

Under Pressure

UK scientists create tomorrow's materials with pressure, CO₂ and fluorinated surfactants

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Have you ever noticed those little paper packets hiding under the wads of crumpled tissue paper in a box of new shoes? You know, the ones that read: Silica gel, Throw Away, DO NOT EAT.

As a kid, I always wondered what would happen if I tore off a corner and popped one of those spheres into my mouth. Now I know.

Silica gel is hydrophilic—it likes water. Through the science of adsorption, the process by which molecules of a liquid or gas contact and adhere to a solid surface, the moisture gets bound to the silica, averting musty wingtips, or, if you deviantly swallowed it, shriveling you up into a dusty corpse like some character in a bad sci-fi flick.

Okay, that second scenario's an exaggeration—it'd take more like a shoebox full of silica gel to cause dehydration—but it brings up a good point. Adsorbants like silica gel can work only as long as they have available surface area. For example, in gas masks the concentration of contaminants will eventually "use up" the adsorbant—activated charcoal.

The surface area of these adsorbants is made up of millions of nano-sized pores. Nanoporous materials offer exponentially more surface area to which molecules can bind. Silica gel typically contains 500 to 1,000 square meters of accessible surface per gram. (In comparison, the area of a basketball court is 420 square meters.)

Scientists around the world are exploiting the power of adsorption by tailoring porous ceramic materials (made primarily of silica) for a number of important applications: catalysis (facilitating chemical reactions), size separation (filtering and capturing molecules based on their size and chemical affinity), and, eventually, thin films. The molecular-level scale of these thin films (1 to 10 microns thick) can significantly alter the way that molecules in air or in liquids interact with a solid on which they are deposited. The long-term applications for these films will be diverse and may include electrical insulators in microelectronics, molecular-level filters, specialized optics, ultra-thin thermal insulation, and miniature biosensors.

But how do you make these porous materials? At the University of Kentucky researchers are using something no one else has tried—a substance called fluori-



nated surfactant—to synthesize new ceramic materials with nano-sized pores. The four-year project is part of the National Science Foundation’s Nanoscale Interdisciplinary Research Team (NIRT) initiative.

“Most organic materials contain carbon with hydrogen bonded to it,” says Barbara Knutson, associate professor of chemical and materials engineering, and a partner on the NIRT project. “In place of the hydrogen, you put fluorine atoms and give the molecules different properties.”

“What’s unique about these fluorocarbons is that they hate both oil and water,” says Steve Rankin, a chemical and materials engineering assistant professor, and the principal investigator on the NIRT grant. “When fluorinated surfactants are placed in water or oil solutions, they look for like molecules, and they end up assembling with each other.”

Fluorinated surfactants (a surfactant is a chemical that acts as a surface active agent—an emulsifier, surface wetting or repellent agent) are used in all kinds of things: non-stick pans, dry cleaning, cosmetics, electronics, paper products, and plastics.

“A unique property of fluorinated

species is that they dissolve in pressurized CO_2 . So a fluorinated surfactant contains something that is CO_2 -philic, likes CO_2 , linked to something that likes organic or water molecules,” says Knutson, who specializes in putting pressure on CO_2 .

CO_2 is a colorless, odorless gas present in the environment. Knutson exploits the solvent properties of CO_2 (its ability to dissolve other substances) at elevated pressures and temperatures, where CO_2 has “supercritical” properties. “Every fluid has a state where it’s not a gas or a liquid, but has a combination of gas and liquid properties. That’s what we call a supercritical fluid. It has some nice properties of gases—the molecules move around quickly and there’s rapid equilibrium. And it has advantageous properties of liquid—it’s dense; liquid can hold a lot more than gas.”

What kind of pressure are we talking about?

“If atmospheric pressure is in units of one atm (atmospheres), we usually conduct supercritical CO_2 experiments in the range of 75 to 250 atm,” says Knutson. This kind of pressure requires special equipment including a view cell (see picture on next page).

Steve Rankin and Barbara Knutson in chemical and materials engineering are using something no one else has tried—a substance called fluorinated surfactant—to synthesize new ceramic materials with nano-sized pores.

Knutson’s instrument, which she describes as the “to-die-for” view cell, is one of very few in the country in an academic setting. That’s because of the cost. A view cell with all of these bells and whistles (temperature control, pressure settings, mixing, density and viscosity measurement) runs about \$290,000.

So what are supercritical fluids good for? All kinds of things, including separating and making chemicals and materials, Knutson says. “The classic example is extraction of caffeine—producing decaffeinated coffee and tea began in the ’80s. Since then, the field has evolved because processing at pressure costs money, and it’s only worthwhile for high-value products,” she says.

“ CO_2 is nonflammable, inexpensive, and environmentally acceptable. A number of pressurized gases are better

solvents than CO₂—high pressure ethane, propane and ammonia—but all of these have consequences for health and safety. In addition, the mild processing temperature of supercritical CO₂ (about 35° C) allows us to work with temperature-sensitive molecules, like biological molecules,” Knutson says.

“Residual solvent is an issue in manufacturing pharmaceuticals. Solvents can contaminate the water used in biotechnology and pharmaceutical processes, as well as the product. Working with a non-contaminating solvent is a main theme of my research. We take the pressure off, and the solvent is gone,” she says.

By changing temperature and pressure, Knutson can “tune” CO₂—change how much of a reactant it can hold, how much of a product is soluble, make something drop out of a solution, or—like a scientist-turned-magician—make the solvent disappear from the products.

In the NIRT project, the researchers are basically mixing together water, components that make silica, alcohol, and the fluorinated surfactant. The surfactant binds to itself (a process called self-assembly) forming tiny geometric structures, such as spheres, cylinders, discs, and complex 3-D networks. Pressurized CO₂ is then used to extract the surfactant.

“Wherever the surfactants were, there are now pores, and everything else has polymerized, becoming a solid material,” Rankin says.

“Other scientists have tried to use CO₂ to remove surfactants from their materials, but CO₂ doesn’t really like



“This is our version of a beaker,” Barbara Knutson says. Her pressurized experiments require this view cell. Inside the cell are several sapphire chambers and an outer layer of water. This high-end view cell costs \$290,000.

surfactants unless they're fluorinated," Knutson says. Most scientists remove surfactants by burning or leaching them out with acid. Both methods can alter the fine structure of the newly created material.

The NIRT project began as a brainstorm. Rankin, Knutson, and Hans Lehmler, an assistant research professor in toxicology, were talking about applications of fluorinated surfactants when, in what Knutson calls "a lightbulb moment," Rankin tossed out an idea about a new way to synthesize nanoporous materials. His concept extended the self-assembly ability of traditional hydrocarbon surfactants to fluorinated surfactants, which have the potential to form smaller and more regular structures.

"We have a strong collaborative team with expertise in making the surfactants, understanding their behavior in solution, and synthesizing novel ceramic materials. The work is going very well," says Rankin.

Rankin's team, including five graduate students, is involved in creating better computer simulations that will predict the way molecules will assemble. Then the team will carry out the final step of taking the surfactants and making the materials. Lehmler is designing the surfactants themselves. Using special pressurized tools, Knutson and her students are testing how surfactants assemble and identifying what their phase behavior is (between the liquid and gaseous states), how they will interact with surfaces, and how to get the surfactants out of the material. Every two weeks everyone on the NIRT project meets to share findings and

brainstorm new ideas.

"The great thing about making materials with fluorinated surfactants is, it gives you materials that have a very well-defined and ordered structure to the pores themselves," Rankin says. "All the pores are the same size." Fluorinated surfactants also assemble more easily than regular surfactants into interesting and useful shapes like cylinders, discs and large flat sheets.

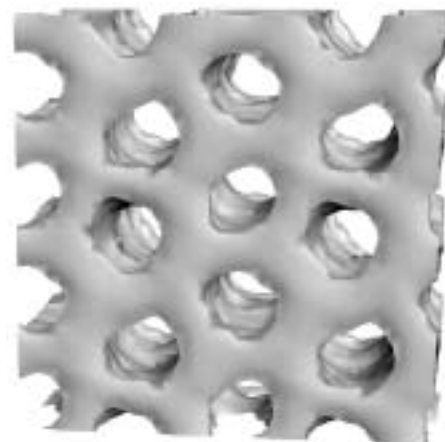
"Some of the original materials people made had pores between 3 and 30 nanometers. The first materials we've made with the fluorinated surfactants have pores that are smaller than that—more like 2 nanometers," he says.

Rankin and Knutson say one application they're very interested in is developing new approaches to making sensors, specifically for the detection of chemical and biological agents.

"We are just getting started in that area, but there are some definite advantages to these fluorinated materials—having defined pore size and being able to put specific chemicals inside those pores that will selectively attract and hold something we're trying to detect," Rankin says. "The process of extracting the surfactants with CO₂ is gentle enough that we can incorporate organic components that bind specifically to target molecules."

"Biosensors are the future of this collaboration," says Knutson. "And the advantages of our process, which combines CO₂ and fluorinated surfactants, suggest that we will find many other applications in the synthesis of advanced materials." ■

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One of Steve Rankin's computer simulations, this 3-D image shows where silica would be found in a porous thin-film material made with fluorinated surfactant. This section of the thin film shows pores aligned perpendicular to the surface of the film.