Researchers shed new light on catalyzed reactions

November 19 2008

Rice University scientists on the hunt for a better way to clean up the stubborn pollutant TCE have created a method that lets them watch molecules break down on the surface of a catalyst as individual chemical bonds are formed and broken.

"We can see the vibrations of the bonds between the atoms of our molecules," said researcher Michael Wong. "By watching the way these vibrations change frequency and intensity with time, we can watch how molecules transform into other molecules step-by-step."

The research is available online in the *Journal of the American Chemical Society*.

This chemical sensing technique relies on nanoparticles consisting of gold and silica called nanoshells, invented 10 years ago at Rice by nanophotonics pioneer Naomi Halas. Nanoshells are about 20 times smaller than a red blood cell, and they can amplify light waves and focus them so tightly that scientists can use them to detect just a few molecules of a target chemical. Building catalysts directly on the surface of the nanoparticles themselves allows researchers to use the nanosensing capabilities of nanoshells to directly follow chemical reactions on the catalyst using light.

"Nanoshells are among the world's most effective chemical sensors, and this study reveals another area where they are uniquely valuable," said Halas, the Stanley C. Moore Professor in Electrical and Computer

Engineering, professor of chemistry and director of Rice's Laboratory for Nanophotonics. "We are aware of no other method that provides this level of detail about metal-catalyzed chemical reactions that run in water. Given the overwhelming interest in biofuels processing and other water-based reactions, we expect this to be a very useful tool in understanding these chemistries in more detail."

TCE, or trichloroethene, is a common solvent and one of the world's most pervasive and troublesome groundwater pollutants. A carcinogen, TCE is found at 60 percent of the contaminated waste sites on the Environmental Protection Agency's Superfund National Priorities List, and the Pentagon has estimated the cost of cleaning up TCE contamination at U.S. military bases to be in the billions.

Wong's research group developed a new palladium-gold catalyst several years ago that helps break TCE into nontoxic components -- unlike methods that just move TCE into the solid phase or gas phase. Early tests showed that the new catalyst worked remarkably quickly. In fact, it was more efficient than predicted, based on the best available theories. "The gold was definitely playing a role that we didn't fully understand," Wong said.

To learn more, Wong approached Halas and Rice theoretical chemist Gustavo Scuseria. Halas had worked for years to develop spectroscopic methods that used gold nanoshells for chemical detection and analysis. Whereas Wong's four-nanometer particles have a gold center covered by palladium atoms, he and graduate student Kimberly Heck wondered if they could cover Halas' much larger gold nanoshells with palladium atoms and then use the nanoshells to detect the elusive TCE chemical reaction. "We also didn't know how the TCE molecules decomposed on the catalyst surface," Wong said.

It took about a year and half to develop the technology and work out the experimental kinks, but Wong said the results were worth waiting for. The method uses surface-enhanced Raman spectroscopy to reveal the structure and makeup of molecules sitting on the palladium-covered gold nanoshell surface. Scuseria, Rice's Welch Professor of Chemistry, and postdoc Ben Janesko provided sophisticated theoretical calculations that helped match the vibrations with the type of chemical bonds.

"We think we parsed it out pretty well," Wong said of the hydrodechlorination reaction. "Millions of surface-bound molecules are reacting simultaneously, but with a lot of work we've uncovered at least seven chemical steps."

Ironically, he said, the reaction the team set out to analyze -- the breakdown of TCE into nontoxic ethane and chloride salts -- happens "way too fast" to be observed by the method. So, the team slowed down the reaction by using a similar molecule called DCE or 1,1-dichloroethene. In fact, DCE is what TCE can become after the catalyst breaks off the first chlorine atom, so by studying the DCE reaction, they are getting a good look at much of what happens with the TCE breakdown.

Wong said the study is helping him better understand TCE catalysis, but he and Halas each think their new method will be especially useful in providing a new level of detail for how molecules are transformed in chemical reactions that take place on catalytic surfaces.

"There was a question of whether we could do Raman spectroscopy and catalysis at the same time," Wong said. "There's no other method that lets you 'see' these catalyzed reactions in water while the reaction is happening, and some of the most interesting of these -- like the reactions needed to upgrade glycerol and cellulose into chemicals and fuels -- occur in water."

Source: Rice University