

Road to greener chemistry paved with nano-gold

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The selective oxidation processes that are used to make compounds contained in agrochemicals, pharmaceuticals and other chemical products can be accomplished more cleanly and more efficiently with gold nanoparticle catalysts, researchers have reported in *Nature* magazine.

A team of 13 U.K. researchers and one U.S. researcher reported in the Oct. 20 issue of the British journal that the carbon-supported gold catalysts can be fine-tuned with high selectivity for desired products through the addition of trace amounts of bismuth.

The gold catalysts can also carry out partial oxidations under solvent-free conditions, the researchers said, making them more environmentally friendly than oxidation processes that use chlorine, and less costly than those employing organic peroxides.

The team, led by Graham Hutchings, professor of physical chemistry at Cardiff University in Wales, included eight other Cardiff chemists, four scientists from the Johnson Matthey chemical company in the United Kingdom, and a materials scientist from Lehigh University in Bethlehem, Pennsylvania.

Their article was titled "Tuneable gold catalysts for selective hydrocarbon oxidation under mild conditions."

Masatake Haruta, a catalyst chemist at Tokyo Metropolitan University

who has been at the forefront of gold nanoparticles research for more than a decade, said in a commentary accompanying the Nature article that the breakthrough by Hutchings's group had the potential to "transform" the chemical industry.

Noting that most industrial oxidation processes use chlorine or organic peroxides, Haruta said, "the chemical industry would be transformed if selective oxidation of hydrocarbons could be achieved efficiently using cheap and clean oxygen from the air. The advancement by Hutchings and colleagues of 'greener' methods for oxidation catalysis using gold is therefore invaluable."

The industrial selective oxidation processes that Hutchings's team catalyzed with gold nanoparticles are used to convert unsaturated hydrocarbons to oxygen-containing organic compounds (e.g., epoxides, ketones), which in turn serve as higher-value compounds that form the basis for many chemical products.

The challenge, says Chris Kiely, professor of materials science and engineering at Lehigh University, is to selectively insert an oxygen atom at specific positions into long-chain or cyclic-ring hydrocarbon carbon molecules, something which nanoparticulate gold achieves effectively.

The gold nanoparticles, which measure 2 to 15 nanometers in width (1 nm equals one one-billionth of a meter) must be distributed evenly over a large surface area support and prevented from coalescing and forming larger particles with weaker catalytic properties.

"The nano-gold catalyst can effectively aid the insertion of an oxygen atom into the unsaturated hydrocarbon," says Kiely, who has co-authored several dozen papers with Hutchings. "Activated carbon provides a viable support for the nanoparticles. The gold catalyst can also be fine-tuned and made more effective, giving a higher yield of epoxides and

ketones, with the addition of occasional atoms of bismuth.

"We're trying to determine the size, distribution and shape of the gold nanoparticles, and to see how these parameters relate to the measured catalytic properties. We are also interested in the interaction of gold with other promoter elements, such as bismuth, and we're trying to identify exactly where the bismuth atoms are going and why they have a beneficial effect."

Kiely, who joined the Lehigh faculty in 2002 after serving on the materials science and engineering and chemistry faculties at Liverpool University, uses transmission electron microscopy and various spectroscopic techniques to characterize the gold nanoparticles.

The recent acquisition by Lehigh University of two aberration-corrected electron microscopes, including a JEOL 2200FS transmission electron microscope, will shed more light on future work in the area of gold catalysis, he said.

"Before, we were able to see nanoparticles and achieve atomic resolution, but not with the same degree of clarity that the new JEOL microscope provides. The new instrument also gives us the capability of doing chemical composition analysis with close to atomic column precision, which will be a big boon."

Gold in recent years has drawn more attention from researchers as a potential catalyst in chemical processing, pollution control and fuel cell applications. Haruta, a pioneer in this area, demonstrated a decade ago that gold nanoparticles could be used, amongst other things, as catalysts to de-odorize restrooms and to convert carbon monoxide to carbon dioxide at low temperatures.

But much remains to be learned for nano-gold to realize its full potential,

says Kiely, who directs the Nanocharacterization Laboratory in Lehigh's Center for Advanced Materials and Nanotechnology.

"Gold is a very useful catalyst for many chemical reactions," says Kiely, "but we're still not sure what happens at the molecular scale during the catalysis process. The more we learn, the better we can fine-tune gold nanoparticle catalysts."

Source: Lehigh University

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