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Structure-Directing Role of Amines in the Ionothermal Synthesis

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Since their discovery, microporous materials have been broadly exploited as shape-selective catalysts and sorbents in different research fields,[1] accompanied by an ongoing search for novel molecular sieve structures and new synthesis methods. For example, Morris and co-workers have recently developed a novel method (ionothermal synthesis) for preparing molecular sieves, which involves the use of ionic liquid as both the solvent and structure-directing agent.[2] By using this method, Morris et al. have prepared several aluminophosphate and cobalt aluminophosphate structures in an imidazolium-based ionic liquid (1-ethyl-3-methylimidazolium bromide ([emim]Br)). Compared with the traditional hydrothermal or solvothermal methods,[1,3] preparations using the ionothermal method can take place at or near ambient pressure because of the negligible vapor pressure of ionic liquids.[4] This eliminates safety concerns associated with high pressures.

The synthesis of molecular sieves often requires the addition of organic molecules, such as amines and quaternary ammonium ions, into the synthesis mixture. The role of these molecules has been described as a structure-directing effect, referring to the complementary shapes of the structure-directing agents and the frameworks they direct. Normally the addition of structure-directing agents to molecular sieve synthesis can affect the rate at which a particular structure is formed. In this work, we report the study of the structure-directing role of amines in the ionothermal synthesis of molecular sieves in 1-butyl-3-methylimidazolium bromide ionic liquid ([bmim]Br).[5] We show that the original crystallization process can be altered by the addition of amine, as summarized in Scheme 1.

Scheme 1. Representation of Crystallization Process Herein

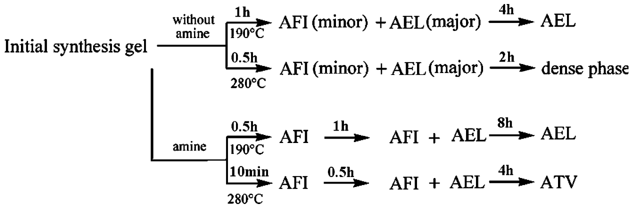

Table 1. Synthesis Details and Conditions for the Preparation of $AlPO_4$ Structures

sample[a]	amine[b]	temp (°C)	time (h)	structure (relative crystallinity, %)
1		190	2	AFI (12.5) + AEL (27)
2		190	4	AEL (100)
3		280	0.5	AFI (15) + AEL (40)
4		280	1.5	$AlPO_4$−tridymite
5	*n*-DPA	190	1	AFI (100)
6	*n*-DPA	190	4	AFI (35) + AEL (38)
7	*n*-DPA	190	8	AEL (90)
8	*n*-DPA	280	0.5	AFI (90)
9	*n*-DPA	280	1	AFI (55) + AEL (30)
10	*n*-DPA	280	3	ATV (100)
11	*i*-DPA	190	1	AFI (51)
12	MIA	190	1	AFI (57)
13	PRD	190	1	AFI (34)
14	*n*-BTA	190	1	AFI (80)
15	DEA	190	1	AFI (37)
16	TEA	190	1	AFI (40)

[a] Molar composition of synthesis mixtures: Al_2O_3:2.55P_2O_5:0.6HF:20[bmim]Br:1.5amine. [b] *n*-DPA, *n*-dipropylamine; *i*-DPA, *i*-dipropylamine; MIA, 1-methylimidazole; PRD, pyrrolidine; *n*-BTA, *n*-butylamine; DEA, diethylamine; TEA, triethylamine.

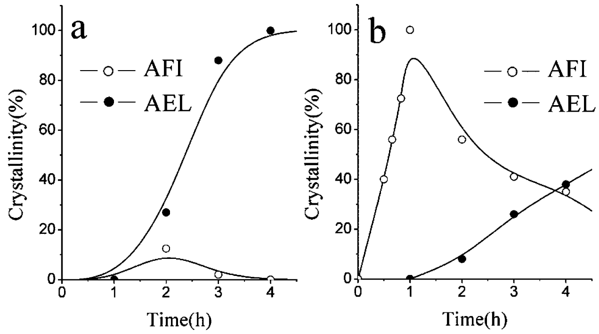

Figure 1. Crystallization curves of AFI and AEL structures grown at 190 °C using synthesis mixtures with composition Al_2O_3:2.55P_2O_5:0.6HF:20-[bmim]Br:x*n*-DPA, where (a) $x = 0$ and (b) $x = 1.5$.

In the absence of amine, $AlPO_4$-11 molecular sieves (AEL-type structure)[6] with minor $AlPO_4$-5 (AFI-type structure)[7] were formed after a short induction period at a temperature between 190 and 280 °C in [bmim]Br (Figure 1a and Table 1). Increasing the crystallization time leads to further growth of the AEL structure, while the amount of the AFI structure passed through a maximum and eventually disappeared after 4 h. Both of the two structures are composed of straight one-dimensional channels with AFI containing 12-membered ring (MR) pores (7.3 × 7.3 Å in size) and AEL containing 10-MR pores (6.5 × 4.0 Å). To date, the only ionic liquid used in ionothermal synthesis was [emim]Br. The pore sizes of all the AlPO and CoAlPO products synthesized ionothermally in [emim]Br are no larger than 10-MR.[2,8] The fact that the 12-MR large-pore AFI structure was formed when [bmim]Br was used as the reaction media instead of [emim]Br suggests the possible structure-directing effect of ionic liquid. (^{13}C CP-MAS NMR indicates that the cation of [bmim]Br is occluded in the pores of AlPOs; see Supporting Information.) Moreover, the cation of ionic liquid may have the major influence on the frameworks it directs. Nevertheless, it seems that $[bmim]^+$ is still suitable for filling the 10-MR channels because the AEL structure was always the major product. The decrease in the amount of the AFI structure with increasing time after 2 h suggests that the AFI structure was not stable and was converted into the AEL structure. According to Davis et al.,[9] microporous AlPO frameworks are energetically less stable than the dense phase, and the relative stability of $AlPO_4$

10.1021/ja061882q CCC: $33.50 © 2006 American Chemical Society

frameworks is in proportion to their framework density (FD = number of tetrahedrally coordinated atoms/nm^3). Therefore, this possible transition of AFI structure (FD = 17.3[10]) to AEL structure (FD = 19.1[10]) along with the decrease in pore size (from 12-MR to 10-MR) obeys Ostwald's rule of successive crystallization.[11]

It should be noticed that the two molecular sieves can be formed simultaneously with a shorter induction time at an elevated temperature of 280 °C. Normally, the upper temperature limit of hydrothermal preparation of molecular sieves is about 200 °C.[1] The microporous framework of a molecular sieve would collapse and convert to the dense phase at the elevated autogenous pressure of water, which increases exponentially with temperature.[12] However, in ionothermal synthesis, the pressure can be maintained at ambient levels even at 280 °C,[4] allowing formation of microporous $AlPO_4$ frameworks. Nevertheless, the frameworks are not stable for a long time and will collapse into $AlPO_4$−tridymite dense phase after heating for 1.5 h (Table 1).

When the same synthesis reaction was carried out in the presence of *n*-dipropylamine (*n*-DPA), the AFI structure was formed within 30 min (Figure 1b), which is shorter than the induction time (1 h) in the absence of amine. In addition, the crystallinity of the AFI structure increased remarkably. The induction time of the AEL structure was unchanged. Thus, the well-crystallized $AlPO_4$-5 can be obtained as a single phase within the first hour. To further clarify the effect of the addition of amine, we selected six other amines (including primary amines, secondary amines, and tertiary amines) as additives to perform the same synthesis experiment. The results show that each of them has a similar effect on the dynamics of the crystallization process, thus making the synthesis of the pure AFI phase sample feasible within the first hour (Table 1). Therefore, it seems reasonable to suppose that amine contributes a structure-directing effect during the crystallization process. To the best of our knowledge, most of the amines we tested can serve as templates for the hydrothermal preparation of both the AFI structure and the AEL structure except for 1-methylimidazole, so there is a possibility that the amine alone can play the role of structure-directing agent. However, taking the structure-directing effect of the ionic liquid into account, we suggest that amine may exert its structure-directing effect together with the ionic liquid. As a potential electron-pair donor, amine may form hydrogen bonds with the imidazolium ring of the ionic liquid. ^{1}H NMR spectra of [bmim]Br and amine liquid mixtures (see Supporting Information) confirmed that the presence of amine causes a downfield shift of the signal corresponding to the proton of the imidazolium ring. This is considered to be strong evidence for the formation of hydrogen bonds between ionic liquid and additives.[13] Through this interaction, the amine may combine with the imidazolium cations of the ionic liquid to form hydrogen-bonded cations of larger size, which might stabilize the large 12-MR channels and facilitate the formation of AFI structure. Moreover, the hydrogen bonding of amine and ionic liquid may disrupt the nonbonding interactions established between the ionic liquid and the inorganic framework during the templating process.[2a] Furthermore, the hydrogen bonding may affect many physical properties of the ionic liquid,[14] such as its self-organization patterns and supramolecular structure.[15] These would lead to a change in the structure-directing properties[16] of the ionic liquid.

The suggested structure-directing effect of amine during the crystallization process was more pronounced at 280 °C. After 3 h heating in the presence of *n*-DPA (Table 1), the two AlPOs were converted to another one-dimensional molecular sieve, that is, $AlPO_4$-25[17] (ATV-type structure, FD = 19.9[10]) containing 8-MR pores (4.9 × 3.0 Å in size). This transformation also resulted in a decrease in pore size and an increase in FD. In contrast, in the absence of amine, the frameworks of AFI and AEL would collapse into the dense phase within 1.5 h at 280 °C. It is possible that the presence of amine inhibits the transformation of microporous $AlPO_4$ framework to the ultimate dense phase. This might be further evidence of a structure-directing effect of amine.

In conclusion, the addition of amine to the 1-butyl-3-methylimidazolium bromide ionic liquid affects the dynamics of the crystallization process and improves the selectivity of the crystallization reaction, leading to the formation of pure AFI and ATV structures. The amine may have a structure-directing effect along with the ionic liquid. This finding extends the usefulness of the ionothermal synthesis method by adding some potential reaction variables.

Acknowledgment. We thank PetroChina (Grant No. W050508-03-03) for financial support, and appreciate Prof. Mark Schlossman at the University of Illinois for helpful discussions.

Supporting Information Available: The details of the characterization (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(5) General synthesis procedure: A round-bottom flask was charged with [bmim]Br (30 g, 0.137 mol), H_3PO_4 (1.00 g, 0.010 mol, 85 wt % in water), $Al[OCH(CH_3)_2]_3$ (0.70 g, 0.003 mol), and HF (0.05 g, 0.002 mol, 40 wt % in water). Amine (0.005 mol) was added if required. Then the reaction mixture was heated to the crystallization temperature between 190 and 280 °C in an oil bath for as long as 5 h. After cooling to room temperature, the products were washed thoroughly with distilled water and acetone.
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JA061882Q