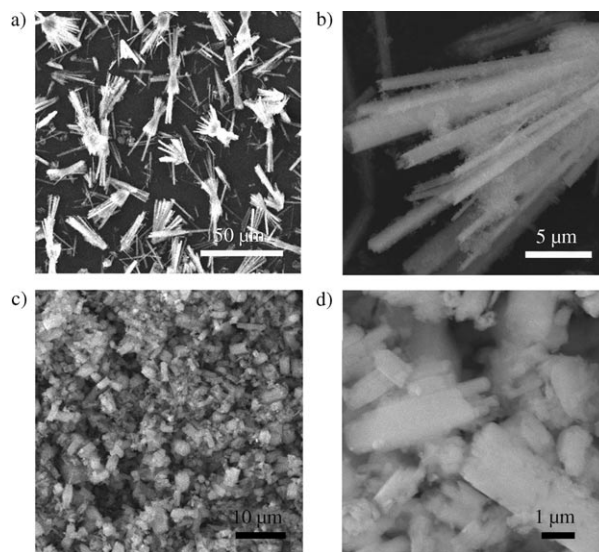


Figure 3. SEM micrographs of aluminophosphate molecular sieves (AEL type) prepared by ionothermal synthesis: a), b) samples after 68 h crystallization with conventional heating; c), d) samples after 20 minutes crystallization with microwave heating. Synthesis conditions: 150 °C, ambient pressure, ionic liquid: [emim]Br.

crystallites grow in an optimal direction as a result of the ionic liquid environment^[25] and form needlelike morphologies. However, under microwave heating, rapid crystallization weakens the optimal directional growth which leads to the formation of cuboidlike crystallites.

The rapid crystallization of molecular sieves during microwave-enhanced ionothermal synthesis is probably a consequence of local superheating. The growth of the molecular sieve generally consists of three periods:^[3,5] 1) digestion and equilibration of reactants, 2) crystal nucleation, and 3) crystal growth. Earlier experimental evidence from hydrothermal synthesis showed that local superheating induced by microwaves could facilitate the reagent digestion to hasten the equilibration of the reactants between the liquid and solid phases.^[5–7] Therefore, crystal nucleation and crystal growth would be faster with microwave heating than with conventional thermal heating hydrothermal synthesis. The local superheating effect of microwaves is caused mainly by the heterogeneity of the reaction mixtures used in hydrothermal synthesis, which leads to several different energy-loss mechanisms coexisting in the bulk phase of hydrothermal synthesis mixtures used in microwave irradiation.^[5] In microwave-enhanced ionothermal synthesis, the situation is similar to the microwave-enhanced hydrothermal synthesis. Ionic liquids have high polarity and good conductivity and can be heated effectively by microwaves.^[23] Ionothermal synthesis mixtures are cloudy liquids and have noticeable heterogeneity. Thus, it is likely that the different energy-loss mechanisms will coexist in ionothermal synthesis, which will lead to local

superheating effects by the microwaves. Therefore, the digestion of reagents will be facilitated and a rapid crystallization rate will be obtained in microwave-enhanced ionothermal synthesis. The product yields obtained with microwave heating is lower than that obtained from ionothermal synthesis with conventional heating (Table 1). The results imply that more reactant exists in the liquid phase under microwave heating than under conventional heating and provides evidence that microwaves facilitate the digestion of the reactant. Therefore, the crystallization during microwave-enhanced ionothermal synthesis is faster than with conventional heating.

Fluoride plays an important role in ionothermal synthesis and affects both the yield of the crystalline product and its crystallinity. Thus, the effect on crystallization of adding HF to the synthesis mixtures with microwave heating was investigated. Table 1 shows that the product yield increased from 10.9% to 47.1% when the ratio of HF was decreased from 1.6:1 to 0.8:1 (molar ratio of F:Al in the synthesis mixtures). The crystallinity of the AEL structure produced increased as the amount of HF was increased (Figure 4).

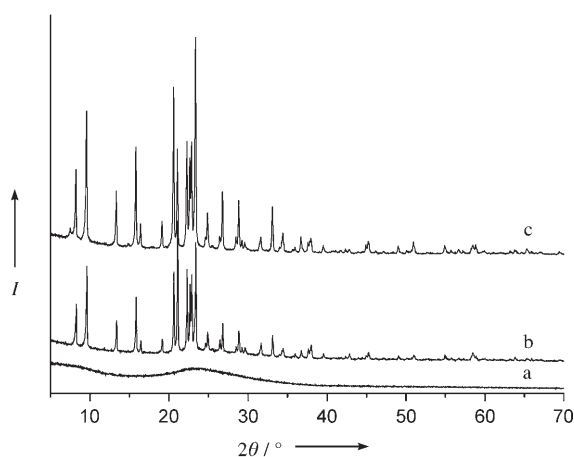


Figure 4. XRD patterns of aluminophosphate molecular sieves (AEL type) prepared by microwave-enhanced ionothermal synthesis with different amounts of HF additive. Molar ratio of F:Al in the synthesis mixtures: a) 0:1, b) 0.8:1, c) 1.6:1. Synthesis conditions: 150 °C, 20 min, ambient pressure, ionic liquid [emim]Br.

However, no aluminophosphate molecular sieves were formed without the addition of HF, although the yield of solid products of Al species could reach nearly 100%. The results indicate that the presence of fluoride was a key factor in the formation of AEL-type aluminophosphate molecular sieves. However, excessive fluoride decreases the yield of crystalline products in ionothermal synthesis. Previous literature reports show that fluoride displays the same effect in hydrothermal synthesis.^[27,28] It is widely accepted that fluoride reacts with the reagent to form soluble fluoride species that remain in the solution after crystallization^[28] and are incorporated with difficulty into the crystalline phase of the molecular sieve. Thus, the yield of the solid product was low when fluoride was involved in the crystallization process. As in the microwave-enhanced ionothermal synthesis, micro-

waves facilitate the process of digestion and equilibration of reactants during crystallization, as discussed above.^[5] Furthermore, according to our results, it seems unlikely that the anion of the ionic liquid (Br^- in the ionic liquid [emim]Br) participated in the digestion period of the molecular sieve crystallization since no AEL-type structure formed after crystallization and the yield of the solid product was almost 100%. Therefore, it seems likely that microwaves enhanced the reaction of F^- ions with Al species, namely, enhanced the digestion of the reactant into the liquid phase, as well as facilitated the formation of the molecular sieve structure during ionothermal synthesis.

In the ionothermal synthesis of aluminophosphate molecular sieves, the introduction of a silicon source (e.g. tetraethyl orthosilicate (TOES)) into the synthesis mixture can result in the formation of AEL-type silicoaluminophosphate molecular sieves (SAPO-11). The molar compositions of the reagents used in the synthesis mixtures are shown in Table 1. The incorporation of silicon into the framework of the molecular sieves is an important indication of the formation of AEL-type silicoaluminophosphate molecular sieves. We used ^{29}Si NMR spectroscopy, energy-dispersive X-ray spectroscopy (EDX), and temperature-programmed desorption of ammonia (NH_3 -TPD) to determine that Si was incorporated into the framework of the AEL molecular sieves (see the Supporting Information).

In contrast to the ionothermal synthesis of AEL aluminophosphate molecular sieves, the introduction of Si into the synthesis mixtures hindered the crystallization of the AEL structure. Figure 5a shows that the crystallinity was very low after one hour of microwave irradiation at 150 °C when TOES was added to the reactions. Under the same reaction conditions the crystallization was almost complete in the absence of Si. The digestion and incorporation of the Si materials into the molecular sieve framework has a close relationship with the amount of fluoride in the synthesis mixtures. It seems that competition between the Si and Al

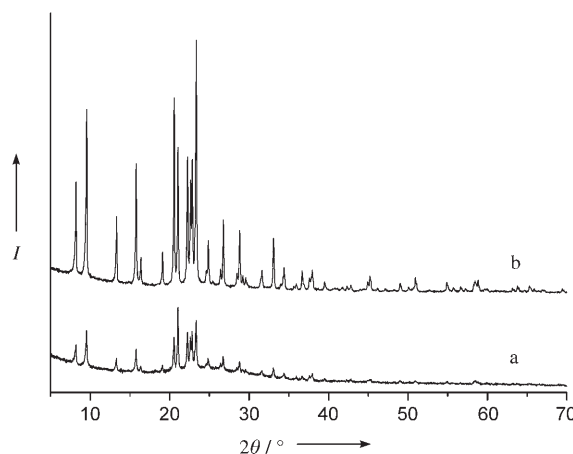


Figure 5. XRD patterns of silicoaluminophosphate molecular sieves (AEL type) prepared by microwave-enhanced ionothermal synthesis with different amounts of HF additive amount. Molar ratio of F:Al in the synthesis mixtures: a) 0.8:1, b) 1.6:1. Synthesis conditions: 150 °C, 60 min, ambient pressure, ionic liquid [emim]Br.

species to react with F^- ions may exist in the crystallization, which has a negative effect on the growth of the AEL molecular-sieve structure. To verify this supposition, twice the amount of HF was added into the reaction. As expected, the AEL structure obtained had a higher crystallinity when microwave irradiation was used (Figure 5b). However, the crystalline yield was very low (decreasing from 74.0% to 17.2%) because of the high degree of digestion of Si and Al materials as a consequence of the large amount of F^- ions.

In a conventional heating ionothermal synthesis process, in addition to the formation of AEL-type molecular sieves, other by-products are produced^[26] (Figure 6a), whose struc-

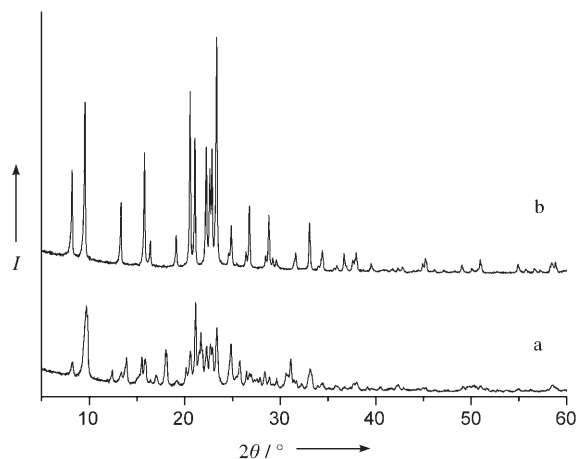


Figure 6. XRD patterns of silicoaluminophosphate molecular sieves (AEL type) prepared by ionothermal synthesis: a) with 68 h of conventional heating and b) with 60 min of microwave heating. Synthesis conditions: 150°C, ambient pressure, ionic liquid [emim]Br.

tures are similar to chabazite. However, when microwave heating was used, the product was nearly pure AEL-type molecular sieve (Figure 6b). The high structural selectivity of microwave synthesis may be related to the local superheating by the microwaves. The growth of AEL-type molecular sieves may be facilitated under such conditions. Therefore, the high crystallization rate of AEL-type molecular sieves under microwave heating depressed the growth of other by-products.

We also investigated another ionic liquid, 1-butyl-3-methylimidazolium bromide ([bmim]Br), as an ionothermal synthesis medium during microwave heating. The results showed that [bmim]Br led to the formation of mixtures of AEL (AlPO₄-11, PDF-410556) and AFI (AlPO₄-5, PDF-410044) aluminophosphate molecular sieves (Figure 7). The crystallinity of the AFI structure decreases with reaction time, while the AEL structure displays the opposite trend.

The ionic liquid plays a dual role in the ionothermal synthesis of molecular sieves: solvent and template.^[9] The size of the cation in the ionic liquids is very important for determining the structure of the molecular sieves. The imidazolium cation [bmim]⁺ is larger than [emim]⁺. Thus, the AFI structure formed with [bmim]⁺ has a 12-ring channel (7.3 × 7.3 Å)^[29] that is larger than the AEL structure formed with [emim]⁺ which has a 10-ring channel (6.5 × 4.0 Å).^[30] This

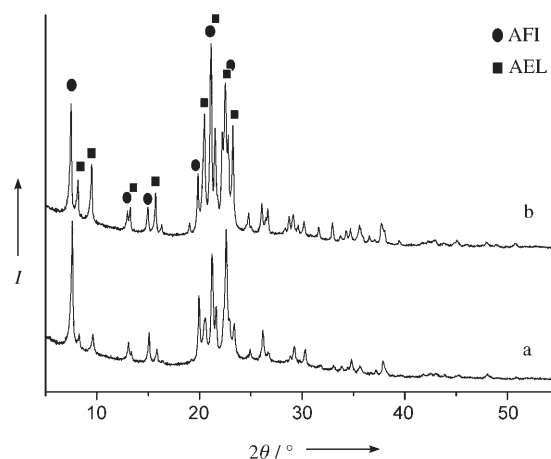


Figure 7. XRD patterns of mixture of aluminophosphate molecular sieves (AEL and AFI types) prepared by microwave-enhanced ionothermal synthesis in [bmim]Br with different crystallization times: a) 10 min; b) 40 min. Synthesis conditions: 150°C, ambient pressure.

result implies a relationship between the cation size of the ionic liquid and the structure of the molecular sieve formed during ionothermal synthesis, which means that a templating effect of the ionic liquid may exist during ionothermal synthesis. Further work on the synthesis of AFI-type aluminophosphate molecular sieves in [bmim]Br is now underway.

In summary, microwave-enhanced ionothermal synthesis is a novel method to prepare molecular sieves. Its advantages are its fast crystallization rate, low synthesis pressure, and high structural selectivity. Ionic liquids are “green” solvents with immeasurably low vapor pressure and good stability. They are also appropriate templates for porous materials and good microwave absorbers that are suitable for microwave dielectric heating. The method reported here will lead to a very promising future for the preparation of molecular sieves by microwave heating.

Experimental Section

Typical preparation of reaction mixtures for ionothermal synthesis: Ionic liquid ([emim]Br or [bmim]Br; 40.0 g) and H₃PO₄ (1.8 g; 85 wt % in water) were mixed in a round-bottom flask, then heated to 100°C with continuous stirring for 10 min. [Al{OCH(CH₃)₂]₃] (1.06 g) and an appropriate amount of HF (40 wt % in water) were added separately to the above mixtures. When the target product was silicoaluminophosphate molecular sieve a certain amount of tetraethyl orthosilicate (TEOS) was then introduced to the liquid mixtures. The molar ratio of ionic liquid to Al in the synthesis mixtures was around 40:1. A small amount of water accompanying the H₃PO₄ and HF existed in the synthesis mixtures at the beginning of synthesis. The final reaction mixtures were stirred at 100°C for 20 min and then were heated to 150°C under microwave irradiation or conventional heating for crystallization of the molecular sieves.

Microwave-enhanced ionothermal synthesis of aluminophosphate and silicoaluminophosphate molecular sieves: The final reaction mixtures prepared at 100°C were placed in a microwave reaction system and heated to 150°C at about 20 K min⁻¹ and kept under ambient pressure for 2–60 min. The microwave reaction system of MARS5 made by CEM Co. (2.45 GHz, maximum power of 1200 W) was used in the experiment. An RPT-300 plus temperature

control sensor was used to measure and control the reaction temperature in the round-bottom flask. The resulting products were washed thoroughly with acetone and water after the synthesis mixtures had cooled to room temperature. The yield of the crystalline product was calculated on the basis of the theoretical amount of AlPO_4 in the synthesis mixtures.

Conventional electric heating ionothermal synthesis of aluminophosphate and silicoaluminophosphate molecular sieves: The final reaction mixtures prepared at 100 °C were heated to 150 °C within about 30 min in an oil bath and kept for an appropriate time for crystallization of the molecular sieves. Treatment of the resultant products and calculation of the yield of the solid product are the same as for the microwave heating process.

Sample characterization: The samples were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD patterns were recorded on a Philips instrument (model CX' Pert PRO, Cu_K radiation, nickel filter, $\lambda = 1.5404 \text{ \AA}$, operating at 40 kV, 40 mA, and with a 2θ scanning speed of 5° min^{-1}). The sample morphology was examined by SEM (JEOL JSN-6460 LV model).

Received: January 6, 2006

Published online: May 9, 2006

Keywords: ionic liquids · ionothermal synthesis · microporous materials · microwaves

- [26] Y. Xu, Z. Tian, Z. Xu, B. Wang, P. Li, S. Wang, Y. Hu, Y. Ma, K. Li, Y. Liu, J. Yu, L. Lin, *Chin. J. Catal.* **2005**, *26*, 446.
 [27] P. A. Barrett, M. A. Cambor, A. Corma, R. H. Jones, L. A. Villaescusa, *J. Phys. Chem. B* **1998**, *102*, 4147.
 [28] S. I. Zones, R. J. Darton, R. Morris, S. J. Hwang, *J. Phys. Chem. B* **2005**, *109*, 652.
 [29] J. M. Bennett, J. P. Cohen, E. M. Flanigen, J. J. Pluth, J. V. Smith, *ACS Symp. Ser.* **1983**, *218*, 109.
 [30] J. M. Bennett, J. W. Richardson, Jr., J. J. Pluth, J. V. Smith, *Zeolites* **1987**, *7*, 160.

- [1] D. W. Breck, *Zeolite Molecular Sieves*, Wiley, New York, **1974**.
 [2] R. Szostak, *Molecular Sieves—Principles of Synthesis and Identification*, 1st ed., Van Nostrand Reinhold, New York, **1989**, 2nd ed., Blackie, London, **1998**.
 [3] C. S. Cundy, P. A. Cox, *Chem. Rev.* **2003**, *103*, 663.
 [4] R. A. van Santen, X. Rozanska, *Adv. Chem. Eng.* **2001**, *28*, 399.
 [5] C. S. Cundy, *Collect. Czech. Chem. Commun.* **1998**, *63*, 1699.
 [6] S. A. Galema, *Chem. Soc. Rev.* **1997**, *26*, 233.
 [7] A. Arafat, J. C. Jansen, A. R. Ebaid, H. van Bekkum, *Zeolites* **1993**, *13*, 162.
 [8] X. Xu, W. Yang, J. Liu, L. Lin, *Adv. Mater.* **2000**, *12*, 195.
 [9] E. R. Cooper, C. D. Andrews, P. S. Wheatley, P. B. Webb, P. Wormald, R. E. Morris, *Nature* **2004**, *430*, 1012.
 [10] E. R. Parnham, R. E. Morris, *J. Am. Chem. Soc.* **2006**, *128*, 2204.
 [11] J. H. Liao, P. C. Wu, Y. H. Bai, *Inorg. Chem. Commun.* **2005**, *8*, 390.
 [12] E. R. Parnham, P. S. Wheatley, R. E. Morris, *Chem. Commun.* **2006**, 380.
 [13] P. Wasserscheid, W. Keim, *Angew. Chem.* **2000**, *112*, 3926; *Angew. Chem. Int. Ed.* **2000**, *39*, 3772.
 [14] T. Welton, *Chem. Rev.* **1999**, *99*, 2071.
 [15] J. A. Boon, J. A. Levisky, J. L. Pflug, J. S. Wilkes, *J. Org. Chem.* **1986**, *51*, 480.
 [16] Y. Chauvin, B. Gilbert, I. Guibard, *J. Chem. Soc. Chem. Commun.* **1990**, 1715.
 [17] M. Antonietti, D. Kuang, B. Smarsly, Y. Zhou, *Angew. Chem.* **2004**, *116*, 5096; *Angew. Chem. Int. Ed.* **2004**, *43*, 4988.
 [18] Y. Zhou, J. H. Schattka, M. Antonietti, *Nano Lett.* **2004**, *4*, 477.
 [19] T. B. Scheffler, C. L. Hussey, K. R. Seddon, C. M. Kear, P. D. Armitage, *Inorg. Chem.* **1983**, *22*, 2099.
 [20] T. M. Laher, C. L. Hussey, *Inorg. Chem.* **1983**, *22*, 3247.
 [21] D. Appleby, C. L. Hussey, K. R. Seddon, J. E. Turp, *Nature* **1986**, *323*, 614.
 [22] F. Shi, J. Peng, Y. Deng, *J. Catal.* **2003**, *219*, 372.
 [23] J. Hoffmann, M. Nüchter, B. Ondruschka, P. Wasserscheid, *Green Chem.* **2003**, *5*, 296.
 [24] N. E. Leadbeater, H. M. Torenus, *J. Org. Chem.* **2002**, *67*, 3145.
 [25] Y. Zhu, W. Wang, R. Qi, X.-L. Hu, *Angew. Chem.* **2004**, *116*, 1434; *Angew. Chem. Int. Ed.* **2004**, *43*, 1410.