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Inorganic-Organic Composite Nanoengineered Films Using Self-Assembled Monolayers for Directed Zeolite Film Growth

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Abstract

This is the final report of a one-year, Laboratory Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). Zeolites, or molecular sieves, are aluminosilicate cage structures that are typically grown from a heterogeneous mixture of organic template molecules, inorganic salts of alumina and silica, and water. These zeolites are used in industry for catalytic cracking of hydrocarbons (gasoline manufacture from oil), and contaminant removal from chemical production processes. Within one year, we developed a viable method for the deposition of a quaternary ammonium salt amphiphile onto silicon wafer substrates. Using a biomimetic growth process, we were also able to demonstrate the first thin-film formation of a zeolite structure from such an organic template. Additionally, we synthesized the precursor to another amphiphile which was to be used for further studies.

Background and Research Objectives

Tailored growth of films and other structures exist in the biological world where nature has developed elegant systems that grow organic-inorganic composites having unique structures of predetermined size, shape, strength, color and porosity. The most familiar example of this biomineralization process is the avian eggshell. Calcite crystals are nucleated by organic molecules (sulfated polysaccharides), and grow in a preferred orientation that is perpendicular to the internal membrane surface. The final columnar shape enhances the compressive strength of the eggshells, while the porous structure allows the growing embryo to respire through the membrane.

This research built upon the biomimetic concept of building nanomaterials by rational design of epitaxial substrates. According to reports published in both *Science* and *Nature*, the synthesis of mesoporous aluminosilicate molecular sieves has been accomplished by templating with lyotropic liquid crystalline solutions of quaternary ammonium amphiphiles (surfactants). Additionally, individual zinc-phosphate molecular

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sieve crystals have been grown from phosphonic acid monolayers deposited on a gold coated silicon wafer, and in reversed micelles, but neither were formed as a contiguous film.

We believe our approach is sound in that we have designed the amphiphile to have a close match to the lattice constants of the ZSM-5 zeolite. Assuming a fluid mosaic model for monolayers and bilayers, we perceive that nucleation will occur over the surface, rather than at random locations. Of course, there is only one way to find out, and that is by perfecting our technique and monitoring crystal nucleation and growth during several timed experiments.

Although zeolites have been around for literally millions of years, our work will directly impact the emerging science of epitaxial growth of inorganic crystals from organic template molecules by providing insight into the mechanisms involved at both the molecular and microscopic level. The oriented films which should result from our work will be a significant development in the field of catalysis research, sensor devices, and separation science. Success in mimicking the biomineralization process, so elegantly performed by organisms in nature, should also help in the design of new nanostructures and nanocomposites that fit form with function.

Our main objective is to make a nanoengineered material comprised of an aluminosilicate zeolite film that is epitaxially grown from a highly oriented substrate. The substrate will be prepared from a Langmuir-Blodgett (LB) film, and later from a self assembled monolayer (SAM) comprised of specially designed amphiphiles which will act as templates for the biomimetic crystallization.

The templates will be designed to meet two stringent requirements: enhanced thermal stability and crystalline lattice constants that match the ZSM-5 zeolite. Simultaneous nucleation should produce a contiguous film of crystalline zeolite having a perpendicular orientation from the surface of the biomimetic template. Success at producing the ZSM-5 zeolite film will be determined by comparing the characterization data obtained from the bulk synthesis to that obtained with our templating technique.

Furthermore, after compiling the synthesis and characterization data, we expected to be able to describe the nucleation mechanism occurring at the organic/inorganic interface during the crystallization process of the zeolite film.

Importance to LANL's Science and Technology Base and National R&D Needs

This research relates to the Laboratory core competency of basic materials research and might have had an impact on the catalysis thrust area. No one else has been using our approach for the growth of contiguous thin films of ordered zeolite structures.

Scientific Approach and Accomplishments

Our biomimetic approach is based on the use of a stable organic amphiphile that acts as a template for the synthesis of the ZSM-5 zeolite.

Design of Amphiphile. The ZSM-5 lattice is orthorhombic with unit cell dimensions of $a = 20.096\text{\AA}$, $b = 19.949\text{\AA}$, and $c = 13.428\text{\AA}$. A trimeric norbornadiene carboxylic acid amphiphile is known to have a hexagonal lattice with a cell length of $5.6\text{\AA}$. The diagonal distance across such a unit cell is $9.7\text{\AA}$. The tripropyl quaternary ammonium salt which will be prepared from this precursor should have a larger unit cell. Two such units will provide an almost exact match to the dimensions of the ZSM-5 axis. Our approach is to be able to use mixtures of the carboxylic acid with the quaternary ammonium salt in order to produce islands of nucleation sites on the surface. We experimentally vary the molar equivalents of each to investigate their effect on the final zeolite film.

ZSM-5 Synthesis. Several recipes exist in the literature for the synthesis of ZSM-5, and include an aqueous combination of amorphous silica, sodium aluminate, and tetrapropylammonium bromide as the template. The mixture is heated to 150°C and crystallization occurs over a period of three days under autogenous pressure. This allows us a broad window to pull samples at various times in order to investigate the growth morphology as a function of time.

Characterization. Initial characterization was performed with both optical and electron microscopy using our facilities in the Materials Science and Technology (MST) Division at LANL. We have excellent scanning electron microscopy (SEM) and transmission electron microscopy (TEM) capabilities dedicated to thin film characterization. The former also has X-ray fluorescence for the determination of the Si/Al ratios in the imaged films. To confirm the crystalline d -spacings, we use the x-ray diffractometer

facilities at the Center for Materials Science (CMS) at Los Alamos. Using these techniques, we are able to fully characterize the nucleation and growth phenomena occurring during the epitaxial crystallization of the zeolite films. Additionally, we will attempt to image the cage structure using our in-house atomic force microscopy or consult with CMS personnel for doing same.

A post-doctoral fellow (Nathaniel Peachey), who had previous experience with LB films, was the driving force behind this work. With his background in organic amphiphiles, Robert Hermes designed and performed the synthesis of the target amphiphile. Additionally, we made arrangements with personnel at Sandia National Laboratories (SNL) for one of our undergraduate program (UGS) students, Matthew Martinez, to work part-time at their Advanced Materials Laboratory while attending the University of New Mexico. He has been responsible for meticulously depositing the LB films that we use in our zeolite synthesis experiments, and uses a computerized Langmuir trough for this purpose.

Amphiphile Synthesis. The target amphiphiles are derivatives of trimeric norbornadiene (Tnbd). We have successfully synthesized Tnbd on a large scale, and subsequently prepared its monoethyl ester, which is the precursor to the rest of the synthetic pathway. Several attempts to hydrolyze this ester to the target carboxylic acid failed. The synthesis of the quaternary ammonium salt amphiphile depends upon the conversion of the carboxylic acid to the free amine, and quaternization with propyl bromide. By the end of FY 1996, we were able to demonstrate the hydrolysis of the monoethyl ester on a very small scale, but gave insufficient amounts for further synthetic work.

Langmuir-Blodgett Films. With several months of training, the UGS participant has become an integral part of our initial success. He has been able to develop his technique to produce monolayers and LB films onto silicon wafer substrates. An LB film of didocecyltrimethylammonium bromide (DDTAB) was deposited in 5 layers, and used for the following zeolite synthesis.

ZSM-34 Zeolite Film. Slotted teflon disks were used to hold the silicon wafers inside a rotating glass jar containing the mixture of ingredients necessary for the growth of ZSM-34. After two days at 80°C, the jar was opened and the wafers were rinsed with deionized water and air dried prior to scanning electron microscopy. The silicon control had no LB film, but had been through the zeolite growth process. A virgin silicon wafer

has the same, relatively featureless structure. The LB-treated silicon had a nice hard film, with relatively good uniformity. We were expecting perhaps just a few crystals that had nucleated from the surface. A few defect areas were encountered, but the rest had a high degree of orientation. To convince ourselves that what we saw was not just etched silicon, a sharp blade was used to scratch the surface. In a subsequent SEM, we could see that the surface was hardly damaged, except in one place where the blade had reached the silicon substrate. Unexpectedly, preliminary x-ray diffraction analysis gave only the peaks associated with the base silicon wafer. We repeated this experiment three more times with a "safer" reaction bomb (stainless steel pressure bomb with teflon liner). All efforts with this new apparatus failed to give results similar to those obtained with the glass jar method.

SM-5 Zeolite Film. We discontinued work on the ZSM-5 because we could not reproduce our work with the ZSM-34 in the new and improved apparatus.

Reference

1. Hermes, R., "Biomimetic Epitaxial Growth of Zeolite Films From Organic Template Monolayers," FY97 LDRD/Individual Projects proposal to the Materials Science Review Committee.