



Molecular sieve synthesis in the presence of tetraalkylammonium and dialkylimidazolium molten salts

Xin Sun, Jonathan King¹, Jennifer L. Anthony*

Department of Chemical Engineering, Kansas State University, Manhattan, KS, USA

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ABSTRACT

Both solvents and structure-directing agents are very important in molecular sieves synthesis. Tetra-butylammonium bromide, tetrabutylammonium hexafluorophosphate, tetrabutylammonium nitrate, tetrapropylammonium bromide, and 1-methyl-3-ethylimidazolium bromide were used to investigate the effect of molten salts/ionic liquids in dilute concentrations on the synthesis of zeolites. Products made include a microporous silicate with MFI-type framework and the layered silicate magadiite.

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1. Introduction

Since the discovery of stilbite ($\text{NaCa}_2\text{Al}_5\text{Si}_{13}\text{O}_{36} \cdot 14\text{H}_2\text{O}$), the first of a group of crystalline microporous aluminosilicates discovered over 200 years ago by the Swedish scientist Crönstedt, molecular sieves have found many applications in water softening, wastewater treatment, odor control, cracking catalysts in oil industry, etc. [1–7]. These stable, crystalline materials with nanometer-sized pores can have a wide range of chemical compositions, including silicate, aluminophosphate, or all-carbon molecular sieves, to name but a few [8–11]. Subsequently, there has been extensive research on the synthesis of new frameworks as well as trying to understand their mechanism of crystallization [12–15].

Crystalline molecular sieves traditionally are prepared using hydrothermal methods. A typical zeolite synthesis would consist of a mixture of water, a source of the framework atoms, a mineralizing agent (e.g. OH^- or F^-), and a structure-directing agent (SDA) [16–20]. Recently, Morris and co-workers developed an ionothermal synthesis method for several aluminophosphate molecular sieves, where an ionic liquid serves as the solvent and/or the structure-directing agent [21–23].

Both the solvent and the SDA are extremely important in the synthetic mechanism of the molecular sieves, with the role of the SDA being most widely studied. Structure-directing agents have several roles during the synthesis of zeolites. They can serve only as space-holders or pore-filling agents, they can have specific interactions

with the zeolite precursors that aid in directing the structure formation, or in some less common cases they can serve as templates for the final structure [24,25]. A proposed mechanism of structure-directing effect on the framework formation suggests that the precursors organize around the SDAs and subsequently assemble into crystalline structures [12,26,27]. As a result, different SDAs usually lead to various structures. For example, in the ionothermal synthesis of AlPOs, the larger imidazolium cation [bmim]⁺ leads to AFI structure which has a 12-ring channel, whereas, the smaller [emim]⁺ leads to AEL framework, which has 10-ring channel [28]. A large number of SDAs take the form of amines or tetraalkylammonium salts (e.g. [TPA][Br], DPA); the structures and sizes of those salts can be easily altered so as to cater to variety of microporous void shapes. These SDA cations are also commonly used in ionic liquids (ILs), such as 1-methyl-3-ethylimidazolium bromide ([emim][Br]) and tetramethylammonium 2,2,2-trifluoro-N-(trifluoromethylsulfonyl) acetamide ([TMA][TSAC]) [29]. Unlike typical structure-directing agents, the low melting points and good solvating properties also allow ILs to serve as the solvent in the synthesis reaction [30–33].

In this work, we replaced a traditional SDA (e.g. [TPA][Br], $T_{\text{mp}} = 270^\circ\text{C}$ [34]) with various salts while maintaining the same synthetic composition ratio. [TPA] and [TBA] are both quaternary ammonium cations and have been used as structure-directing agents in molecular sieves synthesis. They have been chosen to compare the effect of alkyl chain length of SDAs on formation of silicate materials. Salts with [TBA] as the cation and different anions are also used in order to investigate the influence of different anions on the framework. The authors also replaced [TPA][Br] with the common ionic liquid 1-ethyl-3-methylimidazolium bromide [emim][Br]. Two known materials were formed at the completion of the reaction depending on the salt used: either a porous silicate of MFI-type framework or the dense layered silicate magadiite.

* Corresponding author at: 1005 Durland Hall, Manhattan, KS 66502, USA. Tel.: +1 785 532 4321; fax: +1 785 532 7372.

E-mail address: anthonyj@ksu.edu (J.L. Anthony).

¹ Now at the Department of Chemical Engineering, University of California, Berkeley, CA, USA.

Table 1
Molar composition of reagents for preparation of magadiite and MFI in the presence of molten salts.

Product	SiO ₂	H ₂ O	NaOH	SDA	Time (h)	Temp. (°C)	Product type
Sample-1	1.00	24.76	0.195	0.081 [TBA][Br]	44	150	Magadiite
Sample-2	1.00	24.76	0.195	0.081 [TBA][PF ₆]	44	150	Magadiite
Sample-3	1.00	24.76	0.195	0.081 [TBA][NO ₃]	44	150	Magadiite
Sample-4	1.00	24.76	0.195	0.081 [TPA][Br]	44	150	MFI
Sample-5	1.00	24.76	0.195	0.081 [emim][Br]	44	150	Magadiite

2. Experimental procedure

Materials were prepared hydrothermally based on the method used to synthesize pure silica ZSM-5, a zeolite of MFI-type framework [35]. Water, salt (e.g. IL or SDA), base (e.g. NaOH), and silicon dioxide (e.g. Syloid 63 fumed silica) were combined in a molar ratio of 0.072 H₂O:0.030 SDA or IL:0.37 NaOH:9.2 SiO₂. The molten salts/ionic liquids used include tetrabutylammonium bromide ([TBA][Br], $T_{mp} = 102\text{--}104^\circ\text{C}$ [31]), tetrabutylammonium hexafluorophosphate ([TBA][PF₆], $T_{mp} = 244\text{--}246^\circ\text{C}$ [36]), tetrabutylammonium nitrate ([TBA][NO₃], $T_{mp} = 118\text{--}120^\circ\text{C}$ [37]), tetrapropylammonium bromide ([TPA][Br], $T_{mp} = 270^\circ\text{C}$ [34]), and 1-methyl-3-ethylimidazolium bromide ([emim][Br], $T_{mp} = 79^\circ\text{C}$ [38]). After stirring for 2 h, reaction mixtures were charged into Teflon-lined autoclaves, which were placed in an oven at 150 °C for 44 h afterwards. The white precipitate was carefully washed with water, followed by acetone wash (for [TPA][PF₆] only), and dried in air at room temperature. Sample powders were analyzed using an X-ray diffractometer (Bruker AXS D8 Advance), and the resulting patterns were compared to those available in the literature [39,40].

3. Results

Each of the synthesis mixtures with the five different IL/SDAs (shown in Table 1) yielded a powder product; their XRD patterns are shown in Fig. 1. Products synthesized in the presence of either tetrabutylammonium bromide ([TBA][Br]), tetrabutylammonium hexafluorophosphate ([TBA][PF₆]), tetrabutylammonium nitrate ([TBA][NO₃]), or 1-methyl-3-ethylimidazolium bromide ([emim][Br]) all show main XRD peaks at $5.55^\circ 2\theta$, $22.5^\circ 2\theta$, $25.8^\circ 2\theta$, $26.9^\circ 2\theta$, and $28.25^\circ 2\theta$, which are characteristic of magadiite [41]. However, in the case where tetrapropylammonium bromide ([TPA][Br]) is used as the SDA, the pattern is characteristic of MFI, as expected since the reaction composition and SDA used in (4) were comparable to those in reported MFI syntheses [42,43]. For comparison, Table 2 shows several previously reported synthesis conditions for both magadiite and MFI.

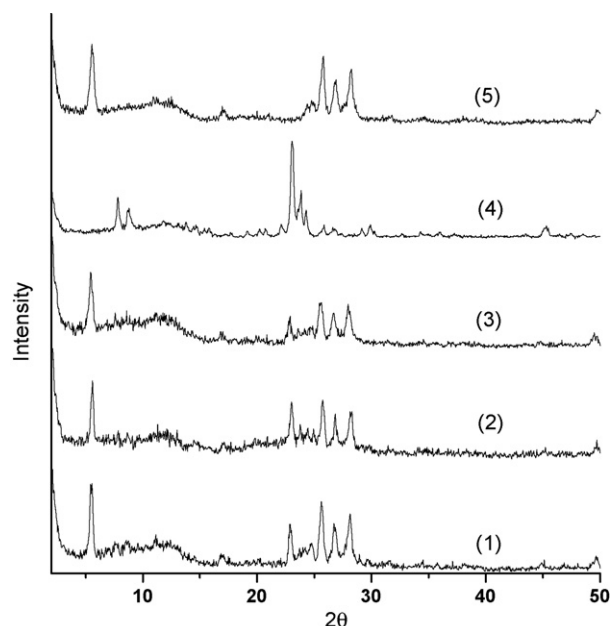


Fig. 1. XRD patterns of products (1)–(5). Their SDAs are (1) [TBA][Br], (2) [TBA][PF₆], (3) [TBA][NO₃], (4) [TPA][Br], and (5) [emim][Br].

4. Discussion

Among the five salts used, only [TPA][Br] yielded a porous pure silica zeolite with the MFI-type framework (Si₉₆O₁₉₂). MFI-type material has a three-dimensional pore system containing sinusoidal 10-ring channels and intersecting straight 10-ring channel [51,52], the structure of which is shown in Fig. 2a. [TPA] is the most common cation for the synthesis of MFI-type structures [53–56]. It has been reported that favorable van der Waals interactions between the organic structure-directing agent and hydrophobic silicon dioxide are the main thermodynamic driving forces for the

Table 2
Literature molar composition of reagents for preparation of magadiite and MFI.

Literature reference	SiO ₂	H ₂ O	NaOH	SDA	Other reagent	Time (h)	Temp. (°C)	Product type
[44]	1.00	16.67	0.333			42	150	Magadiite
[45]	1.00	18.50	0.230			18	170	Magadiite
[46]	1.00	20.00	0.200			48	150	Magadiite
[40]	1.00	33.33	0.111		0.222 Na ₂ CO ₃	72	150–160	Magadiite
[40]	1.00	20.00	0.067	0.750 PEG 200 ^a	0.133 Na ₂ CO ₃	24	150	Magadiite
[47]	1.00	58.00	0.280			96	150	Magadiite
[42]	1.00	22.03		0.108 [TPA][Br]	0.025 Al ₂ (SO ₄) ₃ 0.300 Na ₂ O 0.193 H ₂ SO ₄ 0.500 NaCl	144	180	MFI
[48]	1.00	200		0.8 [TPA][Br]	0.5 NEt ₃	96	130	MFI
[49]	1.00	38.00		0.100 [TPA][OH]		360	110	MFI
[39]	1.00	25.00	0.333		0.067 NaAlO ₂	24	180	MFI
[50]	1.00	58.33	0.277	0.750 PEG 200 ^a	0.167 Al ₂ O ₃	144	150	MFI

^a PEG 200: poly(ethylene glycol).

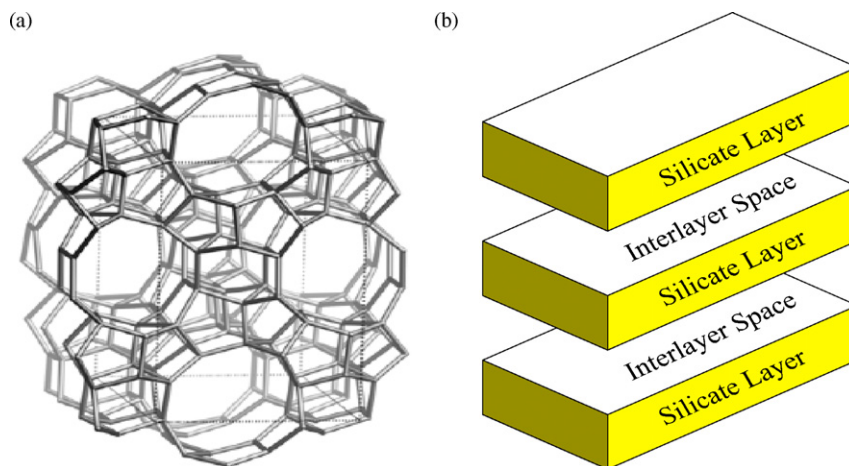


Fig. 2. Schematic diagram of (a) the structure of MFI [57] and (b) the structure of magadiite [58].

assembly of MFI-type or similar zeolites [12]. However, by making a slight change to the cation structure by lengthening the alkyl chains from propyl to butyl (e.g. [TBA][Br]), the MFI-type framework was no longer obtained. Clearly, the larger cation did not provide the necessary van der Waals forces to make MFI.

The syntheses with the remaining salts all resulted in the formation of magadiite ($\text{NaSi}_7\text{O}_{13}(\text{OH})_3 \cdot 4(\text{H}_2\text{O})$), which is a dense material with silicate layer. The terminal oxygen ions of magadiite are balanced by sodium ions located between silicate layers [59]. Schematic diagram of magadiite is illustrated in Fig. 2b. It is suggested that natural Na-magadiite was precipitated from the alkaline brines which were rich in silica, and low in alumina, the absence of which is of critical importance [41]. Due to magadiite's special structure, it can be used in detergent systems and catalyst support [59,60].

According to the literature, Na^+ -magadiite is typically synthesized hydrothermally at 150°C for 42 h with molar ratios ranging from 16 to 58 $\text{H}_2\text{O}:0.1$ to $0.3 \text{ NaOH}:1 \text{ SiO}_2$ [41,44–46]. It is noteworthy that in those reports magadiite can be synthesized without a structure-directing agent. In the current work, all of the precursors and solvents are heated at 150°C for 44 h and with synthetic compositions similar to the conditions employed in producing Na^+ -magadiite. In this respect, the addition of [TBA][Br], [TBA][PF₆], [TBA][NO₃] or [emim][Br] neither enhanced nor inhibited the formation of the magadiite; they merely served as cosolvents. Although the salts did not serve as structure-directing agents, they also did not interfere with the silica chemistry necessary for making the layered silicate. Layered silicates such as magadiite are not porous materials; however, they are recognized as being precursors to the synthesis of porous silicates [41,58]. The fact that dense layered silicates can be synthesized in the presence of ionic liquids bodes well for the possibility of also synthesizing a porous silicate in the presence of ILs.

It is worthwhile to point out that the XRD pattern of product (2) after washing with water only was not the same as that shown in Fig. 2. Although there are peaks characteristic of magadiite at $5.55^\circ 2\theta$, $22.5^\circ 2\theta$, $25.8^\circ 2\theta$, $26.9^\circ 2\theta$, and $28.25^\circ 2\theta$, additional peaks were observed at $8.5^\circ 2\theta$, $11.2^\circ 2\theta$, and $18.1^\circ 2\theta$, which can be seen in Fig. 3a. However, after the sample was washed in acetone for 24 h, additional peaks were no longer visible (Fig. 3b). Those additional peaks are characteristic of the salt [TBA][PF₆]; the XRD pattern of which is shown in Fig. 3c. Although [TBA][PF₆] did not serve as a SDA during the synthesis process, the high intensity peaks indicate it was present in the final post-synthesis product, possibly in the interlayer space of magadiite. Unlike the other salts used in this work, salts composed of the [PF₆] anion and large organic cations

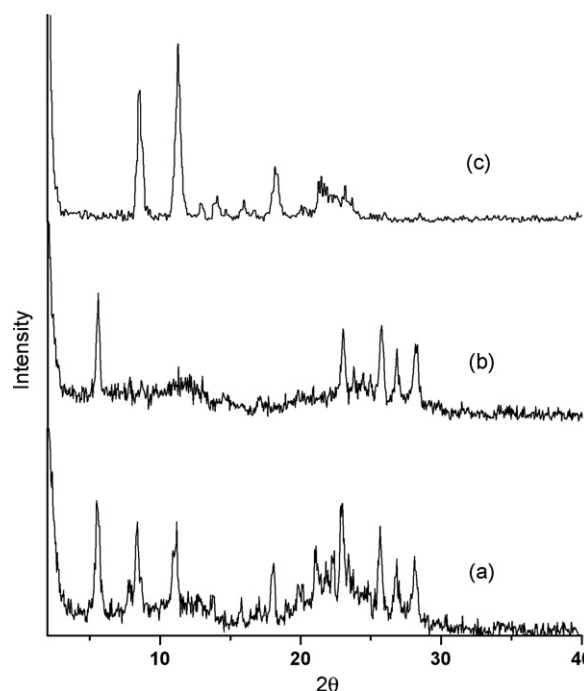


Fig. 3. XRD patterns of (a) water washed product-2, (b) water and acetone washed product-2, and (c) [TPA][PF₆].

are fairly hydrophobic and have a notably lower solubility in water [61–63], which required the use of another solvent (i.e. acetone) to wash the residual [TBA][PF₆] from the final layer.

5. Conclusions

In this paper, the role of different salts with common ionic liquid cations and anions was studied in the synthesis of silicate-based molecular sieves. In the presence of [TPA][Br], a common SDA for MFI, pure silica ZSM-5 is formed. However, with a little change to the alkyl branch of quaternary salts (e.g. [TPA][Br] to [TBA][Br]) another material, magadiite, whose synthesis commonly does not require the presence of SDA, is formed. This result affirms the importance of appropriate van der Waals forces between the precursor and structure-directing agent. Also demonstrated is that the addition of tetraalkylammonium salts to the magadiite reaction mixture does not inhibit the silica chemistry involved in the formation of

magadiite. This is a significant result because pillared layered minerals such as magadiite are often considered precursors to useful porous materials.

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