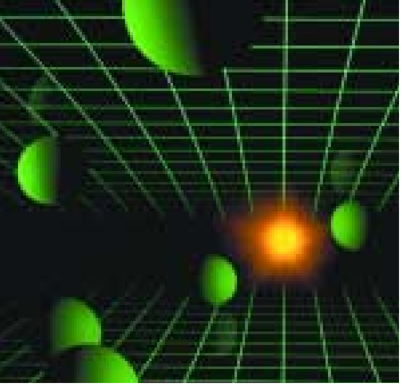

Research & Development Update

Faster, Easier Detection of Fugitive Emissions

The procedure currently used to detect fugitive emissions, known as EPA Method 21, involves moving the probe of a gas sampling instrument along the surface of each piece of applicable equipment and measuring the volatile organic compound (VOC) concentration. If the VOC concentration is above the level defining a leak, the equipment must be repaired or replaced to reduce the concentration to an acceptable level.

However, Method 21 has several shortcomings. It does not provide mass emissions rates of detected leaks, it measures only the total hydrocarbon drawn through its probe, and because of the large number of components to be checked, it is very time-consuming, labor-intensive and expensive.

Among the new technologies being evaluated as alternatives to Method 21 is optical gas imaging, says Michael Smylie, a principal of Environ Corp. (Santa Clara, CA). Smylie spoke at the Air and Waste Management Association Annual Conference, held in San Diego in late June, and reported the results of field studies conducted to evaluate the effectiveness of gas imaging devices for detecting fugitive emissions at ethylene plants.

During the tests, a portable CO_2 laser device based on the backscatter absorption gas imaging (BAGI) technique was employed. This technique can detect leaks instantaneously from a distance — somewhat like "night vision goggles," Smylie explains. The area is illuminated with IR light (in the long-wavelength range of 9–11 µm) and any leaking gas appears in real-time as a "black cloud" on a viewfinder or an attached TV screen.

The technique was able to identify emissions from traditional components (*e.g.*, pumps, valves, flanges, etc.), as well as nontraditional ones (*e.g.*, heat exchangers and process vessels). Furthermore, the CO_2 laser detected all leaks above 1 g/h, which demonstrates a greater control effectiveness than Method 21, Smylie points out.

Ongoing studies are focused on the CO_2 laser's sensitivity to a range of chemicals and quantifying emissions, as well as examining two other technologies — a backscatter camera and a passive IR camera, both of which operate in the mid-wavelength range of 3.5–5 µm. The long-wavelength range is where most olefins are absorbed, while the mid-wavelength range is where aliphatic and some aromatics are absorbed.

Although gas imaging is not yet an EPA-approved alternative to Method 21, Smylie believes that future research could eventually lead to that.

Growing Nanowires and Nanotubes Directly on Microchips

Engineers at the Univ. of California, Berkeley, have devised a process that eliminates the cumbersome middle steps in the manufacturing of sensors, which could lead to cheaper and faster commercialization of a variety of nanotechnology-based devices, predicts Liwei Lin, associate professor of mechanical engineering.

The typical nanowire or nanotube production process occurs in a furnace at temperatures of 600–1,000°C. A 1-cm^2 silicon wafer is coated thinly with a metal alloy. A vapor is directed toward the substrate, and the metal alloy acts as a catalyst in a reaction that eventually forms billions of nanowire or nanotube precipitates. The nanomaterials are then harvested by placing them in a liquid solvent (such as ethanol) and blasting them with ultrasonic waves to loosen them from the wafer surface. Researchers must then sort through the billions of pieces to find the few that meet their specifications.

Using resistive heating, Lin and graduate students Ongi Englander and Dane Christensen were able to precisely localize the extreme heat necessary for nanowire and nanotube growth while protecting the sensitive microelectronics, which remained at room temperature. They passed a current through a wire to the specific locations on the microstructure where they wanted the nanowires or nanotubes to grow. In one experiment, an area was heated to 700°C while another spot just a few µm away remained at 25°C. A gold-palladium alloy and silane vapor were used to create silicon nanowires, and a nickel-iron alloy with acetylene vapor were used to create carbon nanotubes. Nanowires 30–80 nm in diameter and up to 20 µm long, and carbon nanotubes 10–30 nm in diameter and up to 5 µm long, were produced.

"This unique approach," Lin points out, "allows the production of an entire nano-based sensor in a process similar to creating computer chips, with no post-assembly required." His team is continuing their research to fine-tune the temperatures and heating times needed to create the desired lengths of nanowires and nanotubes.

Oxides May Facilitate Small-Scale Hydrogen Production

A unique group of oxide materials that "exhale and inhale" — *i.e.*, that readily give up and accept oxygen atoms with changes in temperature — could be the basis for a small-scale hydrogen-generation system to power fuel cells in homes and vehicles, predicts Zhong Lin Wang, professor of materials science and engineering at Georgia Institute of Technology (Atlanta) and director of the Center for Nanoscience and Nanotechnology.

Scientists have known that oxides of the rare earth elements cerium, terbium and praseodymium can produce hydrogen from water vapor and methane in continuous cycles. Wang and his colleagues have found that doping iron atoms into the oxides significantly enhances the surface chemistry activity of the materials and lowers the temperatures at which these “oxygen pump” materials produce hydrogen.

Traditional reforming processes use metallic catalysts and temperatures above 800°C to produce hydrogen from hydrocarbons such as methane. While suitable for industrial production, this may not be ideal for the small-scale systems needed to power fuel cells in homes or cars, Wang points out.

In the Georgia Tech process, temperatures of 700°C drive oxygen out of the iron-doped oxide, where it oxidizes carbon in the methane to form carbon oxides and free hydrogen. Temperatures as low as 375°C are then used to reduce water vapor, pulling oxygen from water to replenish the crystalline structue and thereby producing more hydrogen. “By cycling the temperature in the presence of methane and water vapor, you can continuously produce hydrogen,” he says.

This approach takes advantage of the oxides’ unique crystalline structure, which allows up to 20% of the oxygen atoms to cycle out of and back into the lattice without structural damage, Wang explains. By providing an oxygen supply, the amount of water required for hydrogen production is reduced.

He believes the reaction temperatures may be lowered further by tuning the iron content and understanding the trade-offs between reaction efficiency and temperature. Lowering the temperature to below 350°C would allow solar energy to supply at least some of the heat needed, which could make the process more attractive, he adds.

Novel Gelling Agent Converts Organic Solvents to Stable Gels

In order for a gel to form, a liquid must contain a gelling agent, whose molecules aggregate into a continual three-dimensional network that holds the liquid together and hinders its flow. In recent years, there has been increased interest in gelling agents that consist of small organic molecules. These low-molecular-weight materials form networks that are held together by weak attractive intermolecular forces, rather than the strong covalent bonds in classic gelling agents such as gelatin, silica gels or polymers, explains Karl Heinz Dötz, professor and director of the Kekulé-Institute of Organic Chemistry and Biochemistry at the Univ. of Bonn (Germany).

Dötz and his colleague Roeland Nolte at the Univ. of Nijmegen in the Netherlands have developed an organometallic complex that acts as a novel gelling agent by converting organic solvents to stable gels. The substance, pentacarbonyl[D-*gluco*-hex(N-*n*-octylamino)-1-ylidene]chromium, consists of a hydrophilic sugar-like head and a lipophilic hydrocarbon tail connected by an organometallic fragemnt of catalytic relevance, a chromium complex bound to a carbon atom. Slight heating (to 70–75°C) followed by cooling to room temperature turns the solvent (in experiments, chloroform, dichloromethane, benzene, toluene, and mixtures of these substances were used) into a stable gel. Further heating causes the gel to dissolve again.

This discovery, says Dötz, could lead to new approaches to catalysis. For example, because the sugar head of the gelling agent contains chiral centers, it may be possible to generate chiral gels, which would be useful for stereoselective syntheses, he speculates. This work is discussed in more detail in *Angewandte Chemie International Edition*, **42,** pp. 2494–2497 (2003).

AIChE JOURNAL Perspective

Complexity in Chemically Reacting Systems

Complexity abounds in chemically reacting systems, where the reaction rate is typically a function of both space and time, notes John L. Hudson, professor of chemical engineering at the Univ. of Virginia (Charlottesville). Interactions among reacting sites, through transport, electric fields, etc., depend on the local reaction rate as well as the range and strength of the coupling of the system’s elements. The coupling, even where it is weak, can produce significant changes in the overall system behavior, Hudson points out.

Considerable progress has been made in the engineering and control of spatiotemporal patterns and in their application to improved reactivity and selectivity through control of local conditions and reaction steps. A host of imaginative techniques have been developed. Transport has been optimized through the use of emulsions, immobilized reactants, flow and electric fields, and external signals and feedback loops have been shown to give detailed control, he reports.

Investigators have also developed creative ways to take advantage of the effects of heterogeneities that arise due to variations in local surface properties. They have designed and manufactured heterogeneous surfaces, such as inert boundaries and active catalytic areas, that produce desired structures and reaction rates, he remarks.

Yet, the rate of development in the area of nonlinear dynamics applied to chemically reacting systems has been, not surprisingly, highly nonlinear, Hudson says. Advancements in chemical structure formation will occur in parallel and in cooperation with developments in spatiotemporal-temporal dynamics in other fields, he believes. And as progress is made on the unraveling of the mechanisms of both the local dynamics and the coupling among sites, the ability to design and operate chemical systems in optimal fashion will grow, he predicts.

Progress, he feels, is likely to be made in the following areas (among others): nanoscale self-organized reactors; the efficient operation of ultra-small-scale networked reactors; the design of networks of controllable and time-varying coupling strengths to optimize structure and reactivity; optimization and control of reacting systems with different time scales; the use of heterogeneities on catalyst surfaces to influence the local and global rates of reaction; open-loop and closed-loop (through spatiotemporal feedback) operation to optimize structure and reactivity; and optimal synchronization of reacting sites by means of external signals or feedback.

Hudson and his colleague István Kiss discuss this topic further in the September issue of the *AIChE Journal*.