The Smallest Chemical Plants

Zeolites–crystalline materials riddled with nanometer-sized cavities–can exert exquisite control over chemical reactions and produce devices on the smallest scale

The stereotypical chemical plant is a big, sprawling complex, full of pipes and reactors and distillation units stretching across thousands of acres. But recently a different sort of chemical factory has been making news. Only a few microns across, it doesn't churn out industrial-sized quantities like its larger cousins. Instead, it specializes in reactions involving only a few atoms at a time, and its small scale offers chemists an entirely new approach to synthesis.

These new chemical plants are zeolites, a class of crystalline materials riddled with tiny, uniform cavities as small as a nanometer or less across—about one hundred-thousandth the diameter of a human hair. By using these cavities as reactor vessels, chemists can exert exquisite control over the reaction products, creating substances that would be difficult or impossible to make with cruder methods. "We look at zeolites as little nanoreactors," says Geoffrey Ozin, a chemist at the University of Toronto and a leader in this growing field. "They're like nano test tubes, all of the same size and shape."

This nanometer structure has Ozin and other chemists excited about zeolites' applications. Already under development are chemical sensors so sensitive they can detect the presence of minuscule amounts of toxins or pollutants and so discriminating they would respond to one particular molecule and no others. More tentative—but potentially more valuable—are electronic and optical devices, such as "molecular wires" that could serve as tiny connectors on computer chips and nanometer-scale semiconductors for use in optical transistors, the essential elements for the much-heralded but hard-to-build optical computer.

What makes zeolites uniquely suited to manufacturing such miniature products, says Du Pont chemist Norman Herron, is their ability to control a reaction. When making small bits of semiconductors or other materials, "you're fighting against thermodynamics—the particles are all trying to grow as fast as they can." Producing the particles in the uniform cavities of a zeolite is the only way to stop the growth at exactly the desired point—in essence, the particles hit a wall and stop.

So far, however, the potential of zeolites is mostly just that—potential—and the difficult transition from promising materials to commercial products is still to come. "It won't happen overnight," says Galen Stucky, a chemist at the University of California, Santa Barbara, who has done extensive work on zeolites. Stucky compares the job of commercializing zeolites to that of bringing thin-film semiconductor devices, such as the integrated circuit chip, to market—except that zeolites are three-dimensional, adding an extra degree of difficulty to the task of turning them into practical devices.

Materials have long been sought to construct special devices, but in this series of news reports, *Science* examines the role of materials as devices unto themselves. In addition to this story on zeolite crystals as microscopic chemical reactors, we look at polymers that emit light on p. 1700, and explore a new breed of oscillators being used to probe the nanoworld on p. 1702. Additional readings for the stories are on p. 1703.

For other news of materials, focusing on interfaces, see Perspectives beginning on p. 1704, and Articles beginning on p. 1710.

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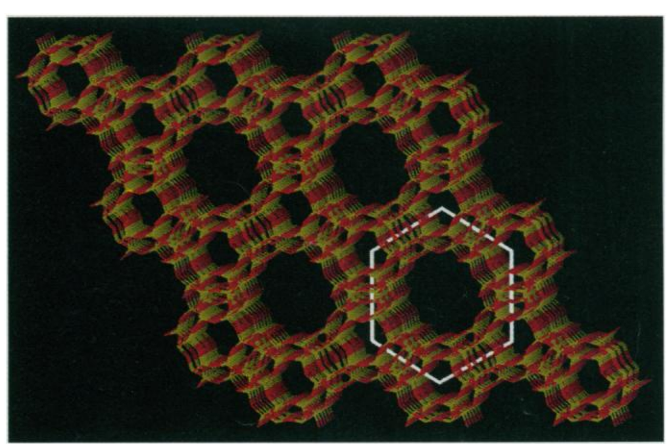
A molecular filter

That three-dimensional structure also holds the key to zeolites' promise. Seen through an electron microscope, a zeolite resembles a bit of crystal that has been worked over by a very neat, organized family of microscopic moles. It has cavities, or voids, at regular intervals; the voids are connected by short tunnels; and each void or tunnel is an exact replica of every other void or tunnel. Depending on the zeolite, the tunnels can be big enough to allow rather large molecules to pass or small enough that nothing much larger than individual atoms can get through.

This ability to work as "molecular sieves" was what first attracted chemists in the petrochemical industry to zeolites several decades ago. The early zeolites were naturally occurring minerals, but chemists have since learned to synthesize them with a wide variety of tunnel and cavity structures, and petrochemical companies now use zeolites extensively—for instance, as filters for separating gas molecules according to size. Over the past few years, however, scientists have realized that zeolites can do much more than process petrochemicals.

At Purdue University, for example, chemist Thomas Bein has employed zeolites to form "molecular wires," strands of conducting molecules a nanometer or less across. A natural approach to forming such miniature electrical connectors is to use conducting polymers—long chains of organic molecules that conduct electrical current (see story on p. 1700). But Bein notes that the usual methods for making conducting polymers won't work for molecular wires: The polymer material is formed with many molecules in a tightly connected mass, from which it is impossible to extract the few needed for a nanoconnector.

Bein's solution, back in 1989, was to make the polymers inside zeolites. He found that if he infused a gas of monomers (the basic building blocks of a polymer) into the tunnels of a zeolite and added a polymerizing agent, the monomers linked into thin polymer strands hundreds of units long. Unfortunately, when Bein analyzed the strands inside the zeolite, he found that they were not conducting.



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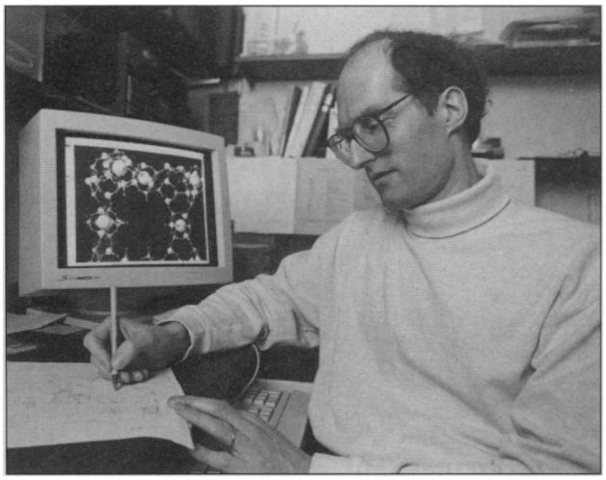
Nanoreactor. The uniform cavities in this zeolite structure, which is called zeolite EMT, are a boon for controlling minute reactions.

The likely reason, he says now, is that the tunnels of the zeolite were too narrow: Only one molecule of the polymer could fit in each tunnel, and single molecules of these polymers are not expected to be good conductors. Bein needed two or more molecules bundled together, so the electrons moving along the strand could jump from one molecule to another, bypassing individual atoms that do not allow electrons to pass easily. However, at the time there were no zeolites with large enough passages to form conducting polymers with more than one molecule in a strand.



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That roadblock was removed 2 years ago, when scientists at Mobil Oil discovered a way to make zeolites with much larger pores. By forming zeolites around "templates" made up of arrays of surfactant molecules that naturally arranged themselves into rod-like shapes, they were able to create zeolites with tunnels of almost any desired size up to 10 nanometers. Before that, the largest available pore size had been about 1.3 nanometers.

Now, working with these "mesoporous" zeolites, Bein has succeeded in producing filaments of conducting polymers worthy of their name: They do conduct electricity. Although it is impossible to remove the individual strands from the zeolite tunnels, the molecular wires can still be put to work. If it were possible, for instance, to grow thin films of zeolite crystals, they and their embedded arrays of molecular wires could be incorporated into semiconductor devices (since thin films are the basis for semiconductor technology) and used on a chip. Bein is now working on growing such thin films.

The road to an optical transistor

The problem of pore size isn't the only hurdle facing zeolite construction; there is also the size of the crystals themselves. Traditionally, zeolites have been produced as powders, with each of the individual zeolite crystals only a few microns in size. But since many of the newer applications will depend on working with single zeolite crystals mounted in devices, practical manufacturing considerations demand much larger crystals.

At Du Pont, for instance, Herron has used zeolites to make cadmium-sulfide materials of a type that might be used in an optical transistor, which would work as a switch for lasers on an optical chip. The materials are well-suited for switching because they are either transparent or opaque, depending on how much light shines on them, and so can be set to block laser light or let it through. But the individual zeolite crystals must be large enough to match the size of the existing semiconductor lasers. "We need zeolite crystals at least tens or hundreds of microns in size," Herron says. That's one or two orders of magnitude larger than those fabricated through the standard method.

Herron makes these materials by injecting first cadmium ions and then hydrogen sulfide gas into a zeolite, to create what he calls a cadmium-sulfide "supercluster"—a three-dimensional array of tiny cadmium-sulfide clusters, one per cavity. The pore size limits each cluster to four cadmium and four sulfur atoms. (Because of the synthesis technique, some of the sulfur atoms are replaced with oxygen atoms, but the practical effect is small.) The supercluster can be made either to transmit or not transmit light from one laser beam depending on the intensity of light from a second beam—the second beam switches the first one.

While this property is not unique to the superclusters—cadmium sulfide in its normal crystalline form will do the same thing—Herron notes that the superclusters perform much better because the individual clusters are both tiny and uniform. That makes for faster switching, since small clusters can change their optical state more quickly, and sharper switching because all the clusters act exactly the same way. He just needs bigger crystals to make the switches work.

Last fall the way was opened for him—and other researchers—to work with zeolites large enough for practical application. In the September issue of *Nature*, Ozin published a method for making single zeolite crystals up to 5 millimeters across. "For 50 years," he says, "nobody really cared about zeolite size" since size wasn't important for the things zeolites were asked to do. Now that it is, Ozin achieved a larger size by replacing water, the usual medium for zeolite crystals, with an organic solvent; he also used what he calls a "magic mineralizer"—the chemical HF-pyridine, which triggers the crystallization but doesn't create too many individual crystals at once. Free from the pressure of a crowd, the crystals grow larger.

Sensors and memories

With Ozin's method for making larger zeolites and the Mobil process for producing large pore sizes, the door to commercial applications seems to be slowly opening. And a few new zeolite products that don't depend on either large crystals or big pores are already getting close to market.

"We see these molecular wires as a start toward assembling more functional devices."

—Thomas Bein

Bein, for instance, has patented a chemical sensor consisting of a thin layer of tiny zeolite crystals affixed to an acoustic wave device, a larger crystal that, because of a feedback mechanism, constantly vibrates at a set frequency. If molecules come along that fit into the cavities of the zeolite, they will subtly change the weight of the whole device, altering its resonance frequency. That change can be detected electronically. By assembling a number of such zeolite sensors, each with pores with different sizes and shapes, Bein says it should be possible to create a sensor that responds only to one or a few closely related molecules.

And Ozin, by creating tiny crystals of a light-sensitive material within a zeolite, is working toward an optical memory that could be used, for instance, in a credit card-sized device that would hold a person's medical history or other types of personal information. He's put crystals of silver halides—the same material used in photographic film—into zeolite cavities. Shining a laser light into one of these cavities would trigger a chemical change in the crystals similar to the change that occurs when film is exposed to light. That change could then be detected—and read as data—by a second laser. But unlike photographic film, the change would be reversible. These silver halide clusters are small enough that their optical states—which are ultimately determined by the position of some of their electrons—could be altered by heating them a little with yet another laser, an infrared one. The heat causes the electrons to revert to their original positions. Thus the optical memory would be erasable.

It's too early to know how many of these schemes will come to fruition, but at the very least, Ozin says, the study of zeolites is changing the way chemists think of their field. With the nearly atom-by-atom control of reactions offered by these little chemical plants, the researchers who work with them have "crossed the boundary between chemistry and physics," he says, and are taking chemical reactions to an entirely new—and much smaller—realm.

–Robert Pool