

Crystal Growth of Faujasitic Microporous Zincophosphate Crystals Using Reverse Micelles as Reactants

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The present study deals with the crystallization of zincophosphate-X (ZnPO-X) from zinc- and phosphate-containing reverse micelles. ZnPO-X has the same topology as faujasite (zeolites X,Y). Reverse micelles are microdroplets of water stabilized in a hydrocarbon medium with the help of surfactants. Successful synthesis of ZnPO-X was possible using reverse micelles made with cationic surfactant dimethyldioctylammonium chloride (DODMAC), 1-decanol as cosurfactant and isoctane as solvent. The composition of the reactants in the water pools of the reverse micelles was about four times more dilute than that in a conventional hydrothermal synthesis. The dilution is necessary since a significant fraction of the water in the reverse micelles is used up for hydrating the headgroups of the surfactant. The crystals appear without the formation of an intermediate amorphous phase. Upon mixing the zinc and phosphate reverse micelles, collisions between them result in exchange of reactants. We propose that only a small fraction of these reverse micelles have the proper supersaturation conditions for nucleation of ZnPO-X. These nuclei then grow into crystals by incorporating nutrients from non-nucleated reverse micelles. In a typical synthesis, only about 15–20% of the possible yield of ZnPO-X was obtained and the rest of the material remained suspended in the organic phase. This clear suspension was an excellent seed solution for ZnPO-X, even from reverse micelle compositions that would not produce ZnPO-X. Using this seed solution and reaction columns of different lengths, crystals of different sizes could be obtained. Reverse micelles as reactants appear to provide a novel way to control supersaturation and thereby influence crystal growth of microporous structures in ways that cannot be readily done with conventional procedures of synthesis of these important materials.

Introduction

Microporous materials include large groups of solids of varying chemical composition as well as porosity. The framework structure is made up of interconnecting T–O–T' bonds where T and T' can be Si, Al, P, As, Ga, Fe, Co, Zn, B, and a host of other elements.^{1,2} Materials with Si–O–Al bonding in the framework are called zeolites and find extensive industrial use. Synthesis of new frameworks has led to new technologies, and considerable effort is being extended in their discovery.^{3,4} Microporous materials are typically synthesized by a hydrothermal process. Study of the nucleation and crystal growth as well as development of new synthesis conditions is an active area of research.⁵ Crystal growth of these materials is a complicated process. Various spectroscopic probes, including Raman, NMR spectroscopies, small-angle X-ray, and neutron scattering has been used to study the mechanism of zeolite crystal growth.^{6–8}

Certain ionic and nonionic surfactant molecules dissolved in hydrocarbon solvents can solubilize water by forming thermodynamically stable microaggregates, gen-

erally designated as reverse micelles or microemulsions. The use of reverse micellar systems in materials synthesis has resulted in a wide range of size-quantized dispersed inorganic nanoparticles.⁹ For example, metallic,¹⁰ semiconductor,¹¹ calcium carbonate,¹² silica,¹³ titanium oxide,¹⁴ and hydroxyapatite¹⁵ have been made. Several crystal morphologies can be formed from synthesis in reverse micelles, for example, cylindrical copper particles,¹⁶ cubic BaSO₄ particles,¹⁷ rod-like and ellipsoidal BaCO₃ particles,¹⁸ tabular shaped and filaments of BaSO₄ particles,¹⁹ and nanowires of BaCO₃.²⁰ The limited thermal stability of reverse micelles requires that reactions using this medium be carried out at ambient temperatures. The most extensively used surfactant for reverse micelle synthesis is sodium bis(2-ethylhexyl) sulfosuccinate (AOT).

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We have reported the synthesis of zincophosphate sodalite using AOT reverse micelles.^{21,22} The zincophosphates were chosen because their synthesis can be carried out under mild conditions.²³ However, all attempts at synthesizing open microporous frameworks, such as the analogue of faujasite, zincophosphate X (ZnPO-X), using AOT reverse micelles were unsuccessful.²⁴ Numerous synthesis reports for inorganic materials using AOT reverse micelles all have dealt with straightforward precipitation chemistry.^{9–20} In the case of microporous framework synthesis, the environment for nucleation and crystal growth is considerably more restricted and the AOT reverse micellar environment was not appropriate for synthesis. This led us to investigate other surfactants, and we have recently reported that the cationic surfactant dimethyldioctylammonium chloride (DODMAC) can be used for reverse micelle based synthesis of ZnPO-X.²⁵

In this paper, we report an optimized synthesis of ZnPO-X using DODMAC-based reverse micelles, including the use of 1,4-diazabicyclo[2.2.2]octane (DABCO) as a structure-directing agent. We propose that in reverse micelle based synthesis, only a fraction of the reverse micelles have the right supersaturation conditions for formation of nuclei, and that these nuclei then grow into crystals by incorporating nutrients from non-nucleated reverse micelles. This process has allowed us to explore seeded synthesis more typical of conventional crystal growth processes in contrast to hydrothermal synthesis of microporous materials.

Experimental Section

Materials. The surfactant Bardac-LF-80 which contains about 80% of dioctyldimethylammonium chloride (DODMAC) in an ethanol/water solution was a gift from Lonza, Inc. (Fair Lawn, NJ). Isooctane (HPLC grade, Fisher), zinc nitrate hexahydrate (Aldrich, 98%), H₃PO₄ (AR Grade, Mallinckrodt, 85%), 1,4-diazabicyclo[2.2.2]octane (DABCO) (Aldrich, 98%), sodium hydroxide pellets (NaOH) (Baker Analyzed), and 1-decanol (Aldrich, 99%) were used as received. The surfactant DODMAC was concentrated by evaporation under reduced pressure and dried under vacuum overnight.

Preparation of Micellar Solutions. The micellar solutions were prepared by the injection method, which involved injecting a known volume of aqueous solution of the reactants into the surfactant solution and resulting in formation of a single phase. The surfactant solution used was 0.2 M DODMAC and 0.33 M 1-decanol in isooctane. Results on two different reverse micellar compositions are being reported in this paper. Composition A was made with two reverse micellar solutions, involving 0.16 M Zn(NO₃)₂ as one solution and 0.11 M NaOH, 0.58 M DABCO, and 0.27 M H₃PO₄ solution as a second solution. Composition B was made with three reverse micellar solutions: 0.2 M Zn(NO₃)₂ as the first solution, 0.11 M NaOH and 0.27 M H₃PO₄, as the second solution, and 0.58 M DABCO as the third solution. In a typical reverse micelle preparation, 100 mL of surfactant solution was placed in a bottle, 2 mL of an aqueous solution containing the appropriate reactants was added, and the bottle was vigorously hand shaken for about 1 min and then kept aside to equilibrate at room temperature (25 °C). A different micelle solution was made with each set of reactants. After 24 h of equilibration, the reverse micelle reactant solutions were used for synthesis. No phase separation was observed at any stage of the reverse micelle solution preparation.

Preparation of Zincophosphate-X. The zinc- and phosphate-containing reverse micellar solutions were mixed in various ratios as outlined in the text. All the reactions were carried out at room temperature (25 °C). The column experiments were done in a glass column of 12.6 mm i.d. and varying lengths, as discussed below. It was necessary to silylate the glass tubes with a dilute solution of octadecyltrichlorosilane in toluene in order to prevent the growth of crystals on the glass surface.

Characterization. Micelle size was monitored by a quasi-elastic dynamic light scattering (DLS) method. These experiments were carried out using a digital correlator from Brookhaven Instruments (model BI-9000 digital correlator) with an argon ion laser (Coherent) operating at 514 nm. All experiments were performed at 25 °C with a laser power of 200 mW at a scattering angle of 90°. Prior to light-scattering experiments, dust particles were filtered out from the micellar solutions using a 0.45 μm Teflon membrane filter. By use of software supplied by the vendor, particle sizes were obtained by using the method of cumulants.

The X-ray power patterns were determined with a Rigaku, D-Max-2B X-ray diffractometer using nickel-filtered Cu Kα (λ = 1.5405 Å) radiation. Particle sizes and morphology were determined by scanning electron microscopy (SEM) using a JEOL JSM-820 scanning microscope. Prior to examination, the samples were mounted with double-sided carbon paste tape on aluminum or copper pegs and coated with a film of evaporated gold.

Results

Optimization of Conventional Synthesis. Detailed studies of the crystallization of zincophosphates from zinc- and phosphate-containing solutions, including the synthesis of the open pore faujasitic ZnPO-X, have been reported.^{23,26–28} DABCO has also been reported as the templating agent in the synthesis of ZnPO-X.²⁹ Since reverse micelle synthesis needs to be carried out at ambient temperature and previous hydrothermal synthesis of ZnPO-X was reported at low temperatures, we needed to optimize the reaction conditions. The optimum procedure involved mixing two solutions, a 0.8 M Zn(NO₃)₂·6H₂O aqueous solution and a solution containing 0.43 M NaOH, 2.33 M DABCO, and 1.13 M H₃PO₄. Upon mixing equal volumes of these solutions at room temperature (25 °C), a white gel was immediately formed. Within 2 h, complete settling of the product was observed. The isolated product had the characteristic octahedral-shaped morphology and diffraction patterns as zincophosphate-X crystals reported in the literature.²⁹

Preparation and Properties of Reverse Micelles. Reverse micelle formation by the surfactant dioctyldimethylammonium chloride (DODMAC) in isooctane using 1-decanol as cosurfactant has been reported.^{30,31} The two typical methods for preparation of reverse micelles include either equilibration of the hydrocarbon and water phase or injection of the required amount of water into the hydrocarbon. In this study, we have primarily focused on the injection method of preparation of reverse micelles, whereas our earlier work has used the equilibration method.^{21,22} The advantage of the injection method is that the composition of the aqueous phase in the reverse micelle is well-defined, since all of the solution is taken up in the organic medium, though the choice of the aqueous composition has to be well controlled. On the other hand,

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Table 1. Composition of Reactants Used for ZnPO-X Synthesis

conventional synthesis	aqueous solution used to prepare micellar solution	
	composition A	composition B
[Zn ²⁺] = 0.8 M	[Zn ²⁺] = 0.16 M	[Zn ²⁺] = 0.20 M
[Na ⁺] = 0.43 M	[Na ⁺] = 0.11 M	[Na ⁺] = 0.11 M
[PO ₄ ³⁻] = 1.13 M	[PO ₄ ³⁻] = 0.27 M	[PO ₄ ³⁻] = 0.27 M
[DABCO] = 2.33 M	[DABCO] = 0.58 M	[DABCO] = 0.58 M

the equilibration method is simpler, since the water uptake is controlled by the equilibrium between the organic and aqueous phases, though the composition of the aqueous phase in the micelle may be different from the aqueous solution.

To optimize the synthesis of ZnPO-X, we have investigated several reverse micellar compositions. Two of these are presented here. These involved reaction between a two-micelle system (referred to as composition A), one containing zinc and the other the phosphate along with the structure-directing agent. The second system involved reaction between three micelles (referred to as composition B), a zinc, a phosphate, and a structure-directing agent micelle. The concentrations of the various constituents of the reverse micelles for these two compositions are shown in Table 1 along with typical compositions used in the conventional hydrothermal synthesis.

All the reverse micelle solutions formed by the injection method were found to be visually stable against phase separation for several weeks. Dynamic light scattering experiments show that the diameters of the zinc- and phosphate-containing reverse micelles were 8 and 6 nm, respectively, for composition A. The size of the reverse micelles was monitored by dynamic light scattering over a period of 4 weeks and remained constant during this period.

Zincophosphate-X Formed by Reaction of Zinc and Phosphate Micelles. (a) Reaction with Two Reverse Micelles. Reaction was carried out by mixing zinc and phosphate micelles (composition A) with volume ratio of 1:1 and placing the container aside after gentle shaking, avoiding foam formation. The reaction mixture remained clear throughout the reaction. After about 8 h of reaction, particles were found at the bottom of the reaction vessel. This settling process was complete in 3–4 days. The products were separated by centrifugation and washed. Figure 1 shows the characteristic powder diffraction and electron micrograph of the products, typical of ZnPO-X. The yields of the products were in the range of 15–20%, indicating that a significant fraction of zinc and phosphate species were still present in the organic medium.

(b) Reaction with Three Reverse Micelles. By use of composition B, ZnPO-X was obtained only when the volumes of the micellar solutions were in the ratio of 3:4:4 for zinc, DABCO, and phosphate solution, respectively. The morphologies of the crystals were similar to that obtained from composition A. When the reaction was carried out by mixing zinc, phosphate, and DABCO reverse micelle solutions with a volume ratio of 1:1:1, the earliest appearance of a solid product was delayed until 2 days. As seen from the X-ray diffraction (XRD) and scanning electron microscopy (SEM) in Figure 2a, ZnPO-X was not produced in this reaction. We have not characterized the solid product further. The compositions from which ZnPO-X could be obtained were in a reasonably narrow range.

Seeded Synthesis in the Reverse Micellar System. ZnPO-X crystals grown from the reaction composition A

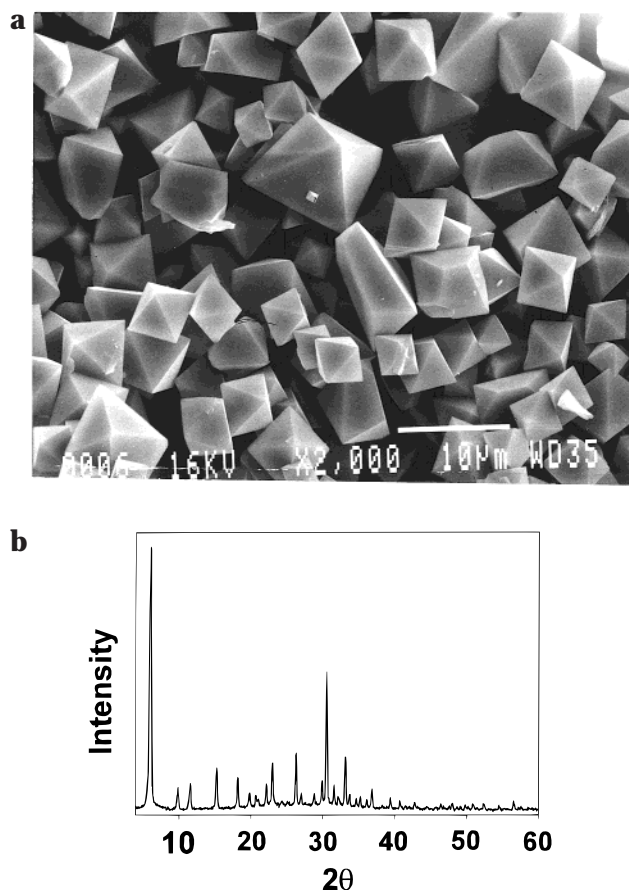


Figure 1. (a) XRD pattern and (b) SEM image of ZnPO-X obtained from the reverse micelle reaction of composition A.

were washed well and added to a fresh mixture of zinc and phosphate reverse micelles (composition A), and crystal growth was examined in a rotating cell. The use of the rotating cell allowed the crystals to be suspended for longer periods of time.²² The SEM image of the products obtained is shown in Figure 3. It is observed that the seed crystals do not grow further, instead a new crop of small crystals of uniform crystal size grow on the surface of the seed crystals.

In another experiment, ZnPO-X crystals were grown from the reaction composition A and, after crystallization, the solids were filtered out. The mother liquor was used as seed solution and added to the 1:1:1 volume ratio of the reactants from composition B, a composition that does not form ZnPO-X. However, upon addition of the mother liquor, product appeared within hours. The diffraction pattern and the SEM pictures are shown in Figure 2b. Clearly, ZnPO-X is being formed, promoted by the mother liquor addition. The crystal growth was monitored by dynamic light scattering methods over a period of time. The results are presented in Figure 4 and indicate that the size of the initial clusters is of the order of 15 nm and grew rapidly to micrometer sizes within an hour.

To obtain information on the nature of the particles that were present in the mother liquor, isolation of these particles was attempted by disrupting the reverse micelles by treatment with acetone followed by centrifugation. Figure 5 shows the SEM of these particles along with the diffraction pattern. These particles do not have the ZnPO-X structure and are agglomerated with sizes greater than 1 μm, whereas light scattering indicates that the system from which they were extracted were of

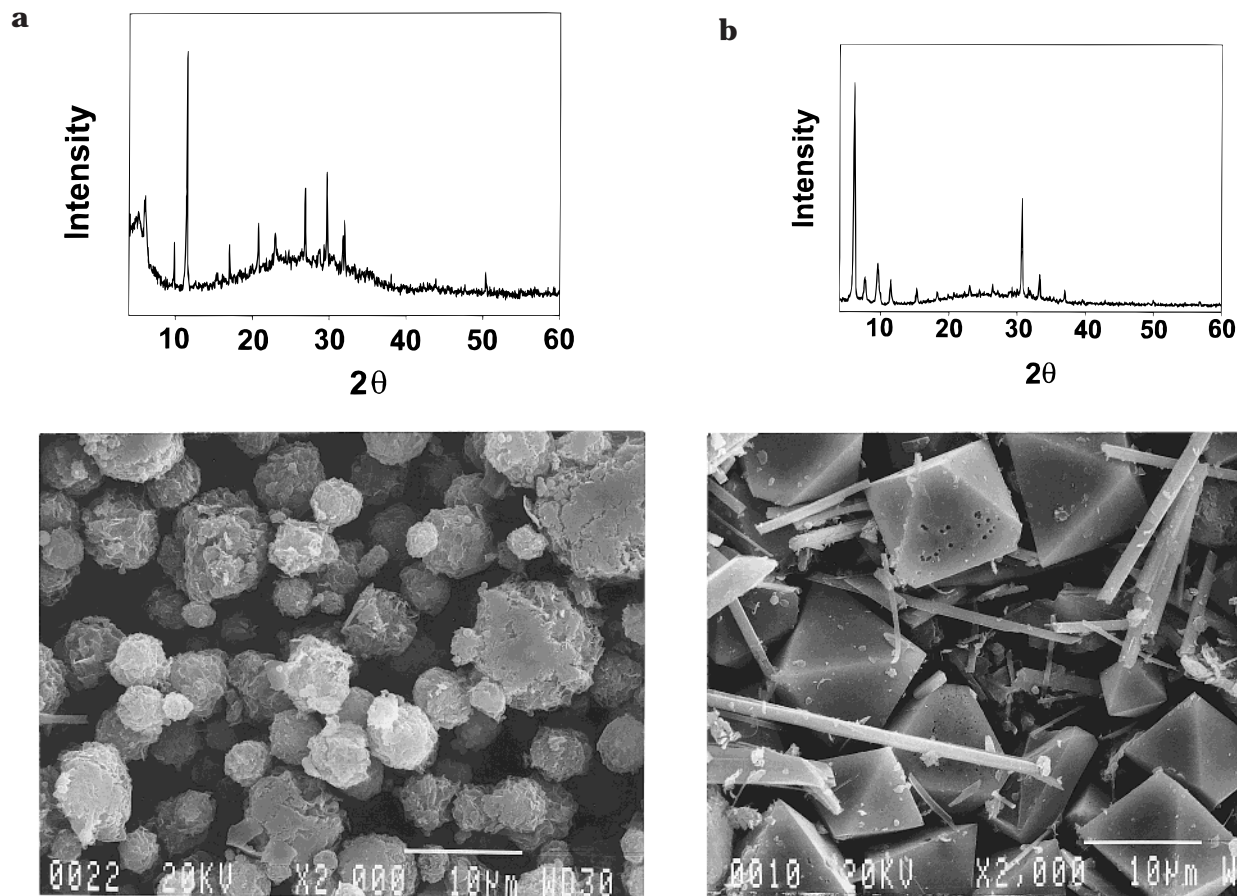


Figure 2. XRD and SEM images of the product made from (a) composition B (1:1:1 ratio) and (b) composition B (1:1:1 ratio) with mother liquor as a seed solution.

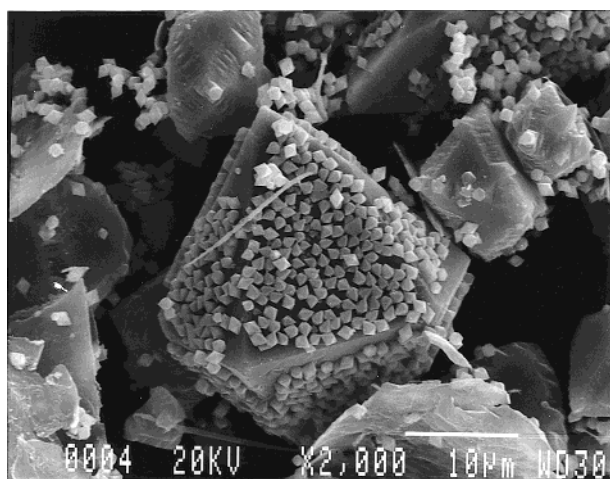


Figure 3. SEM image of ZnPO-X obtained with seed crystals using a rotating cell and composition B in 1:1:1 ratio.

the order of 15 nm. When these isolated particles were used as seeds with composition B, no ZnPO-X was formed. It appears that the extraction process is changing the nature of the particles present in the mother liquor.

Crystal Growth in Columns. The mother liquor from a completed composition A synthesis was added to composition B (volume ratio 1:1:1) in narrow columns of varying lengths. Three such experiments were performed with columns of height 0.71, 1.78, and 2.62 m. Products were collected from the bottom of the column after 1 day for the two shorter columns and after 2 days for the longer

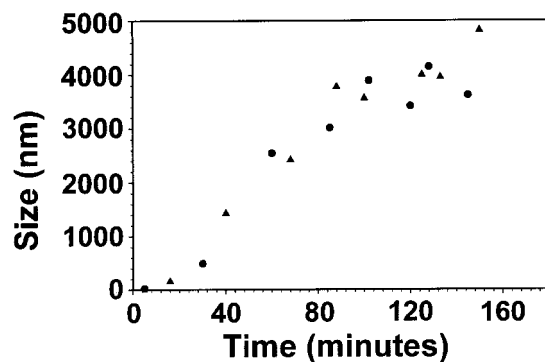


Figure 4. Plot of the particles size (nm) vs time of the seeded reactions measured by using light scattering: (▲) 1:1:1:1 volume ratio of zinc, phosphate, DABCO, and seed solutions; (●) 1:1:1:0.1 volume ratio of zinc, phosphate, DABCO, and seed solutions.

column. The SEM images of the three samples are shown in Figure 6. From these micrographs, we calculated average sizes of 3, 6, and 15 µm with increasing column height, respectively. Figure 7 plots the average crystal size versus the column length.

Discussion

Comparison of Composition between Conventional and Reverse Micelle Synthesis. The reactant composition necessary for successful synthesis of ZnPO-X from reverse micelles was obtained by trial and error and is compared to the composition for the conventional synthesis in Table 1. For the reverse micelle synthesis, the reactant ratios were similar to conventional synthesis,

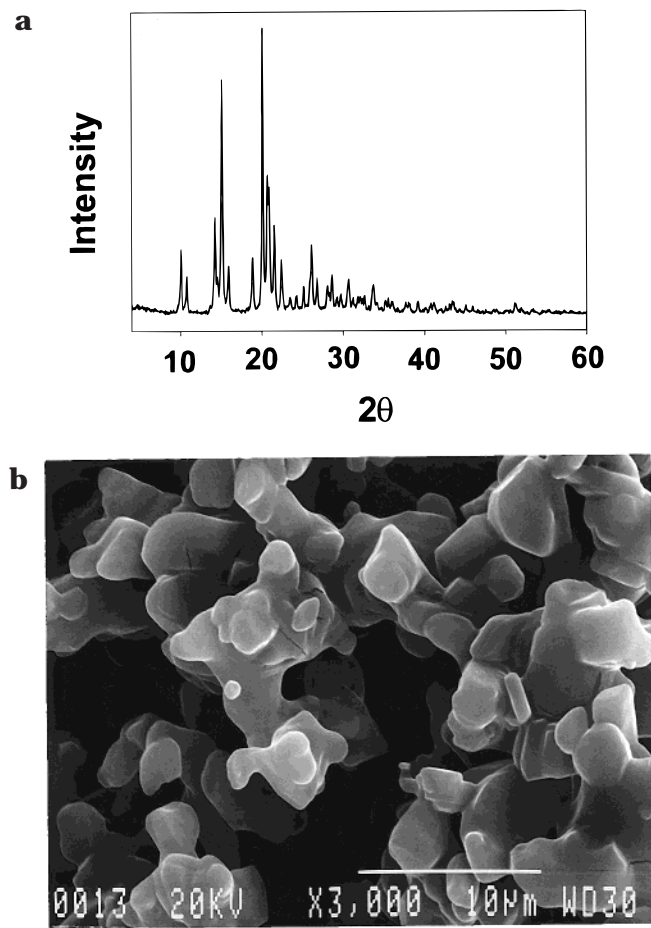


Figure 5. Material isolated from the mother liquor after disruption of reverse micelles with acetone: (a) XRD pattern and (b) SEM image.

but a factor of 4 dilute. If such diluted aqueous solutions were used for the conventional hydrothermal synthesis, then no ZnPO-X was crystallized. It is well-known that in reverse micelle formation, water is used for the moistening of the headgroups of the surfactant.⁹ The present results indicate that a significant fraction of the water is used up via interaction with the surfactants. These observations also provide some guidelines for choosing appropriate concentrations for reverse micelle synthesis for materials where composition is crucial to the synthesis.

Growth Process in Reverse Micelles. The initial step in crystal growth in reverse micelles begins with the collision of zinc and phosphate micelles, a result of which is formation of new micelles that share the contents of the colliding micelles.²² As these collisions proceed, reverse micelles with a distribution of zinc and phosphate concentrations will be formed. It can be expected that supersaturation conditions will be exceeded in only a certain fraction of these reverse micelles and will result in formation of zincophosphate nuclei. These nuclei can then grow into crystals by incorporating nutrients from non-nucleated reverse micelles. We have proposed such growth processes in reverse micelle based growth of sodalite and ZnPO-X using TMA as structure directing agent.²⁵ Crystal growth will stop once the nutrients are depleted.

Nature of Species Left Behind after Crystal Growth. In the ZnPO-X synthesis, only about 15–20% of the zincophosphate is recovered as crystals from the bottom of the reaction vessel, and the rest of the species remain suspended in the organic medium. The size of the

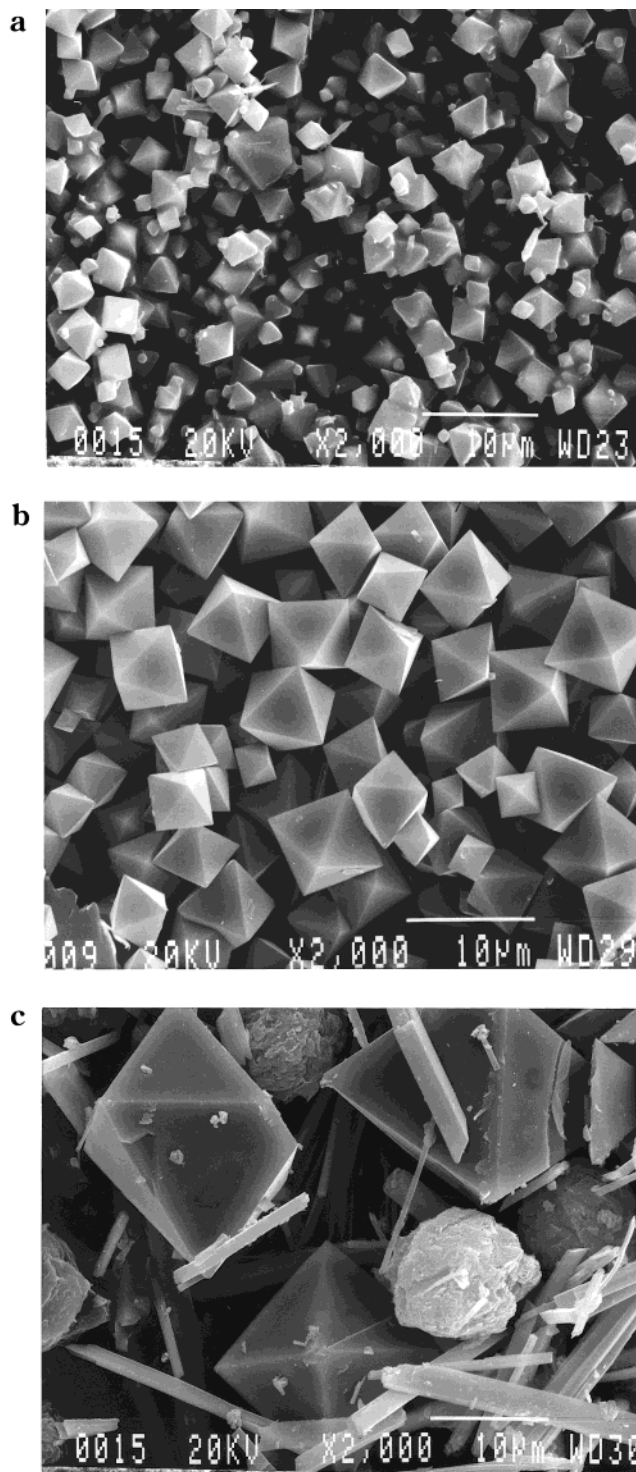


Figure 6. SEM image of the products obtained from columns of different heights: (a) 0.71; (b) 1.78; (c) 2.62 m.

clusters present in the mother liquor is around 15 nm. The solution with these clusters acted as an excellent seed system for growth of ZnPO-X, with crystal growth beginning immediately after addition to a reverse micelle system that would not form ZnPO-X. This is evidence of the fact that the mother liquor contains nuclei which will immediately grow if provided with a source of reverse micelles as nutrients. To verify if these clusters were embryonic nuclei of ZnPO-X, we attempted to break up the reverse micelles and extract the small particles. As Figure 5 shows, zincophosphate aggregates of micrometer size with weak diffraction features that are definitely not assignable to

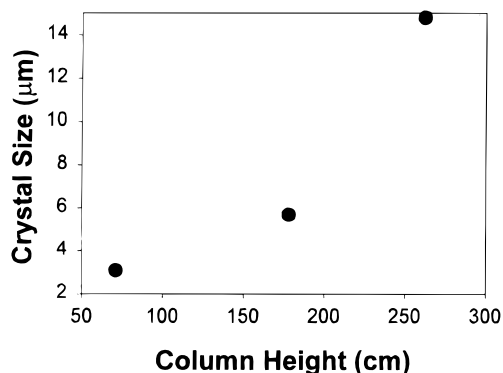


Figure 7. Plot of crystal size vs length of the column.

ZnPO-X were obtained. These particles also did not act as seeds for ZnPO-X. Clearly, the extraction process is destroying the nuclei structure.

The formation of these nuclei can be understood based on the exchange processes in reverse micelles. Initially, only a small fraction of the micelles have the right supersaturation to form nuclei of ZnPO-X and these nuclei commence crystal growth using up the non-nucleated reverse micelles. But, the composition of the non-nucleated reverse micelles also changes with time via collisional exchange, and eventually more of these will have the right composition to form ZnPO-X nuclei. So, with time, the non-nucleated reverse micelles are decreasing and, thereby, the nutrients available for growth. We propose that this is the condition at the very end of the synthesis, where all of the crystals have settled, and what is remaining behind are primarily clusters of nuclei. If these nuclei are then brought in contact with fresh non-nucleated reverse micelles, then they will immediately commence growth to ZnPO-X, even if the composition is not optimized, as with composition B.

Seeding in Reverse Micelle Synthesis. Our attempts to grow larger crystals by using well-formed ZnPO-X as seeds were unsuccessful, rather the surface of the seed crystals acted as nucleation sites of small crystallites, typical of secondary nucleation. Previous studies in conventional zeolite crystallization have also noted that it is not possible to make seed crystals larger by suspending them in the crystallization medium.³² Surface nucleation, like the example shown in Figure 3 was reported by Culfaz and Sand for seeded mordenite synthesis.³³ For systems in which independent nucleation in the medium can occur, the addition of seed crystals appears to provide surface sites for the nuclei to anchor and grow, rather than growth of the seed crystals themselves.

However, by using the small 15 nm clusters present in the mother liquor as seed nuclei, and a composition where nucleation is slowed, as in composition B, we find that the size of the crystals can be increased by controlling the

time they spend in the medium. In our case, this was accomplished by using narrow columns of different heights, the height of the reaction column determining how long the crystals remain suspended in the column. Figure 7 shows a plot of the average crystal size versus the column length from which the crystals were obtained. The size dependence provides further clues on the crystal growth process. It appears that as the column length increases, the crystal size gets bigger, but in a nonlinear fashion. The nonlinear growth can be understood based on the mechanism of formation of these crystals from reverse micelles. Only a few nuclei are formed initially, which then grow. If the column length is short, these crystals reach a certain size and they settle. New crystals are then formed from the remaining reverse micelles over time. Thus, the recovered samples from short columns are a reflection of crystals formed at different times. On the other hand, if the column is very long, then the earliest crop of crystals will continue to grow larger and use up the non-nucleated reverse micelles as nutrients. In this case, the recovered crystals arise from the nuclei that were formed at the earliest times.

In conventional synthesis of zeolites, it is well recognized that nanometer particles can play a role in the nucleation process.³⁴ The addition of "clear aqueous nuclei" to promote zeolite synthesis was recognized 2 decades ago.³⁵ The mother liquor in the reverse micelle containing the embryonic nuclei of ZnPO-X is conceptually similar to these zeolite systems, though its isolation occurs at the end of a synthesis, whereas in zeolitic systems, the reaction system is exhausted of all nuclei by the end of the synthesis. Thus, in the reverse micellar system, the nuclei get an opportunity to mature well, as is evident from the immediate growth of these nuclei on exposure to nutrients and exist by virtue of the uniqueness of reverse micelles.

Conclusions

We have shown that it is possible to grow an open framework zincophosphate-X structure from reactants initially contained in reverse micelles. The composition needs to be carefully controlled since a significant fraction of the water in the reverse micelles is used up for hydrating the surfactant headgroups. The crystal growth process begins with a few nuclei that grow by incorporating nutrients from non-nucleated reverse micelles. This gives rise to a system where at the end of the crystallization, the solution is filled with nuclei which act as excellent seeds if a source of nutrients is provided. This crystal growth route results in formation of larger crystals if the growing crystals can be kept in suspension for longer periods of time.

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