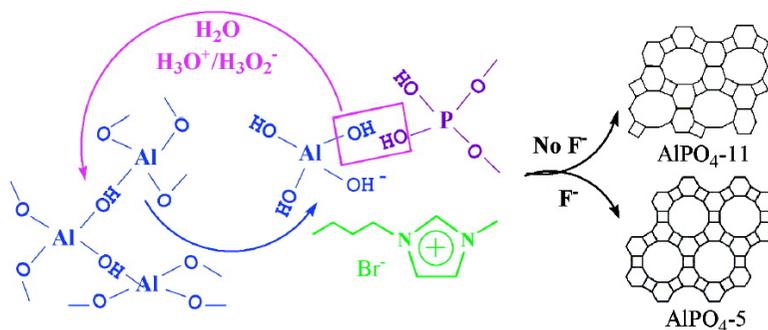


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Effect of Water on the Ionothermal Synthesis of Molecular Sieves

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Molecular sieves are three-dimensional open frameworks of corner-linked TO_4 tetrahedra ($T = \text{Si}, \text{Al}, \text{P}, \text{etc.}$).¹ They are extensively used in industry for ion-exchange, separation, gas adsorption, and, in particular, catalysis. Normally these materials are prepared under hydrothermal or solvothermal conditions.^{1,2} In 2004, Morris et al. reported a new ionothermal method, in which ionic liquids (ILs)³ were used instead of water or organic solvents.⁴ Ionothermal synthesis can be performed at ambient pressure in open vessels and is currently attracting great interest. In our laboratory, microwave-enhanced ionothermal synthesis is used,^{5a} and the effect of the addition of amines into the ionothermal synthesis is studied.^{5b}

A new synthetic method should have unique capabilities, such as the preparation of new structures or materials with particular morphologies, or the ability to address questions that are difficult to study using existing methods. An open issue in hydrothermal, solvothermal,^{1,2,6} and “dry”^{1,7} synthesis of molecular sieves is the determination of the effect of water on the crystallization process. Here, we use ionothermal synthesis to address this issue.

Ionothermal synthesis of molecular sieves is normally “wet” due to the usage of hydrous starting materials, such as aqueous solutions of H_3PO_4 and HF .^{4,5,8} Morris and co-workers prepared SIZ-3^{4a} in 1-ethyl-3-methylimidazolium bromide ([Emim]Br)⁹ IL. However, prebaking the mixture of Al, P, and F sources at 50 °C for 2 h led to the production of SIZ-4^{4a} in the same IL. The change in product structures was attributed to the amount of water present in the reaction mixtures.^{4d} Therefore, questions about the effect of water also exist in ionothermal synthesis. In the present work, we report quantitative studies of the effect of water on the synthesis process of aluminophosphate (AlPO_4)¹⁰ molecular sieves utilizing an ionothermal synthesis system in which AlPO_4 molecular sieves can be prepared without addition of water.¹¹ Anhydrous starting materials are used in the synthesis, such as $\text{NH}_4\text{H}_2\text{PO}_4$ (no crystal water), pseudoboehmite (AlOOH , 78.6 wt % Al_2O_3 , dried at 110 °C for 24 h in dry air), and NH_4F (no crystal water). Results indicate that addition of reagent quantities of water ($\text{H}_2\text{O}/\text{Al} = 1$, molar ratio) to this reaction system has a remarkable effect on the crystallization kinetics.

The two ILs most commonly used in previous ionothermal syntheses,^{4,5,8} [Emim]Br and [Bmim]Br,⁹ are selected as reaction media to study the effect of water in the present work. The method of heating could affect the crystallization process greatly.^{5a} Therefore, both conventional heating and microwave heating^{5a,12} are employed. In the case of [Emim]Br, AlPO_4 -11 is prepared under microwave heating (Figure 1), while SIZ-6^{4b} is produced when conventional heating is employed (see Table S1, Supporting Information). When [Bmim]Br is used as the reaction medium, AlPO_4 -11 is obtained in the absence of NH_4F (Figures 2A and 3A), while addition of NH_4F results in either pure AlPO_4 -5 (Figure 2B) or a mixture of AlPO_4 -11 and AlPO_4 -5 (Figure 3), depending upon the heating methods.

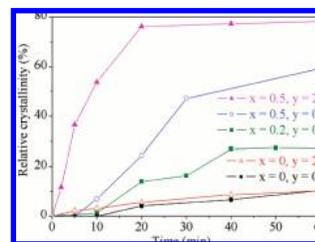


Figure 1. Crystallization curves of AlPO_4 -11 obtained in [Emim]Br under microwave heating at 200 °C. Initial gel composition: $1\text{AlOOH}:3\text{NH}_4\text{H}_2\text{PO}_4:x\text{NH}_4\text{F}:y\text{H}_2\text{O}:40$ [Emim]Br (molar ratio).

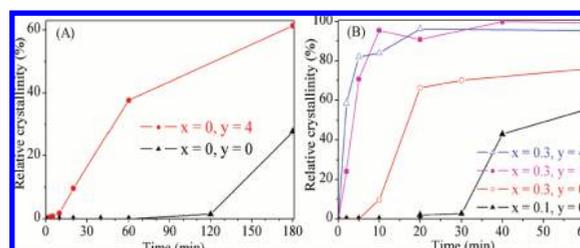


Figure 2. Crystallization curves of products obtained in [Bmim]Br under microwave heating at 200 °C: (A) AlPO_4 -11 in the absence of F^- and (B) AlPO_4 -5 in the presence of F^- . Initial gel composition: $1\text{AlOOH}:1.2\text{NH}_4\text{H}_2\text{PO}_4:x\text{NH}_4\text{F}:y\text{H}_2\text{O}:40$ [Bmim]Br (molar ratio).

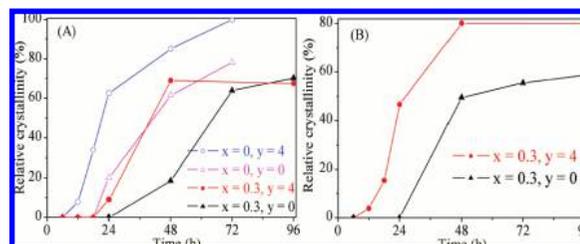


Figure 3. Crystallization curves of products obtained in [Bmim]Br under conventional heating at 200 °C: (A) AlPO_4 -11 and (B) AlPO_4 -5. Initial gel composition: $1\text{AlOOH}:1.2\text{NH}_4\text{H}_2\text{PO}_4:x\text{NH}_4\text{F}:y\text{H}_2\text{O}:40$ [Bmim]Br (molar ratio). Note that a mixture of AlPO_4 -5 (major phase) and AlPO_4 -11 (minor phase) is obtained in the presence of F^- .

F^- is usually used in the ionothermal synthesis of molecular sieves^{4,5,8} as well as in conventional synthesis.^{1,13} Therefore, the effect of water is studied both in the presence and in the absence of F^- . A reagent amount of NH_4F ($\text{NH}_4\text{F}/\text{Al} = 0.2$ or 0.3 , molar ratio) acts as a mineralizer to promote the crystallization kinetics (Figures 1 and 2). In addition to its mineralizing role, F^- may play a structure-directing role along with [Bmim]⁺ cations in the case of AlPO_4 -5, which is produced only in the presence of NH_4F (Figures 2 and 3). The existence of the additional peak at -23.5 ppm in the ³¹P MAS NMR spectrum of AlPO_4 -5 (see Figure S8,

Supporting Information) indicates that F^- is incorporated into the framework of $AlPO_4-5$.¹⁴

Water is added quantitatively into the reaction mixtures, which have different compositions and are crystallized under different conditions (Figures 1–3). Recent work indicates that strong interactions exist between water molecules and the anions of ILs,¹⁵ which could lead to the deactivation of water. In the present work, however, both the induction and growth time of crystallization curves are dramatically reduced after the addition of reagent quantities of water (Figures 1–3). This indicates that the water added to the reaction systems is unambiguously involved in the crystallization of the molecular sieves. The water promotes both the nucleation and the crystal growth process.

NH_4F and $NH_4H_2PO_4$ dissolve easily in the ILs used in the present work, so the solution-media transformation is most probable rather than solid-phase transformation. Formation of solution active species and their transformation into final products are the fundamental steps in solution-media transformation.^{1b,16} Hydrolysis and condensation are basic reactions in the formation and transformation of solution active species.¹ As a nucleophilic reagent, the added water would improve hydrolysis reactions and thereby facilitate the formation of solution active species.^{6b} Therefore, the induction time is reduced after the addition of water. Furthermore, H^+ or OH^- is also expected to induce hydrolysis and condensation reactions, depending on the pH.^{6b} Recent molecular simulations indicate that both H^+ and OH^- exist as hydrates, and the transport of these hydrates depends strictly on the involvement of water.¹⁷ Therefore, the added water could also promote the synthesis kinetics by promoting both the production and the transport of H^+ and OH^- hydrates. When no water is added, the induction time of the crystallization curve is quite long. This suggests that the formation of solution active species is the rate-controlling step of the overall crystallization process. A trace amount of water would be produced slowly in the reaction of $NH_4H_2PO_4$ with $AlOOH$. However, the content of self-generating water is so low that the solution active species form at an ultralow rate. After the induction period, the relative crystallinity increases sharply, which could be attributed to the release of more water in the condensation reactions.¹⁶ Thus, the synthesis of molecular sieves appears to be an autocatalytic process. Admittedly, a trace amount of water might have been introduced from other sources. However, compared with the water that we added, its amount and effect could be ignored.

In hydrothermal synthesis of molecular sieves, it is difficult to study the effect of water due to the presence of excess water. Under solvothermal conditions, addition of a certain amount of water has a marked effect on the crystal size of the products.^{6a} Ozin et al. studied systematically the effect of water by varying its amount (from that added with H_3PO_4 up to 6 times the molar quantity of the glycol) in a reaction system based on tetraethylene glycol and obtained a considerable range of $AlPO_4$ products.^{6b} It was suggested that the amount of water determined the extent of hydrolysis reaction and thereby the resulting structure types.^{6b} However, no results obtained at a water content lower than that added with H_3PO_4 were taken into account. Chen and Huang detected that ¹⁷O-enriched water induced bond breaking and re-forming of $Al-O-P$ by ¹⁷O solid-state NMR spectroscopy in the dry-gel conversion synthesis of $AlPO_4-11$.⁷ However, no attention was given to the effect of the amount of water present. In the present work, when no water is added, $AlPO_4$ molecular sieves are ionothermally produced at a low rate in the presence of only a trace amount of self-generating water. Addition of reagent quantities of water ($H_2O/Al = 1$, molar ratio) or NH_4F ($NH_4F/Al = 0.2$, molar ratio) results in greatly enhanced crystallization kinetics. Therefore, we conclude that the

presence of water or other polar substitutes is necessary for the successful synthesis of molecular sieves and that reagent quantities of these agents accelerate the hydrolysis and condensation reactions and, consequently, the crystallization kinetics. These results indicate the usefulness of ionothermal synthesis in the study of the effect of water on the crystallization process of molecular sieves.

In conclusion, the present work provides unambiguous evidence that water has a remarkable effect on the ionothermal synthesis of molecular sieves. Addition of reagent quantities of water can enhance the crystallization kinetics of molecular sieves greatly. Ionothermal synthesis allows one to address fundamental questions that are difficult to study in conventional methods of synthesis.

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Supporting Information Available: Details of the characterization. The materials are available free of charge via the Internet at <http://pubs.acs.org>.

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