CATALYSIS

MRI Visualization Could Aid Catalyst Development

Using para-hydrogen-polarized gas, researchers at the U.S. Dept. of Energy's Lawrence Berkeley National Laboratory (www.lbl.gov) and the Univ. of California (UC) at Berkeley have successfully applied magnetic resonance imaging (MRI) to the study of gas-phase reactions on the microscale — a significant step toward improving the design of catalysts and catalytic reactors, they say.

Their technique uses para-hydrogen-polarized gas to make an MRI signal strong enough to provide direct visualization of the gas-phase flow above active catalysts in packed-bed microreactors. In this way, gases and liquids can be tracked in microfluidic devices, such as a "lab-on-a-chip," as well as in the void spaces of a tightly packed catalyst reactor bed.

"This is the first time hyperpolarized gas has been used to directly study catalytic reaction products on such a small scale and without the use of tracer particles," comments Louis Bouchard, a UC chemist on the team. "It opens the door for future studies of heterogeneous catalysis in which all the unique benefits of MRI, such as velocimetry and spatially dependent quantities are available."

MRI and a similar technology, nuclear magnetic resonance (NMR) are powerful analytic tools, and could be valuable for characterizing catalytic reactors and reactions in microfluidic devices. However, the low sensitivity of conventional MRI/NMR techniques has limited their applicability to microscale catalysis research.

The scientists used para-hydrogen to overcome the low sensitivity. At standard temperature and pressure, hydrogen exists as approximately 75% ortho-hydrogen and 25% para-hydrogen. In the para- form, the protons in the nucleus have opposite spins. Increasing the fraction of para-hydrogen in the gas mixture leads to a spin-polarized product after a hydrogenation reaction. Under the right conditions, this hyperpolarization can be passed on to nuclei of interest and used to substantially boost the strength of their MRI/NMR signals by several orders of magnitude.

Bouchard and his colleagues have found a way to use gas enhanced with para-hydrogen in combination with propylene gas and a heterogenized catalyst to achieve a strong MRI/NMR signal from samples in the gas phase — something that has only been done before using hyperpolarized noble gases and expensive polarization equipment. A mixture of propylene and para-hydrogen-enriched gas (about 40% p-H_2), is passed through a reactor cell containing a rhodium-based catalyst immobilized on modified silica gel, where hydrogenation takes place. This produces spin-polarized propane gas that is transferred to an MRI/NMR magnet. The catalyst-free hyperpolarized propane gas can then be used to enhance MRI/NMR signals.

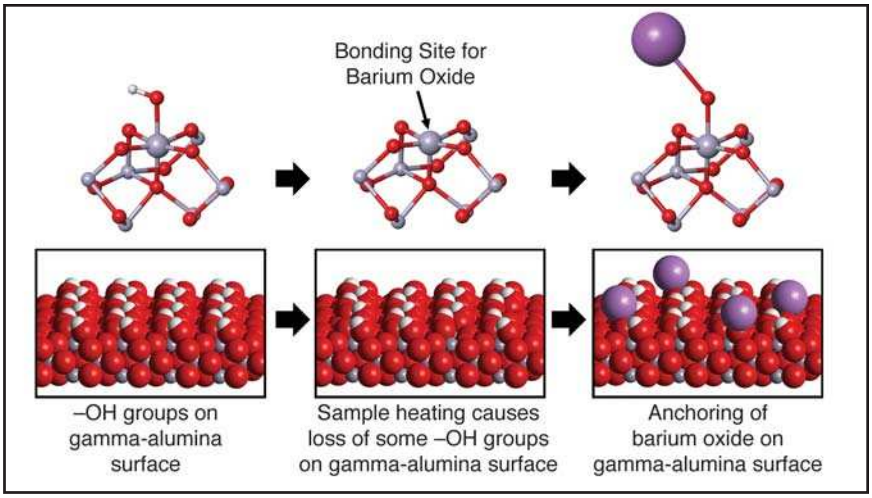
The technique is ready to be used now for the study of hydrogenation reactions. In the future, the researchers would like to extend its application to study other types of catalysts and reactions.

The Berkeley team also developed an NMR-based method to control the spatio-temporal aspect of delivering the polarized product in a microreactor. This enables precise control of how subsequent chemical reactions are visualized and studied.

Understanding the Formation of Emission-Control Catalysts

Researchers at the U.S. Dept. of Energy's Pacific Northwest National Laboratory (PNNL; Richland, WA; www.pnl.gov) have recorded the first observations of how certain catalyst materials used in emission-control devices are constructed. The PNNL team observed how barium oxide, which absorbs NO_x from tail-pipe emissions, attaches itself to the surface of gamma-alumina, a common catalyst support material.

The manner in which barium oxide anchors onto alumina suggests the exact site where catalytic materials begin to form — and where they can be available to absorb NO_x emissions. "Understanding catalysts in molecular and atomic detail can help us identify new ways to improve them," says PNNL researcher Janos Szanyi.



In the presence of water, aluminum ions (gray) on the surface of alumina bond to six oxygen ions (red). Heating removes the water and leaves some aluminum ions with only five oxygen ions, creating a bonding site for the barium oxide. Image courtesy of PNNL.

Aluminum ions in alumina bond to either four or six oxygen ions. When water is present, approximately 15% of the aluminum ions on the surface bond to six oxygen ions — one underneath to the bulk of the alumina, four in a square on the surface, and one on top to an oxygen ion in the water molecule. Removing the water by heating leaves the aluminum ion with only five oxygen bonds. In this penta-coordinated state, the aluminum is open for bonding to the barium oxide. Using nuclear magnetic resonance (NMR) spectroscopy to study the bonding, the researchers learned that the barium oxide filled every available penta-coordinated site, atom-for-atom.

The team is now examining the interaction of gamma-alumina with other metal and metal oxide particles to determine if penta-coordinated aluminum ions are suitable bonding locations for other catalytic materials.

This discovery may help remove a barrier to widespread use of diesel and other fuel-efficient "lean-burn" vehicle engines. Lean-burn engines deliver up to 35% better fuel economy because they mix more air with gasoline than standard internal combustion engines. However, the more-efficient engines can't meet strict emission standards because their pollution-control devices do not effectively reduce NO_x emissions. By capitalizing on the learnings obtained from the PNNL work, new catalyst designs may enable the benefits of lean-burn engines to be realized.

BIOENGINEERING

MIT Engineers Work to Heal With a New Bandage ...

Inspired by geckos, Jeff Karp, an instructor of medicine at Brigham and Women's Hospital and Harvard Medical School, and Robert Langer, chemical engineering professor at the Massachusetts Institute of Technology (Cambridge, MA), created a waterproof bandage that may soon be used to patch surgical wounds.

The surface of the bandage has nanoscale hills and valleys, like those on a gecko's paws that allow the lizard to cling to walls and ceilings. Layered over this landscape is a thin coating of glue that helps the bandage stick in wet environments, such as to the heart, bladder or lung tissue. And