Reverse Micelle Based Synthesis of Microporous Materials in Microgravity

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Objective

The goal of this research program is to enhance the fundamental understanding of the crystallization of the technologically important class of microporous materials. Major strides have been made in conventional hydrothermal synthesis of microporous materials, including the discovery of about 100 different topologies. Many of these materials find uses in chemical petroleum and consumer industries. However, because of the complexity of the synthesis process, correlation between molecular events and crystal growth has been difficult. This has held up progress in synthesis of new frameworks and control of morphologies.

Significant Results

We have designed a new procedure for growing microporous materials. Research over the past several decades has demonstrated that small droplets of water in oil (i.e., reverse micelles) can be used as the site for growth of metals, semiconductors, minerals, polymers and biomimetic materials. The major advantage of this process is controlling size of particles, down to nanometer scales. Our contribution has been to show that reverse micellar systems can also be used to grow microporous materials. Unlike the previous systems mentioned above, mere supersaturation effects do not lead to formation of open framework microporous materials. The appropriate chemical environment for nucleation is essential. Three surfactant systems for making reverse micelles have been examined. These include an anionic surfactant, bis(2-ethylhexyl oxy carbony)-1-ethanesulfonate (AOT), a neutral surfactant, poly(oxoethylene) sorbitan trioleate (Tween 85) and a cationic surfactant, dioctyldimethylammonium chloride (DODMAC). Zincophosphates were the choice of the framework in all reverse micellar systems.

In the AOT system, condensed structures such as hopeite and hexagonal zinc phosphate along with the microporous framework sodalite was synthesized. By careful control of the composition of the zinc and phosphate containing reverse micelles, sodalite crystals were formed by three distinct pathways. These include a slow growth by a layer-by-layer mechanism, a process formed by aggregation of growing nuclei and a crystal growth pathway through a restructuring of surface of amorphous zincophosphate particles. Even though such crystal growth pathways have been postulated to occur in conventional synthesis, a clear separate demonstration of each pathway as observed for the reverse micellar system has not been reported. Considerable effort has been spent in trying to synthesize a framework structure more open than that of sodalite, such as zincophosphate with the faujasite topology (ZnPO-X) in the AOT system, but these experiments have been unsuccessful. Detailed chemical composition and vibrational spectroscopic studies led us to the conclusion that the presence of sodium cations in the AOT reverse micelle led to disruption of ZnPO-X nucleation.

This led us to examine Tween-85 as an alternative detergent for ZnPO-X nucleation. In this system, too, only condensed structures such as hopeite and microporous structure of sodalite

were formed. Like the AOT system, control over morphology could be exercised by choice of reactant compositions.

Recently, we have been successful in synthesizing ZnPO-X from the DODMAC reverse micellar system. This is a major breakthrough for this project, because it establishes that reverse micelles can indeed nucleate open framework structures, thereby establishing the generality of the procedure. Experiments are underway to determine the exact role of the DODMAC reverse micelle in the nucleation of ZnPO-X.

Along with synthetic procedures, we have also developed the use of laser light scattering and microprobe laser Raman spectroscopy for analysis of the crystal growth process. In addition, electron microscopy and diffraction methods have also been used.

Benefit of Microgravity to this Project

There are two effects of microgravity that will be exploited in this research. First, the settling rate in microgravity can be slowed down by 4 to 6 orders of magnitude. Second, the effect of buoyancy-driven convection will be reduced, leading to a predominantly diffusion controlled process.

In all three surfactant systems, we find a crystal growth process in which a few nuclei are formed and grow into crystals which settle by gravity with sizes of a micron. More crystals are then formed and the process continues. In microgravity, the growth process of the initial crystals is expected to continue until the nutrients are exhausted, resulting in larger crystals.

Convection alters attachment kinetics, as well as enhances mass transfer. In the ZnPO-X we find the presence of octahedral as well as singly twinned crystals. We expect that defects are going to be significantly reduced under microgravity conditions. In addition, the influence of seeding and epitaxial growth on seed crystals will be examined in microgravity. The feasibility of growth of mixed microporous materials, such as zincoarsenate on zincophosphate is an exciting possibility.