Hydrothermal Synthesis of Molecular Sieve Fibers: Using Microemulsions To Control Crystal Morphology**

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Microporous crystals with pore sizes near molecular dimensions, such as zeolites and molecular sieves, are widely used in shape-selective catalysis and separations, and are being developed for applications in membranes, sensors, and optics.[1, 2] Because many emerging applications of microporous materials require precise control of crystal size and orientation,[3, 4] there is significant interest in developing new strategies to control crystal structure and morphology. Reverse microemulsions have been used to control the size and shape of some inorganic materials by confining the reaction within surfactant assemblies.[5, 6] Microporous zincophosphates have also been crystallized at room temperature from reactants enclosed in reverse microemulsions.[7, 8] Zeolites and molecular sieves usually require hydrothermal synthesis conditions ($T > 100^\circ C$), at which microemulsion formation is difficult to achieve. Here we report the use of reverse microemulsions to control the morphology of crystals of a common aluminophosphate molecular sieve ($AlPO_4$-5) during hydrothermal synthesis at 180 °C. Very long fibers are obtained in the microemulsion-based synthesis, a morphology not observed previously for $AlPO_4$-5. These fibers have linear micropores parallel to the long axis of the fibers. We believe that the high aspect ratio of the fibers should allow their incorporation into materials with controlled crystal orientation. The microemulsion approach could be used to control morphology of other complex materials.

Aluminophosphates are a widely studied class of microporous materials containing a variety of structural types.[9] We chose to synthesize aluminophosphate number five ($AlPO_4$-5) because of it is one of the most common molecular sieves and has found application in catalysis, nonlinear optics, and membrane separations.[10] The crystal structure has the IUPAC name AFI and forms parallel linear pores with uniform diameters of 0.7 nm. The normal route for synthesis of $AlPO_4$-5 begins with a mixture of water, an aluminum source, a phosphorus source, an organic structure-directing agent, and hydrofluoric acid. We conducted phase behavior measurements on several surfactant systems to identify surfactants capable of solubilizing all of the components of the $AlPO_4$-5 synthesis mixture into a water-in-oil microemulsion. The mixture was treated as a pseudo-ternary system, with oil, "aqueous," and "surfactant" components. Toluene was chosen as the oil phase. The "aqueous" phase was an $AlPO_4$-5 synthesis mixture consisting of water, aluminum triisopropoxide, phosphoric acid, hydrofluoric acid, and triethylamine in a molar ratio of 50:0.8:1.0:0.5:1.2, respectively.[11] The "surfactant" phase was a mixture of an ionic surfactant and *n*-butanol. The alcohol was added as a cosurfactant to improve microemulsion formation.[12] Three ionic surfactants were investigated; sodium dodecyl sulfate, cetyltrimethylammonium bromide, and cetylpyridinium chloride. Various concentrations of "surfactant" and "aqueous" phases in toluene were examined to determine regimes where an optically transparent, single-phase microemulsion formed at room temperature. It was determined that cetylpyridinium chloride in a 2:1 weight ratio with *n*-butanol had the largest single-phase region, and was capable of solubilizing the greatest amount of the $AlPO_4$-5 synthesis mixture.

The mass fractions of components used for hydrothermal synthesis were 0.219 cetylpyridinium chloride, 0.109 *n*-butanol, 0.492 toluene, and 0.180 $AlPO_4$-5 synthesis mixture. The microemulsion was formed by first mixing water, phosphoric acid, and triethylamine together at room temperature for five minutes. Then, cetylpyridinium chloride, *n*-butanol, and toluene were added and the mixture was vigorously shaken for two minutes. At this point, a single-phase microemulsion formed. The microemulsion was aged overnight while stirring at room temperature. Aluminum triisopropoxide was then added and the mixture was shaken vigorously for one minute. After the addition of the aluminum source, the microemulsion was aged at room temperature for two hours. Hydrofluoric acid was then added and the microemulsion was aged for an additional two hours. At room temperature, this mixture forms a transparent single-phase microemulsion, unlike the traditional $AlPO_4$-5 synthesis mixture that appears milky white. Hydrothermal synthesis was conducted by heating the microemulsion to 180 °C in a teflon-lined autoclave for 6 h while stirring. A control was also performed by using the same synthesis conditions, but without toluene, surfactant, and butanol. The solid product was collected by centrifugation, washed with ethanol, and dried overnight in a vacuum oven at 50 °C.

The microemulsion-based synthesis resulted in the formation of long fibers approximately 200 – 300 nm in width and 15 – 30 microns in length (Figure 1a), with some groups of fibers aggregated into parallel bundles. The widths of the fibers are very uniform, while the lengths of the fibers vary a great deal. The blunt ends observed on many fibers (Figure 1b), as opposed to sharp points, suggest that these fibers may have been broken during transfer to the scanning electron microscopy stage. By comparison, the traditional synthesis resulted in the formation of irregular hexagonal columns approximately 4 – 8 microns in width and 5 – 12 microns in length (Figure 1c). The hexagonal columns appear in a wide variety of sizes. The surfaces of the columns are rough, indicating that they are likely composed of multiply twinned crystals. The powder X-ray diffraction pattern for the material

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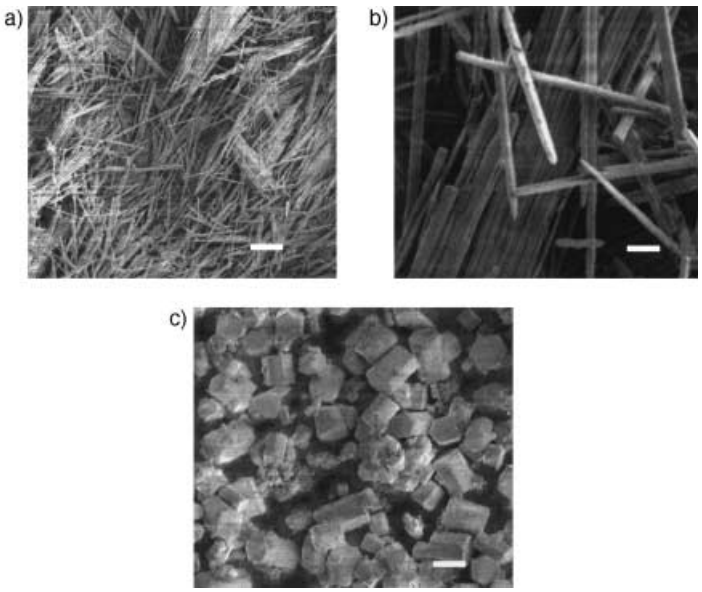

Figure 1. Scanning electron micrographs of $AlPO_4$-5 synthesized in an autoclave at 180 °C for 6 h. a) $AlPO_4$-5 from microemulsion-based synthesis (bar equals 10 microns); b) close-up of fiber ends of $AlPO_4$-5 from microemulsion-based synthesis (bar equals 1 micron); c) $AlPO_4$-5 from traditional synthesis (bar equals 10 microns).

synthesized through the microemulsion-based synthesis is consistent with the AFI structure, and appears similar to the $AlPO_4$-5 diffraction patterns in the literature.[13] The one notable difference is the greatly reduced intensity of the (002) peak located at a Bragg angle 2Θ of 21.3°. The loss of intensity of the (002) peak indicates that the fibers are preferentially oriented horizontally, which is consistent with the observed orientation in Figure 1a. From the preferred orientation of the fibers, it can be concluded that the linear micropores are parallel to the long axis of the fibers.

Microwave heating was explored as an alternative route for the synthesis of $AlPO_4$-5 from reactants enclosed in water-in-oil microemulsion droplets. Microwave heating often reduces the crystallization time and/or temperature required for hydrothermal synthesis of zeolites and molecular sieves, including $AlPO_4$-5.[14, 15] Microemuslions were prepared by using the same procedure described above and then heated in a Teflon-lined vessel to 180 °C for 17 min in commercial microwave. Figure 2a shows the scanning electron micrograph of the product formed within the microemulsion after microwave heating. As with the synthesis in the autoclave, a fibrous product is produced. However, the particle size is much smaller, with widths of approximately 150 nm and lengths of up to 2–3 microns. The smaller fibers also display some tendency to aggregate into parallel bundles. For comparison, Figure 2b shows the product formed from heating the traditional synthesis mixture in the microwave. The product appears as multiply twinned crystals up to 50 microns in length and 10–15 microns in diameter, and is similar to the "barrel-like" morphology described by Wilson in the original synthesis of $AlPO_4$-5.[16] The powder X-ray diffraction patterns for the products from both the traditional synthesis and the microemulsion synthesis confirm the AFI crystal structure (not shown). There is a slight reduction in the intensity of the (002) peak located at a Bragg angle 2Θ of 21.3° for both products, but not as much as observed for the longer fibers synthesized in the autoclave. Apparently, the smaller aspect ratio of the fibers produced in the microwave (10 compared to 100 for the fibers produced in the autoclave) reduces the preferred horizontal orientation.

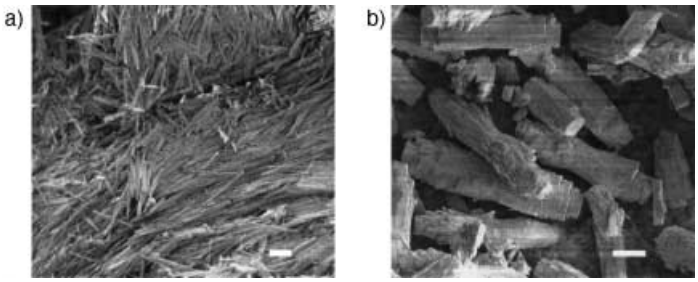

Figure 2. Scanning electron micrographs of $AlPO_4$-5 synthesized by microwave heating at 180 °C for 17 min. a) $AlPO_4$-5 from microemulsion-based synthesis (bar equals 1 micron); b) $AlPO_4$-5 from traditional synthesis (bar equals 10 microns).

The formation of microporous materials during hydrothermal synthesis is a complex process of self-assembly coupled with several simultaneous chemical reactions. The mechanism of nucleation and growth is poorly understood, but a recent study has shown that Zeolite A crystals are nucleated within amorphous precursor particles.[17] The size and shape of the final crystal was the same as the amorphous precursor particle, but further crystal growth could be attained upon heating through Ostwald-ripening type mechanism. It has been proposed that $AlPO_4$-5 crystallization occurs through a similar route where an amorphous precursor consisting of a self-assembled array of inorganic and organic (structure-directing agent) material converts to $AlPO_4$-5 crystals upon heating.[14] Concentrated water-in-oil microemulsions often form cylindrical aggregates, and these aggregates have been used as templates to form rod-shaped materials.[18] We believe that a similar templating mechanism may be operative in the molecular sieve synthesis. Such a mechanism would involve "dual" templating: the structure-directing agent templates the micropores within the crystal, while the surfactant aggregate surrounding the amorphous precursor templates the crystal size and shape. While we believe the surfactant aggregates template crystal nucleation, the final crystal size is much larger than typical surfactant aggregates, so crystal growth must continue outside the microemulsion droplets. The microporous $AlPO_4$-5 fibers synthesized in the microemulsion may find application in optics, sensors, or membranes, where the high aspect ratio of the fibers will allow deposition onto substrates with controlled crystal orientation.

Experimental Section

Phase behavior measurements: An $AlPO_4$-5 synthesis mixture consisting of water, aluminum triisopropoxide, phosphoric acid, hydrofluoric acid, and triethylamine in a molar ratio of 50:0.8:1.0:0.5:1.2, respectively, was formed and aged for at least 4 h at room temperature. In a second container, surfactant, butanol, and toluene were added in concentrations of 60 wt% toluene and 40 wt% surfactant + butanol. The $AlPO_4$-5 synthesis mixture was added in 50 μL increments to 5 g of the surfactant, toluene, and butanol

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mixture. After each addition of the $AlPO_4$-5 synthesis mixture, the container was stirred for several minutes before making visual observations. The minimum amount of $AlPO_4$-5 synthesis mixture required to form the microemulsion was determined by the observation of a transparent single-phase. The maximum solubility of $AlPO_4$-5 synthesis mixture in the microemulsion was defined by the onset of visual turbidity. The ratio of butanol to surfactant was varied from 2:1 to 1:2. The single-phase microemulsion did not form in the absence of butanol.

Hydrothermal synthesis: Autoclave synthesis was counducted in a teflon-lined pressure vessel (Parr, model 4744) wrapped in heating tape and controlled to a temperature of 180 °C for 6 h. The reactor contents were stirred continuously using a magnetically coupled teflon stir bar. Microwave synthesis was conducted in teflon acid digestion vessels in a CEM MDS-2000 oven. The vessels were heated to 180 °C for 17 min without stirring.

Powder X-ray diffraction spectra were collected by using a Scintag XDS2000 diffractometer using an accelerating volatge of 45 kV and intensity of 40 mA. The diffraction pattern was collected from an angle 2Θ of 5 to 50°, using a step size of 0.02° and a collection time at each step of 3 s. Scanning electron micrographs were obtained by using a JEOL 6300FX high-resolution scanning electron microscope operating at an accelerating voltage of 1.0 kV.

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Biomimetic NAD^+ Models for Tandem Cofactor Regeneration, Horse Liver Alcohol Dehydrogenase Recognition of 1,4-NADH Derivatives, and Chiral Synthesis**

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In memory of Dr. E. Steckhan

The biocatalysis discipline has the potential to generate important chiral organic compounds, by the use of enzymes, usually in the presence of critical cofactors.[1, 2] Therefore, practical methods for the regeneration of the coenzyme 1,4-NADH are significant in biocatalysis.[3–5] In this manner, a variety of transition metal hydrides have been evaluated as catalysts for the regioselective reduction of NAD^+ and NAD^+ models to the corresponding 1,4-NADH derivatives to develop faster rates and a more economical regeneration process.[6–9] In the most significant example, Steckhan et al. described the in situ generation of $[Cp^*Rh(bpy)(H)]^+$ ($Cp^* = \eta^5$-C_5Me_5, bpy = 2,2′-bipyridyl) for the regiospecific reduction of natural NAD^+ to 1,4-NADH,[7] and then demonstrated the cofactor regeneration process in enzymatic chiral reduction reactions with horse liver alcohol dehydrogenase (HLDAH).[10–12]

More importantly, we recently reported the source of this unusually high regioselectivity for 1,4-NADH and other mechanistic aspects with a model NAD^+ compound, 1-benzylnicotinamide triflate (**1**; Scheme 1). The reaction in H_2O/THF (1:1) used $[Cp^*Rh(bpy)(H_2O)](OTf)_2$ (**2**) as the catalyst precursor, and sodium formate as the hydride source to provide exclusively the kinetic product, 1-benzyl-1,4-dihydronicotinamide (**3**).[13]

Furthermore, we also recently used an aqueous NAD^+ model, β-nicotinamide-5′-ribose methyl phosphate (**4**) and demonstrated its similar regioselective reduction with $[Cp^*Rh(bpy)(H)]^+$, formed in situ, to give the corresponding 1,4-dihydronicotinamide-5′-ribose methyl phosphate (**5**) at pH 6.5.[14] NAD^+ model **4** bears a structural resemblance to NAD^+ (a monoribose phosphate moiety, but with no pyrophosphate or adenosine substituents), while NAD^+ biomimetic **1** has a simple 1-benzyl group instead of the ribose, pyrophosphate, and adenosine groups.

The initial rates (r_i) of the regioselective reduction of both **1** in H_2O/THF (4:1) and **4** in H_2O at pH 6.5 with $[Cp^*Rh(bpy)(H)]^+$ (generated in situ) to give their corre-

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