The sweet smell of nano-success

January 27 2006

Materials scientists at Lehigh University and catalyst chemists at Cardiff University have uncovered secrets of the "nanoworld" that promise to lead to cleaner methods of producing, among other things, spices and perfumes.

The materials scientists, headed by Christopher Kiely of Lehigh, have determined the structure of a type of gold-palladium nanoparticle, which is the active component of a new environmentally friendly catalyst that promotes the oxidation of primary alcohols to aldehydes.

The researchers reported their results Jan. 20 in *Science* magazine, one of the world's top science journals. The article was titled "Solvent-free oxidation of primary alcohols to aldehydes using titania-supported gold-palladium catalysts."

The oxidation of primary alcohols to aldehydes is of fundamental importance to the chemical, pharmaceutical and perfume industries.

The oxidation of aromatic primary alcohols, such as vanillyl and cinnamyl alcohol, is of particular importance in the manufacture of perfumes and flavorings. Almost 95 percent of the worlds' vanilla (vanillyl aldehyde) is synthetically manufactured.

Benzaldehyde is also a key intermediate in the production of many fine chemicals in the agrochemical and pharmaceutical industries.

Such oxidation reactions have always been performed using permanganates or chromates, but these reagents are expensive and have serious toxicity issues associated with them. This new catalyst, consisting of gold-palladium nanoparticles dispersed on a titanium oxide support, allows this reaction to take place using oxygen under mild solvent-free conditions.

The new catalyst system was developed by a group headed by Prof. Graham Hutchings at Cardiff University in the United Kingdom.

"Determining the structure of the gold-palladium nanoparticle will help us understand how this catalyst works at the atomic level," says Kiely, who directs the Nanocharacterization Laboratory at Lehigh University in Bethlehem, Pa.

"This will inevitably enable us to optimize its performance and will subsequently lead to the development of other gold-based catalysts."

Samples of the catalyst were studied by Andrew Herzing, a Ph.D. candidate in materials science and engineering in Lehigh's Center for Advanced Materials and Nanotechnology (CAMN). Herzing used Lehigh's VG HB 603 aberration-corrected scanning transmission electron microscope (STEM), which enables energy dispersive x-ray data to be collected from individual nanoparticles.

"Our aberration-corrected STEM is unique in that it has an extremely small and intense electron probe. It also has a very high collection efficiency for the x-rays generated," says Kiely.

The original microscope was purchased almost a decade ago but was fitted only last year with a spherical aberration corrector designed to overcome distortions in the lenses that focus the electron beam. This has led to a significant improvement in resolution.

"Before being fitted with the aberration corrector, this microscope held the world record for spatial resolution in x-ray elemental mapping at two nanometers (two billionths of a meter)," says Kiely.

"Now, with the aberration corrector, it achieves an elemental mapping resolution of half a nanometer, approximately the width of two atoms."

Even so, obtaining chemical information from the tiny gold-palladium particle is difficult because the x-ray signal from a palladium atom is far weaker than the signal from a gold atom. There are also signals from the titanium oxide support. Under normal circumstances, the palladium signal would be lost in the noise.

To overcome this, Masashi Watanabe, a research scientist in the CAMN, has developed software based on multivariate statistical analysis combined with a spectrum imaging technique. While scanning for a particular element, Watanabe's software compares all the signals generated from an area and automatically identifies features in a particular signal dataset (in this case, a characteristic palladium X-ray signal).

Watanabe's automated approach significantly reduces the amount of random noise both in the signal and background. While a similar methodology has been in use for some time, Watanabe's program reduces the data analysis time from several hours to a few minutes.

Elemental maps collected from individual nanoparticles revealed that the palladium signal originates from a slightly larger spatial area than that of the corresponding gold signal. From this, Kiely's team concluded that the nanoparticles have a core-shell structure in which a palladium-rich shell surrounds a gold-rich core.

Even though the outer shell is palladium rich, this gold-palladium catalyst significantly outperformed a similar catalyst comprised solely of palladium. It is proposed that the gold acts as an electron promoter for the palladium, thus enhancing the nanoparticle's catalytic properties.

"Correlating a particular catalyst's performance with detailed structural and compositional data consistently proves to be a powerful methodology for understanding catalytic reactions," says Kiely.

Kiely has been collaborating with Hutchings for more than 10 years. The Lehigh-Cardiff team published an article titled "Tuneable gold catalysts for selective hydrocarbon oxidation under mild conditions" in *Nature* magazine on Oct. 20.

Source: Lehigh University