

An Interdisciplinary Approach to Understanding the Growth of Nanoporous Materials [1]

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Background:

The ability to fabricate complex, nanostructured materials tailored for specialized applications remains an elusive goal of the National Nanotechnology Initiative. An exciting strategy for such materials synthesis involves hierarchical assembly of supramolecular precursors, to form complex organic-inorganic structures with long-range order. These materials can yield nanoporous solids with applications in traditional areas like catalysis or separations or in emerging areas like sensors and optoelectronics [2]. Unfortunately, tailoring such syntheses usually requires costly trial-and-error modifications to reagents and conditions, because of a lack of fundamental understanding regarding the structures and mechanisms that control hierarchical assembly. To address this issue, we have assembled a Nanoscale Interdisciplinary Research Team to elucidate the growth of pure silica zeolites: a class of materials with both fundamental importance and wide-ranging applications.

The synthesis of pure silica zeolites in the presence of organic cations is one of the simplest examples of such a hierarchical assembly process. It involves interactions that are weak but cooperative (e.g., van der Waals or electrostatic forces between the inorganic fragments and the organic ions) directing the formation of a covalently linked periodic oxide framework. Although the organic cations are incorporated in the final structure, they are not bonded to the inorganic framework by strong chemical bonds. As a result, they can be removed by calcination or extraction without destruction of the inorganic framework. For their role in directing the framework formation around them, and in creating after their removal the network of nanopores, these organic cations are often called templates or structure directing agents.

A multitude of framework topologies consisting of periodic arrangement of silicate tetrahedra have been synthesized by templated hydrothermal growth. They include 1-, 2-, and 3-dimensional nanopore networks with pore openings ranging from 0.4 to 1.0nm. With over 100 framework topologies synthetically available—each with its own range of compositions—zeolites offer molecular recognition at the subnanometer scale resulting in applications such as shape selective catalysis, adsorption and ion-exchange. Templated hydrothermal synthesis of nanoporous materials is fundamentally important because of its similarities with other routes to hierarchical assembly such as biological morphogenesis and biomimetic synthesis (e.g., formation of enamel). The current and emerging applications of crystalline nanoporous frameworks indicate that templated hydrothermal synthesis is of great technological significance as well.

In this project we are developing and employing a unique combination of theoretical and experimental techniques to elucidate at the nanometer scale, for the first time, the self-organization processes that control the formation of high silica zeolites. Understanding and controlling the synthesis of the silica polymorph silicalite from ~3nm subcolloidal silicate-template particles represents the central theme of the effort. Synthesis of silicalite can be

accomplished by heating a mixture prepared from tetraethyl orthosilicate (TEOS), tetrapropyl ammonium hydroxide (TPAOH) and water. After crystallization the tetrapropyl ammonium cation (TPA) occupies the channel intersections with each of the four propyl groups extending into one of the four surrounding channel segments. Preceding zeolite nucleation and growth, and immediately after the dissolution of the silica source in the TPAOH solution, a stable suspension of ~3nm composite silicate-TPA particles is formed.

Despite the recent progress made in understanding the formation of silicalite/TPA, we still lack the fundamental understanding needed to *control* this growth process, and to use subcolloidal silica particles to *facilitate* the growth of new materials with advanced performance. To develop this understanding, we seek more atomistic experimental and theoretical perspectives on silicalite/TPA growth.

Results:

It has been recently proposed that the subcolloidal nanoparticles formed during the hydrothermal synthesis are crystalline MFI nanoblocks [3]. Since this issue lies at the center of our project Lobo, Tsapatsis, Vlachos and their coworkers [4] have reinvestigated this question by carrying out the synthesis protocol used in reference [3] and making a careful structural characterization of the resulting nanoparticles using various techniques. They conclude that the existence of MFI nanoblocks is not supported by empirical evidence. In fact, other plausible structures can explain the available experimental information just as well. Thus the structure and composition of subcolloidal nanoparticles observed during zeolite synthesis remains an open problem and our group's investigations of this are ongoing.

We have conducted a series of contrast-matching small angle neutron diffraction experiments on the suspension of nanoparticles. Analysis of these data indicate that the particles have, on average, cylindrical shape with a radius of ~2 nm and 6 nm long. These experiments have also revealed that the surface of the particles has a high concentration of the TPA+ molecules. We are in the process of refining the analysis of the SANS data to extract additional information

about particle structure. We are planning to combine these results with ongoing NMR spectroscopy measurements and the simulated annealing technique to develop models that are fully consistent with all available experimental evidence.

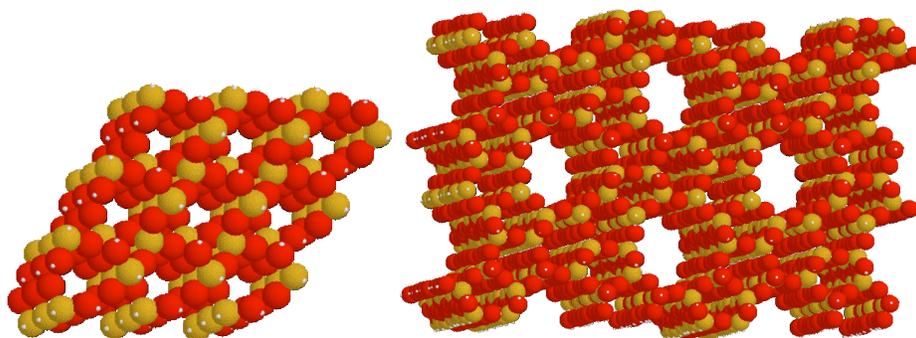


Figure 1. Computer graphics visualizations of mechanically stable quartz (left) and MFI (right) structures generated with our atomistic model of silica.

In order to develop a fundamental modeling approach to these systems, UMass members of the group have built a computationally efficient atomistic model of silica that includes the effects of short range repulsion, strong association and low coordination number [4]. This model is based on ideas that have previously been used in modeling the effects of strong association in

hydrogen bonded fluids. Results to this point indicate that the base case model is capable of forming mechanically stable solids that correspond structurally to quartz, cristobalite and silicalite-1, to name a few (see figure 1). The thermodynamic stability and phase behavior of the model is currently being investigated using rigorous statistical mechanical simulation methods. This model will be used in studies of subcolloidal particle structure, and also in simulations of silicalite-1 structure and formation.

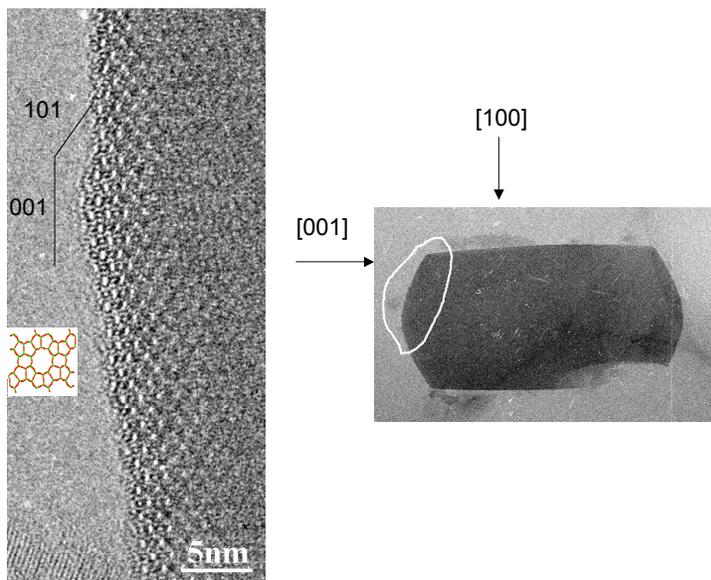


Figure 2. HRTEM's of MFI crystals prepared with a monomer TPA template. The surfaces exhibit 101, 010, 001 and 100 crystal planes.

crystals has been determined by use of HRTEM (see figure 2). This is important for determining how surface structure influences growth. There is a pronounced effect on MFI crystal growth kinetics and MFI crystal habit when the synthesis is performed with the dimer and trimer of TPA. In addition to its fundamental significance this finding has allowed, in a related project, the Tsapatsis group to prepare b-oriented MFI membranes for the first time. These membranes exhibit superior fluxes and selectivities compared to all MFI membranes reported up to now.

References

- [1] Further information about this project is available via email to any of the PI's: monson@ecs.umass.edu, auerbach@chem.umass.edu; tsapatsi@ecs.umass.edu, lobo@che.udel.edu; vlachos@che.udel.edu
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