Microemulsion-Directed Synthesis of Molecular Sieve Fibers

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The aluminum phosphate molecular sieve $AlPO_4$-5 with the AFI crystal structure was synthesized in a novel fibrous morphology through confined synthesis within water-in-toluene microemulsion droplets. The surfactant cetylpyridinium chloride with the cosurfactant butanol forms a thermodynamically stable single-phase microemulsion with the $AlPO_4$-5 synthesis gel at room temperature. Several pseudo-ternary phase diagrams were constructed to map the single-phase microemulsion region. The phase diagrams were used as a guide for hydrothermal synthesis at various microemulsion compositions. Crystallization of $AlPO_4$-5 was achieved at 180 °C either by conventional heating of the microemulsion for 6 h or microwave heating for 17 min. The crystals are much larger than the microemulsion droplets, so that the microemulsion does not simply act as a template, but rather directs crystal growth into fibers presumably by interacting with the surface of the growing crystal. The $AlPO_4$-5 crystal morphology changes from individual fibers to "fan-like" fiber aggregates as the ratio of $AlPO_4$-5 gel to surfactant increases. As the ratio of toluene to surfactant increases, nonporous Berlinite becomes the favored product due to partitioning of the structure-directing agent into toluene. Microwave heating produces smaller fibers and less nonporous $AlPO_4$ than conventional heating. The microemulsion approach presented is applicable to hydrothermal synthesis of a variety of zeolites and molecular sieves to potentially control crystal morphology.

Introduction

Zeolites and molecular sieves are materials whose crystalline frameworks form nanometer or subnanometer scale pores.[1,2] A variety of different crystal structures are known having a range of pore sizes.[2,3] Because the pore diameters are on a molecular scale, diffusion of molecules within the crystals can be restricted. Depending on the relative dimensions of the pores and molecules, diffusion within the pore may be prevented completely, allowed with restricted rotation, or allowed freely. These microporous materials are widely used in separation and catalysis because of their ability to discriminate between molecules on the basis of size or shape. Recent research has focused on emerging applications in areas such as optics, microelectronic devices, and even medical diagnosis where the ability to spatially orient molecules within the porous crystal is advantageous.[4,5] For example, incorporation of dye molecules into the channels of molecular sieve crystals enables the formation of microlasers.[6−8] Porous materials also can be used as low-dielectric materials in microelectronic devices.[9,10] An application in medical diagnosis is zeolite-enclosed metal ions used for magnetic resonance imaging (MRI).[11] One of the main limitations in building advanced devices containing molecular sieves or zeolites as components has been the ability to precisely control crystal size, shape, and orientation.

One promising route to control crystal size and shape is through confined synthesis from reagents dissolved in water-in-oil microemulsions. Under appropriate conditions, surfactants in oil−water systems will self-assemble to form thermodynamically stable microemulsion droplets.[12] These small droplets can be viewed as nano-reactors for synthesis of materials from aqueous reactions.[13,14] Microemulsions droplets are usually in the shape of spheres. However, different structures can also be formed such as cylinders, flat sheets, and bicontinuous structures.[12,15] Aqueous reactions that produce solid products may be confined within the droplets, and thus the size and shape of the product may be affected by

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confinement within the microemulsion.[13,14,16] Dutta and co-workers first attempted to synthesize zeolites within a water-in-oil microemulsion more than a decade ago but the microemulsion was unstable under hydrothermal conditions and did not significantly alter crystal growth.[17] Successful alteration of crystal growth by nucleation in microemulsions was first reported for a zincophosphate molecular sieve synthesized at room temperature.[18] Here we report a synthetic strategy that uses a microemulsion to affect the crystal morphology of a common molecular sieve, aluminum phosphate number five ($AlPO_4$-5), under normal hydrothermal synthesis conditions. The microemulsion approach provides a new synthetic route to zeolite nanocrystals that are of increasing interest,[19] and that may be deposited onto surfaces to create nanostructured films.[20,21]

Because microemulsions typically have droplet diameters much smaller than the wavelength of visible light, they can be characterized by the formation of an optically transparent single phase that can be identified visually. Usually at least four components are required for microemulsion formation; water, oil, surfactant, and cosurfactant.[15] For chemical reactions, the aqueous phase also contains the reagents used for synthesis. In the case of $AlPO_4$-5 synthesis, there are five components in the aqueous phase; an aluminum source, phosphorus source, water, mineralizing agent, and structure-directing agent. To simplify the characterization of microemulsion phase behavior in multicomponent mixtures, systems are usually treated as pseudo-ternary with “oil”, “aqueous”, and “surfactant” components.[12,15] In the present study, the “aqueous” phase was a standard $AlPO_4$-5 synthesis gel, containing water, aluminum triisopropoxide, phosphoric acid, triethylamine, and hydrofluoric acid.[22] The “surfactant” phase was a mixture of cetylpyridinium chloride and a short chain alcohol, and the “oil” phase was toluene. Several phase diagrams were determined visually and then used as a guide for selecting compositions for crystallization of $AlPO_4$-5 from the optically transparent single phase.

As with most common zeolites and molecular sieves, $AlPO_4$-5 crystallization is usually carried out under hydrothermal conditions ($T > 100$ °C). The elevated temperatures and pressures required for crystallization have limited the use of microemulsions in zeolite and molecular sieve synthesis because of the difficulty in maintaining a stable microemulsion.[17] Microemulsion-based synthesis has been successful with a class of zincophosphate molecular sieves that crystallize readily near room temperature.[18,23,24] In the present study microemulsions were formed at room temperature with all reagents used for synthesis to avoid the difficulty in maintaining stability at elevated temperatures. After aging for some time at room temperature, the microemulsion was heated to hydrothermal conditions to initiate crystallization. Our preliminary study demonstrated that this approach dramatically alters $AlPO_4$-5 crystal size and shape, producing a fibrous morphology not previously observed.[25] Previous studies have demonstrated the ability to “tailor” crystal dimensions of $AlPO_4$-5 during hydrothermal synthesis by adjusting the gel composition, but the traditional synthesis route never produced a fibrous morphology.[26] The highly anisotropic morphology afforded by microemulsion-based synthesis may allow oriented deposition onto substrates to form nanoporous thin films useful in membranes and optics.[27−29] Our preliminary study was based on only a single microemulsion composition. The present study expands upon the initial work by determining several phase diagrams of microemulsion formation with the $AlPO_4$-5 synthesis gel. Reactions were conducted over a wide range of microemulsion compositions in the single-phase region. The results show that the morphology and crystal structure of $AlPO_4$-5 varies widely with microemulsion composition. Some improvements were made to the synthetic procedure in our initial study to more reproducibly obtain $AlPO_4$-5 fibers in high yield. A series of control experiments were also conducted to explore whether the individual components of the microemulsions are influencing crystal morphology through adsorption onto the growing crystal.

Several studies have shown that microwave heating offers advantages over conventional heating during zeolite and molecular sieve synthesis, including reduced reaction times and improved crystal quality.[30,31] Materials produced by conventional heating have larger crystals but usually have a wide size distribution and higher concentration of byproducts.[7] Microwave heating offers more rapid crystallization than conventional heating and it is believed more nuclei are generated simultaneously, thus the growth of the crystals is homogeneous.[31] Microwave heating of microemulsions also has the added advantage that many oils are transparent to microwaves so that aqueous droplets are selectively and rapidly heated. For each microemulsion composition examined, parallel crystallization studies were conducted with microwave versus conventional heating to examine the effect of heating on crystal structure and morphology.

Experimental Section

Materials. Phosphoric acid (85%), triethylamine (99.5%), butanol (99.4%), toluene (99.5%), hydrofluoric acid (48%), cetylpyridinium chloride (CPC, 98%) and aluminum triisopro-

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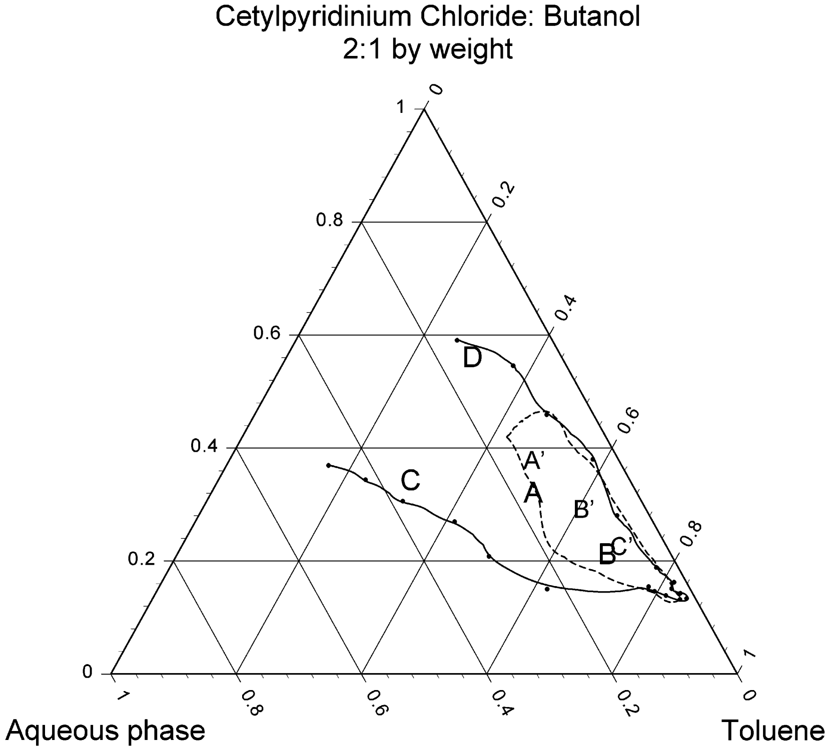

Figure 1. Phase diagrams with the surfactant CPC and cosurfactant butanol in the ratio of 2 to 1 by weight. The region enclosed in the black line has double the standard molar ratio of structure-directing agent (1.2:1.0 triethylamine/ phosphoric acid). The dashed-line region represents standard molar ratio of triethylamine in the aqueous phase (0.6:1.0 triethylamine/phosphoric acid). A–D are compositions chosen for hydrothermal synthesis with double the molar ratio of triethylamine. A′-C′ are compositions chosen for hydrothermal synthesis with the standard molar ratio of triethylamine.

poxide (99.99%) were purchased from Aldrich and used as received. Because of its sensitivity to moisture, aluminum triisopropoxide was stored in a desiccator.

Determination of Phase Diagrams. Measurement of the single-phase region of microemulsion formation was described previously.[25] The molar ratio of the components in the aqueous phase was kept constant and based on a synthesis gel composition for $AlPO_4$-5 from the literature.[22] For standard condition, the aqueous mixture is composed of water, aluminum triisopropoxide, phosphoric acid, triethylamine, and hydrofluoric acid in a molar ratio of 50:0.8:1.0:0.6:0.5. The phase diagram was also investigated with double the molar ratio of triethylamine (1.2 mol per mol phosphoric acid). First, the aqueous $AlPO_4$-5 synthesis gel was formed and stirred at room temperature for 4 h. In a second vial, CPC, butanol, and toluene were added. The $AlPO_4$-5 synthesis mixture was added in increments to the second vial. After each addition of the aqueous mixture, the vial was stirred for a few minutes before visual observation. As the aqueous mixture was added, there was a sharp transition from a turbid mixture to an optically transparent single phase. Further addition of the aqueous mixture eventually led to the return of a turbid multiphase mixture. The single-phase region can be mapped on a ternary phase diagram by repeating the process with different toluene/ surfactant weight ratios. The phase diagram was used as a guide in selecting different compositions within the optically transparent single phase region for hydrothermal synthesis.

Hydrothermal Synthesis. Deionized water, phosphoric acid, and triethylamine were first mixed together. It is important to mix triethylamine and phosphoric acid together first to allow the acid–base reaction and minimize the solubility of triethylamine in the oil phase by formation of a salt with phosphoric acid. Then, cetylpyridinium chloride, butanol, and toluene were added, and the mixture was shaken for 1 min to disperse the surfactants. At this point, a clear single-phase microemulsion had formed. The microemulsion was stirred overnight at room temperature. Then the microemulsion was put on ice for 5–10 min prior to adding aluminum triisopropoxide to get better crystallization.[32] Aluminum triisopropoxide was then added and the mixture was shaken vigorously for 2 min then aged at room temperature for 2 h. Hydrofluoric acid was then added and the microemulsion was aged for another 2 h at room temperature. The optically transparent, single-phase microemulsion was then transferred to a Teflon vessel for hydrothermal synthesis.

For control experiments without the microemulsion, all aqueous components except aluminum triisopropoxide and hydrofluoric acid were mixed at room temperature. The mixture was then placed on ice for 5–10 min prior to addition of aluminum triisopropoxide. After adding aluminum triisopropoxide, the mixture was shaken for 2 min and stirred for 2 h at room temperature. Hydrofluoric acid was then added and the mixture was aged an additional 2 h before hydrothermal synthesis.

Conventional Heating. The Teflon-lined vessel (45 mL, model 4744, Parr Instrument Company) was wrapped in heating tape then heated to 180 °C and kept at this temperature for 6 h without stirring.[22]

Microwave Heating. The microemulsion was heated in a microwave oven (Milestone Ethos Plus, with 6 100-mL Teflon vessels) to 180 °C over 2 min and kept at 180 °C for 17 min without stirring. The maximum power output of the microwave was adjusted to 500 W.

For both heating methods, the product was collected by centrifugation after the temperature of the liquid decreased to room temperature. The liquid was then transferred to a 28-mL centrifuge tube and centrifuged at the speed of 14 500 rpm for 30 min. The collected solid was then washed with ethanol twice with the same centrifugation conditions. Finally, the product was dried overnight in a vacuum oven at 50 °C.

Characterization. The morphology of the products was examined with scanning electron microscopy (LEO 982 FE-

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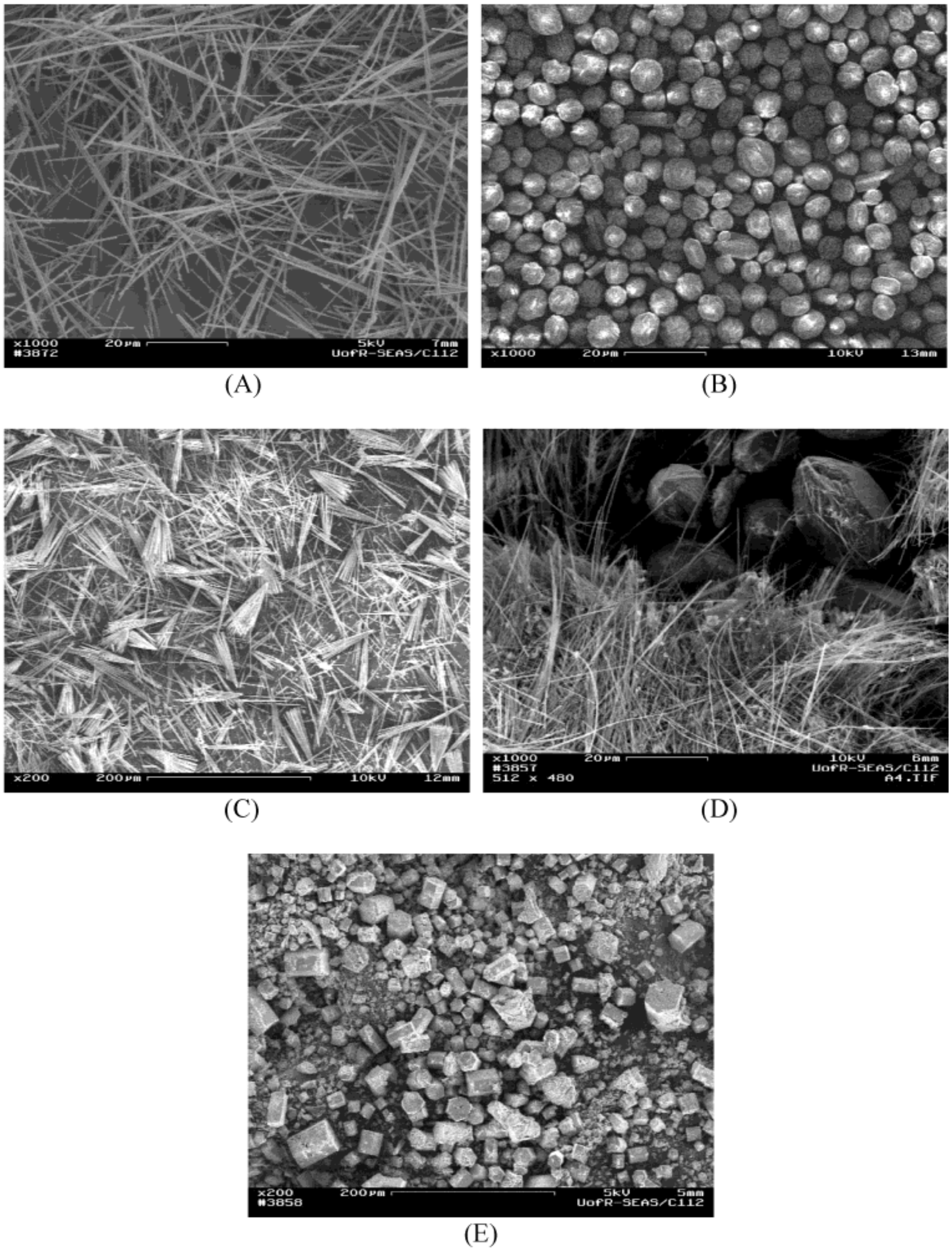

Figure 2. Products from conventional heating (6 h at 180 °C) with double the standard amount of triethylamine. Figure 2A–D correspond to microemulsion compositions A to D, respectively, from Figure 1. Figure 2E is the control experiment without the microemulsion. The scale bars are 20 microns for A, B, and D; 200 microns for C and E.

SEM) after coating with 800–1000 Å of metal (Au 60%, Pd 40%). The crystal structure was determined by powder X-ray diffraction (Philips PW3020) with an integration time of 2 h and a step size of 0.02 degree/3 s.

Results

Figure 1 shows the phase diagram for the surfactant CPC and cosurfactant butanol in the ratio of 2:1 by weight. The area between the lines on the diagram is where the single-phase microemulsion forms. Two single-phase regions are shown corresponding to two different molar ratios of triethylamine structure-directing agent in aqueous phase. Phase behavior was determined using the standard molar ratio from the literature of 0.6 mol triethylamine per mol phosphoric acid and double the standard ratio (1.2 mol triethylamine per mol phosphoric acid). The larger single-phase region (enclosed with black line) corresponds to double the standard amount of structure-directing agent. The differences in the two phase diagrams are likely due to pH changes in the aqueous phase which can strongly affect phase behavior. There is an acid–base equilibrium between triethylamine and phosphoric acid in the synthesis gel. The pH will thus be strongly dependent on the ratio of triethylamine to phosphoric acid. The ammonium salt formed when triethylamine reacts with phosphoric acid is soluble only in the aqueous phase. However, the unprotonated triethylamine is soluble in toluene. Therefore, there is also likely an equilibrium partitioning of triethylamine between the oil and aqueous phases that can affect pH as well as change the actual triethylamine concentration in the aqueous phase. We did not investigate triethylamine partitioning or the effect of pH on phase behavior in detail. However, triethylamine and phosphoric acid were mixed together to ensure salt formation prior to the addition of toluene to minimize the solubilization of triethylamine in the oil phase. The bold letters A−D on the phase diagram represent compositions chosen for hydrothermal synthesis within the single-phase region with twice the standard molar ratio of triethylamine. Similarly, A′−C′ are the compositions chosen for hydrothermal synthesis within the single-phase region with the standard synthesis gel. The points were selected to sample a wide range of single-phase microemulsion compositions.

The crystal morphologies obtained by hydrothermal synthesis from the microemulsions with conventional heating are shown in Figure 2. Figure 2A−D correspond to compositions A−D, respectively, from Figure 1. Figure 2E is the control experiment using traditional hydrothermal synthesis without the microemulsion, which shows hexagonal columns with wide size distribution in the range from 5 to 40 μm wide and 5 to 55 μm long. As in our preliminary study,[25] composition A (49 wt % toluene, 33 wt % CPC/butanol, and 18 wt % synthesis gel) produces crystals in the shape of long fibers (Figure 2A), which range from 20 to 70 μm long and from 250 to 700 nm wide. The products obtained for composition B (70 wt % toluene, 20 wt % CPC/butanol) have spherical or football-like shapes with sizes from 5 to 20 μm (Figure 2B). Synthesis at composition C (30 wt % toluene, 34 wt % CPC/butanol) also produces fibrous crystal morphology (Figure 2C). The morphology of these particles is similar to those synthesized at composition A (Figure 2A) except that many of the fibers are aggregated together in a “fanlike” formation. The product obtained from composition D (30 wt % toluene, 56 wt % CPC/butanol) is a mixture of fibers and football-shaped crystals. The fibers are thinner than those obtained at composition A and in some cases appear to bend.

Powder X-ray diffraction was used to investigate the crystal structure of samples shown in Figure 2A−E. The diffraction patterns are given in Figure 3A−E, and correspond to crystals shown in Figure 2A−E, respectively. The patterns shown in Figure 3A and C are that of the AFI crystal structure of $AlPO_4$-5, and are consistent with the pattern of the control experiment shown in Figure 3E. The diffraction pattern in Figure 3B is that of berlinite, the aluminum phosphate iso-structural analogue of alpha quartz. Figure 3D has features of both the AFI and berlinite patterns and thus indicates that the sample is a mixture of berlinite and $AlPO_4$-5. By comparison of Figures 2 and 3, it can be seen that the $AlPO_4$-5 crystals are fibrous, whereas the berlinite crystals are football-shaped or near spherical.

Berlinite is a dense phase material slightly more thermodynamically stable than $AlPO_4$-5.[33] In fact, we have observed that the $AlPO_4$-5 fibers undergo structural transformation to berlinite during the synthesis. For the reaction conducted at the composition B in Figure 1, the collected product is a mixture of berlinite and $AlPO_4$-5 fibers when the reaction time is reduced to 2 h (data not shown). The fraction of fibers observed gradually decreases as reaction time is increased. At a reaction time of 6 h, fibers are no longer observed and the product is pure berlinite (Figures 2B and 3B).

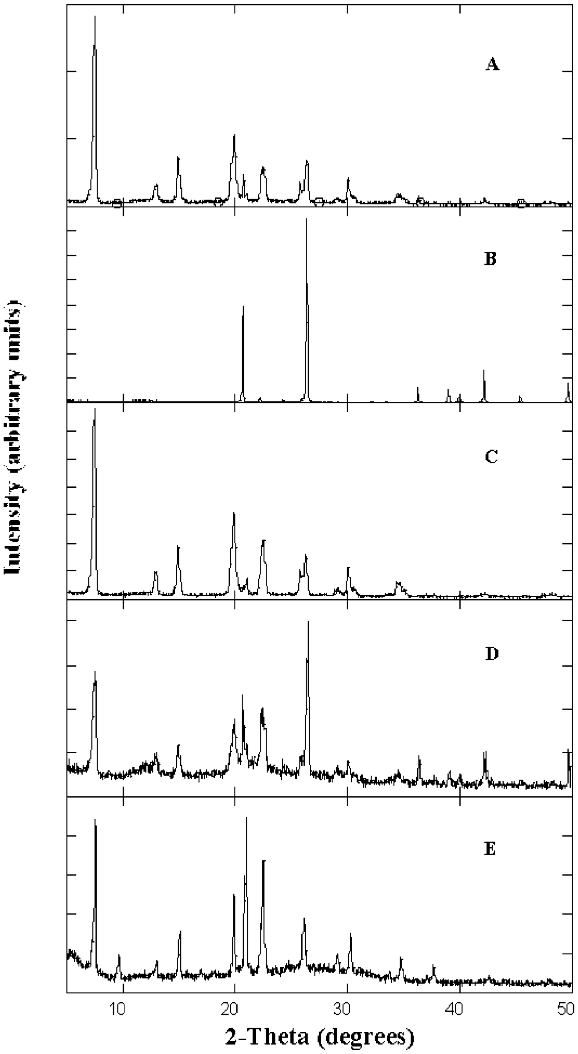

Figure 3. (A−E) X-ray diffraction patterns for products shown in Figure 2A−E, respectively.

Because of the complex nucleation and growth mechanism of molecular sieves, the results are often influenced by many factors. For example, keeping the autoclave vessel agitated or static sometimes leads to different crystal structures in the synthesis of zeolite Beta.[34] In our investigation, we found that under some conditions stirring with a magnetically coupled stir bar can influence crystal quality and in some cases results in a different crystal structure. Stirring during the heat-up period has little effect as long as the reactor is maintained static after reaching 180 °C. However, if the vessel is stirred at 1100 rpm throughout the reaction, the product at the microemulsion composition of point A (Figure 1) is transformed from nanoporous $AlPO_4$-5 to dense phase berlinite.

For the hydrothermal synthesis conducted in a microwave oven, $AlPO_4$-5 fibers were obtained for all four compositions A−D as shown in Figure 4A−D. Some fibers produced at composition A with microwave heating reveal the same fanlike morphology as those pro-

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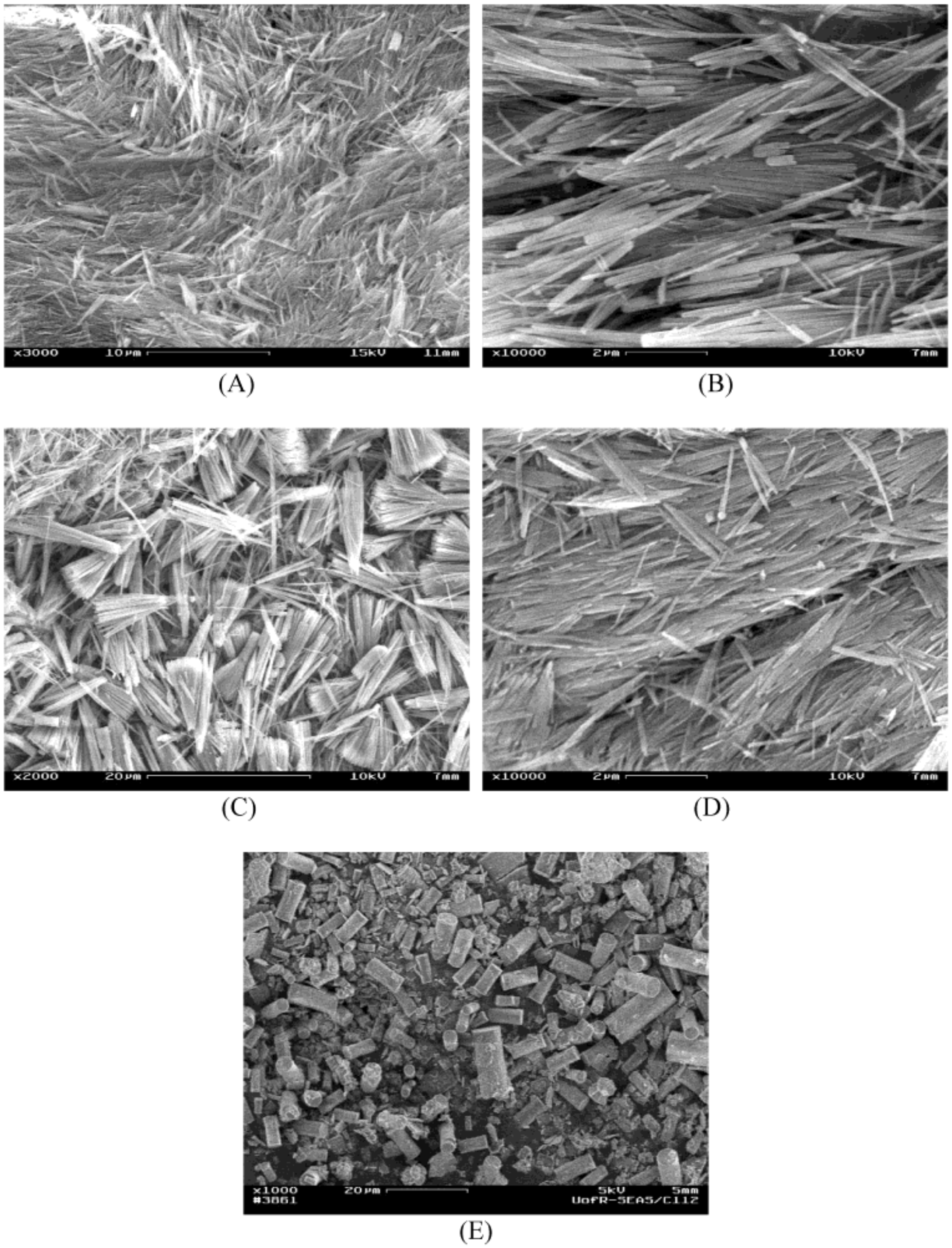

Figure 4. Products from microwave heating (17 min at 180 °C) with double the standard amount of triethylamine. Figure 4A–4D corresponds to microemulsion compositions A to D, respectively, from Figure 1. Figure 4E is the control experiment without the microemulsion. The scale bars are A 10 μm; B 2 μm; C 20 μm; D 2 μm; and E 20 μm.

duced at composition C with conventional heating. By tuning the maximum power output and the time required to heat to 180 °C as described in the Experimental Section, the number of aggregated fibers could be suppressed to a low level. For composition C, many fanlike fiber aggregates were observed. For compositions B and D, the resulting materials are also $AlPO_4$-5 fibers but appear to have poorer crystallization. There is amorphous material in the product, as determined by electron microscopy. The size of the fibers is around 2–4 μm in length and ~150 nm in width for compositions A, B, and D. The fanlike shaped fibers have the largest particle size: around 10 μm long and up to 500 nm wide. Figure 4E is the control experiment without the microemulsion. Unlike the fibers obtained for all compositions with microemulsion, the $AlPO_4$-5 crystals appear in the shape of circular columns with the size up to 20 μm in length and 8 μm in width. The X-ray diffraction patterns for all five reactions are consistent with the AFI structure and are shown in Figure 5A–E. For Figures 3E and 5E, a small peak at angle 2θ of approximately 10 degrees is observed. This peak is consistent with $AlPO_4$-8 and may come from a small amount of side product. The coexistence of two phases has been observed in the literature.[7]

The single-phase microemulsion region becomes smaller by changing the molar ratio of triethylamine to the standard value of 0.6 mol per mol phosphoric acid (dashed line in Figure 1). Three points were chosen for hydrothermal synthesis to represent the whole single-phase region. The compositions are point A′ (50 wt % toluene, 35 wt % CPC/butanol), point B′ (60 wt % toluene, 30 wt % CPC/butanol), and point C′ (68 wt % toluene, 24 wt % CPC/butanol). All three reactions

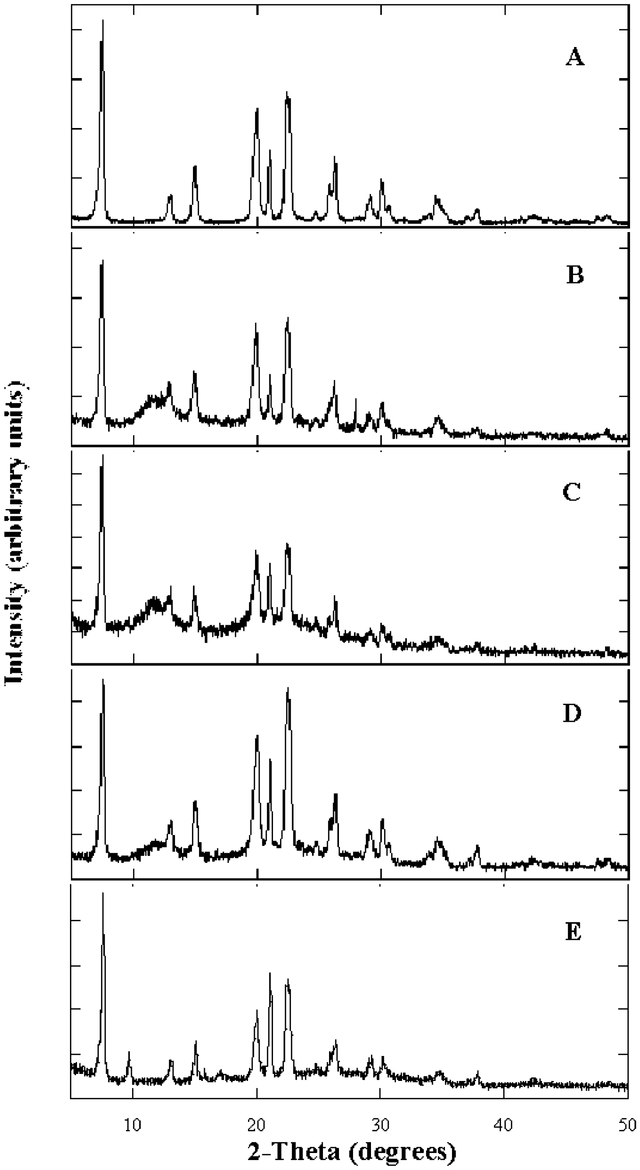

Figure 5. (A−E) X-ray diffraction patterns for products shown in Figure 4A−E, respectively.

produced berlinite by conventional heating. Figure 6A is a selected picture for composition C′. The control reaction without the microemulsion produced hexagonal $AlPO_4$-5 crystals 4−15 μm wide and 30−70 μm long with some multiply twinned crystals (Figure 6B). By microwave heating, pure $AlPO_4$-5 crystals were produced for composition A′ mostly in the shape of circular columns with a small amount of fibers (Figure 7A). For compositions B′ and C′, the products also contain columns and fibers (not shown). However, the X-ray diffraction shows that the products from compositions B′ and C′ contain an impurity of cristobalite. Cristobalite is a dense-phase material with a slightly higher enthalpy of formation than berlinite.[33] Figure 7B shows that the control experiment produced multiply twinned crystals in the formation of "dumbbell" and "half-dumbbell" shapes. The twinned crystals also appear as hexagonal columns in some cases. The crystals are approximately 20 μm long and 10 μm in diameter, which is very similar to the dimensions of the product obtained for the control experiment by microwave heating with a double amount of triethylamine.

A very small single-phase region can be formed when the weight ratio of CPC to butanol is changed to 3:1 with double standard molar ratio of triethylamine. A reaction from this microemulsion (48 wt % toluene, 40 wt % CPC/butanol) demonstrated a poor crystallization for conventional heating. There were fibers with a large amount of amorphous material and some crystals of berlinite and cristobalite. However, pure $AlPO_4$-5 was obtained by microwave heating. The image (Figure 8) revealed small fibers with lengths from 1 to 2 μm and widths from 30 to 55 nm.

Discussion

The mechanism of nucleation and growth of nanoporous materials is a complex process of simultaneous chemical reactions and self-assembly.[1,35] The triethylamine "directs" the crystal growth into the metastable AFI structure of $AlPO_4$-5. In addition to the structure-directing agent influencing crystal structure, confinement within the microemulsion affects the overall crystal morphology. However, the microemulsion does not act as a simple "template" inside which the crystal grows. The dimensions of the crystals produced by the reaction are many times larger than the typical dimensions for microemulsion droplets of around 5−100 nm.[36] Thus, the crystals must continue to grow outside of the microemulsion droplets. It is clear from the data, however, that confinement of the gel within the microemulsion has a strong impact on the overall crystal morphology. In particular, microemulsion confinement tends to "direct" the growth of $AlPO_4$-5 crystals into a fibrous morphology. The $AlPO_4$-5 fibers were first reported in our preliminary communication.[25] To our knowledge, the fibrous morphology has been observed only in this microemulsion-based synthesis. The linear nanopores within the $AlPO_4$-5 crystals are oriented along the long axis of the fibers.[3,25] The fibers thus offer intriguing possibilities of producing "pseudo single crystals" by oriented deposition onto surfaces.

Although it is clear that the microemulsion influences crystallization, it is unclear at what stage in the reaction the microemulsion directs crystallization into the fibrous morphology. The mechanism of crystal nucleation and growth for zeolites and molecular sieves is still an open area of investigation. It is generally accepted that zeolites and molecular sieves crystallize either in solution via a solution-mediated transport mechanism or within solid gel particles through reorganization of an amorphous hydrogel precursor.[1] Recent investigation of the synthesis of Zeolite A shows that even in an optically transparent synthesis gel there are nanometer-scale amorphous precursor particles that act as nucleation sites.[35] Once the nanometer scale amorphous particles completely crystallized, further growth of Zeolite A occurred through solution transport of soluble species in an Ostwald ripening type mechanism.[35] For $AlPO_4$-5, the synthesis gel is initially milky white in appearance due to light scattering from amorphous gel particles. When dissolved in the microemulsion, however, the gel appears transparent because it is confined in

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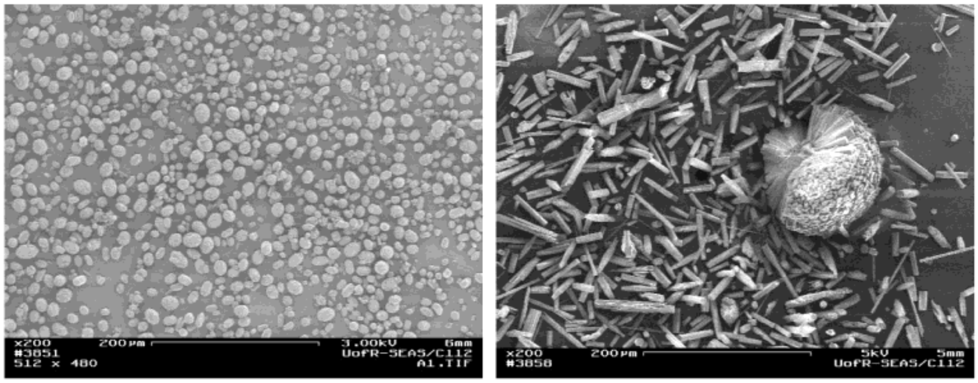
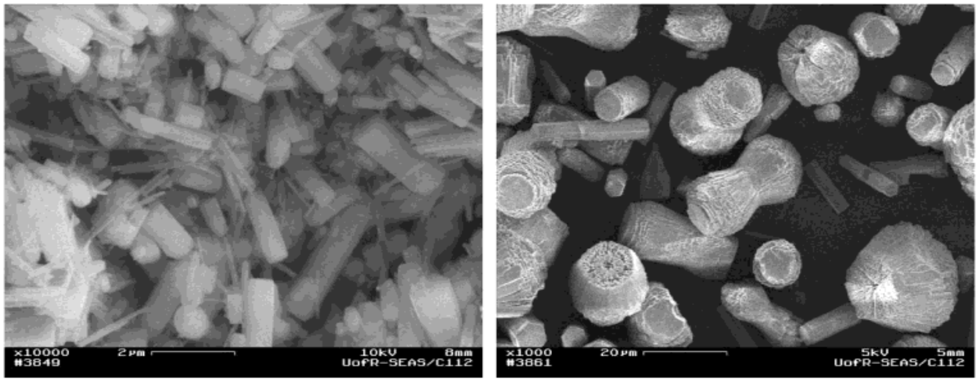


(A) (B)

Figure 6. Products from conventional heating (6 h at 180 °C) with standard triethylamine concentration. 6A is from a microemulsion with composition C′ in Figure 1. 6B is the control experiment without the microemulsion. The scale bars are 200 μm.



(A) (B)

Figure 7. Products from microwave heating (17 min at 180 °C) with standard triethylamine concentration. Figure 7A is from a microemulsion with composition A′ in Figure 1. Figure 7B is the control experiment without the microemulsion. The scale bars are A, 2 μm; and B, 20 μm.

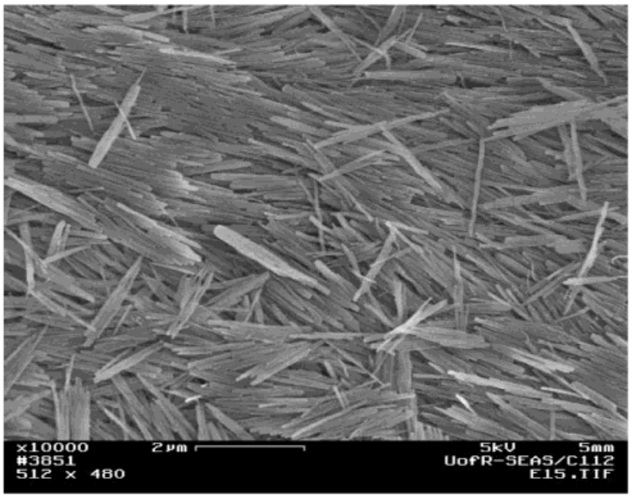


Figure 8. $AlPO_4$-5 fibers crystallized by microwave heating (17 min at 180 °C) with double the standard amount of triethylamine from a microemulsion with the weight ratio of CPC/butanol is 3:1. The scale bar is 2 μm.

microemulsion droplets that are much smaller than the wavelength of visible light. It is possible that the microemulsion influences the nucleation process by confinement of the amorphous gel precursor particles at the earliest stages of the reaction, even during the aging step at room temperature. The characterization of microemulsions structure is possible by techniques such as X-ray diffraction. Future study of the microemulsion structure at room temperature may shed light on the effect of confinement on nucleation. However, the growth of $AlPO_4$-5 crystals will prevent the study of the microemulsion structure at the reaction conditions.

It is clear from the results that the components of the microemulsion influence crystal growth during the hydrothermal synthesis period because both crystal shape and size are dramatically altered. It should be noted that all phase behavior measurements were made at room temperature, whereas crystal growth occurs at 180 °C. Because the reactions must be contained in a sealed Teflon autoclave, visual observation was not possible and it is unknown whether the microemulsion maintains stability under hydrothermal conditions. In fact, the final crystal size is larger than the microemulsion droplets themselves so that growth must continue outside of the microemulsion. Crystal growth in the latter stages of the reaction may occur through solution transport of soluble species either through intermicellar exchange with surfactant aggregates, or by solution transport in bulk water droplets if the microemulsion is destabilized.

One way that the microemulsion may influence crystal growth is through the interaction of one or more of the components with certain faces of the growing crystal so that growth is directed primarily in one direction. Adsorption of solvent or other additives onto one face of a crystal can slow growth on that face and

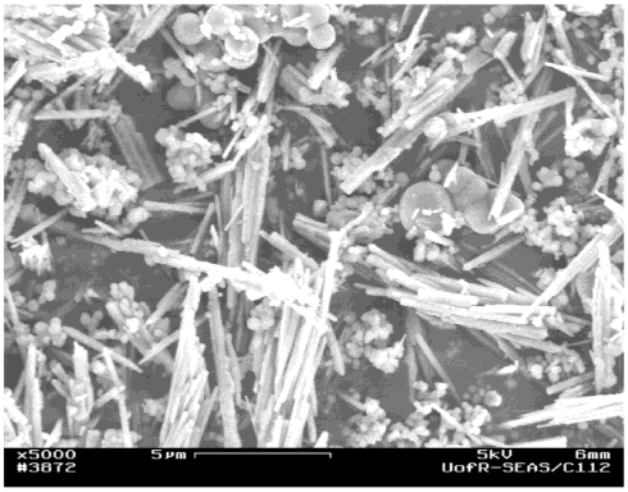


Figure 9. Fibers and amorphous material produced by microwave synthesis control with CPC only (no microemulsion formation). The scale bar is 5 μm.

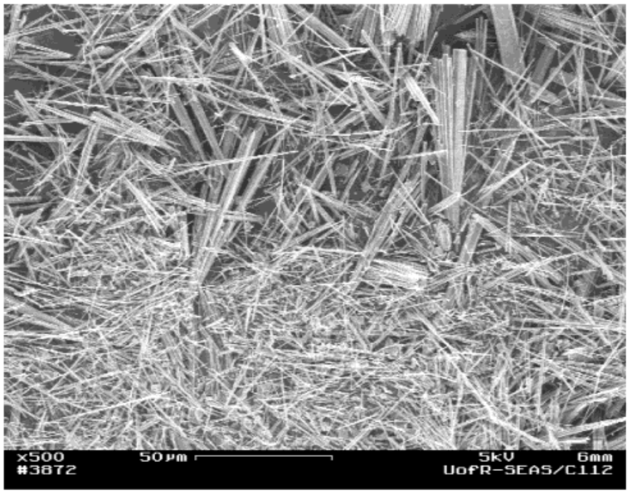


Figure 10. Fibers synthesized by conventional heating with toluene and butanol only. Note the broad crystal size distribution. The scale bar is 50 μm.

may be exploited to "engineer" crystal morphology.[37−39] Growth normal to faces with strongly adsorbed compounds is retarded, resulting in a relative increase in the surface area of that face. A somewhat similar mechanism was proposed for the growth of zincophosphate sodalite crystals nucleated in reverse microemulsions at room temperature.[18] It was shown that zincophosphate sodalite grows primarily along the (110) or (111) faces and it was proposed that surfactant adsorption and interaction with reverse micelles controls growth.

The surfactant and oil phase for microemulsion has three components (toluene, butanol, and CPC) and it is possible that one or a combination of these may influence crystal growth by preferential adsorption on one of the crystal faces. To explore whether adsorption was influencing crystal growth, a series of six control experiments were conducted (three reactions containing only one of the microemulsion components, and three reactions containing only two of the microemulsion components). The six control experiments were conducted using both microwave and conventional heating. The majority of these control experiments produced a large fraction of amorphous material and the few $AlPO_4$ crystals that were visible had the "dumbbell" or hexagonal column morphologies described above for experiments without the microemulsion (not shown). There were two notable exceptions, however, where fibrous $AlPO_4$ crystals were produced. By microwave heating, the addition of the surfactant CPC alone caused some small fibers a few μm in length to form with a significant fraction of the product remaining amorphous (Figure 9). Conventional heating with CPC alone produced an entirely amorphous product. By conventional heating, fibers with a large size distribution (widths ranging from 500 nm to more than 3 μm) were produced with the addition of toluene and butanol without CPC (Figure 10). The size distribution is larger than any observed for products synthesized from the microemulsion. Microwave heating with toluene and butanol did not produce fibrous crystals, but rather produced hexagonal columns and dumbbell shapes. Although some fibers can be produced by adding only one or two components of the microemulsion, the crystal quality is generally poor. In the one case were crystallization appears good, the particle size distribution is large.

When only one or two components are added, the synthesis gel is inhomogeneous. There is either an excess solid surfactant phase or an excess oil phase present because all three components are required to form a single-phase microemulsion. Formation of the microemulsion is necessary to obtain fibrous $AlPO_4$-5 crystals with low levels of impurities and a narrow size distribution. It seems likely that the microemulsion affects both nucleation and growth events. Confinement of the amorphous gel particles can affect nucleation and allow the components of the microemulsion to adsorb on the growing crystal surface. Surface adsorption can then affect crystal growth. The control experiments discussed above indicate that CPC, butanol, and toluene all play a role in adsorbing onto the crystal surface to direct morphology. The most important components for producing fibers appear to be different depending on the type of heating used for synthesis. CPC alone produces some fibers during microwave synthesis, but not with conventional heating. Toluene and butanol produce fibers during conventional heating without CPC, but no fibers are formed without CPC by microwave heating. It is still unclear at this stage why heating methods result in different morphologies with microwave versus conventional heating in control experiments. Further studies are needed to clarify these phenomena.

Comparison of the phase diagram in Figure 1 to the products in Figures 2 and 4 shows that the formation of "fanlike" aggregates of fibers are favored as the microemulsion composition is shifted to a higher fraction of the aqueous phase. Inspection of these crystals with high-magnification electron microscopy shows that the fibers extend radially from a common point of attachment. The mechanism of formation of these multiply twinned crystals is unknown at this point. A series of microwave reactions show that the "fanlike" aggregates are favored as the microwave power is increased and the heatup time is decreased. A maximum power of 500

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(37) Berkovitch-Yellin, Z.; van Mil, J.; Addadi, L.; Idelson, M.; Lahav, M.; Leiserowitz, L. *J. Am. Chem. Soc.* **1985**, *107*, 3111.
(38) Lahav, M.; Leiserowitz, L. *Chem. Eng. Sci.* **2001**, *56*, 2245.
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W with a heatup time of 2 min was found to minimize twinning of the fibrous crystals during microwave synthesis. It is likely that many factors are at play in determining the formation of the “fanlike” structures including the growth rate, degree of supersaturation, and rate of adsorption of compounds onto the growing crystal faces.

The overall amount of structure-directing agent required to form nanoporous $AlPO_4$-5 is higher for the microemulsion-based synthesis than that for the control experiment without the microemulsion. By comparing the phase diagram in Figure 1 to the crystallization results in Figures 2 and 6, it can be seen that the product composition changes from $AlPO_4$-5 to berlinite as the microemulsion composition is adjusted closer to the toluene end of the phase diagram. Because unprotonated triethylamine is soluble in toluene, it is likely that some of the triethylamine partitions from the aqueous phase into the oil phase. Thus, as the microemulsion composition is changed to higher toluene concentration, there is less triethylamine in the aqueous phase. With insufficient structure-directing agent, nanoporous crystal formation is not possible, and dense-phase berlinite is produced. The hypothesis that triethylamine partitioning to the toluene phase reduces the concentration of triethylamine in the aqueous phase also explains why, when the standard molar ratio of triethylamine to phosphoric acid is used, conventional heating produces berlinite at all compositions investigated, even though $AlPO_4$-5 is produced by traditional hydrothermal synthesis without microemulsions. It is interesting to note that berlinite was never formed in reactions conducted in microwave. Another dense-phase material, cristobalite, was observed in microwave synthesis but it is unclear at this time why cristobalite is preferred over berlinite. It may be due to the much shorter reaction time of 17 min versus 6 h for conventional heating, as berlinite has the lowest free energy and would be favored at long reaction times.

Conclusions

The molecular sieve $AlPO_4$-5 was synthesized in a new fibrous morphology by hydrothermal synthesis in a water-in-oil microemulsion. The surfactant cetylpyridinium chloride with cosurfactant butanol solubilizes the standard aqueous $AlPO_4$-5 synthesis gel into a single-phase microemulsion in toluene that is thermodynamically stable at room temperature. Several pseudo-ternary phase diagrams were measured to map the single-phase microemulsion region at room temperature and used as a guide for hydrothermal synthesis. By changing the composition of microemulsions, the crystal size and shape could be varied. The $AlPO_4$-5 crystal morphology changed from individual fibers to “fanlike” aggregates of fibers as the ratio of aqueous gel to surfactant was increased. As the ratio of toluene to aqueous gel increased, the formation of the dense-phase aluminum phosphate Berlinite was favored. As the organic structure-directing agent is not only soluble in aqueous phase but also in the toluene phase, the concentration of the structure-directing agent in the aqueous phase decreases with increasing amount of toluene and dense-phase aluminum phosphate becomes the favored product. Doubling the standard triethylamine concentration allows $AlPO_4$-5 synthesis from the microemulsion.

Similar trends in crystal morphology were observed using microwave synthesis and conventional synthesis. The crystal size was typically smaller for microwave synthesis and there was less dense-phase aluminum phosphate formation. Microwave energy offers faster crystallization time, 17 min versus 6 h for conventional synthesis. Microwave heating of water-in-oil microemulsions also offers the unique advantage of selective heating of the microemulsion droplets. Because many oils are transparent to microwaves, the aqueous droplets are rapidly and selectively heated within the oil.

The mechanism of the modification of crystal morphology is not simple templating by confinement within microemulsion droplets. The microemulsion may influence crystal nucleation by influencing the amorphous precursor particles that form at room temperature and act as nucleation sites. The final crystal size is larger than the microemulsion droplets, so continued growth must occur through solution transport outside of the microemulsion. Control experiments show that preferential adsorption of some of the components of the microemulsion onto certain crystal faces may influence crystal growth. The novel fibrous $AlPO_4$-5 morphology may allow oriented deposition onto substrates for formation of membranes or optical devices. The microemulsion approach presented here should be applicable to the synthesis of many zeolites and molecular sieves that are synthesized under hydrothermal conditions to form novel crystal morphologies.

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