Gases from grasses: Simulations on Ranger supercomputer help researchers understand biofuel react

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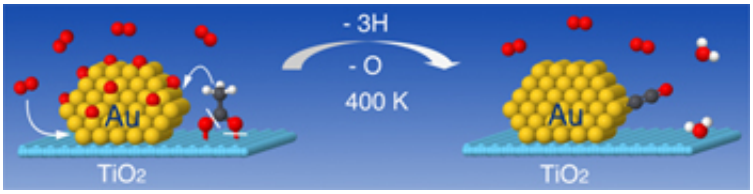

This shows the conversion of acetate to ketenylidene at the perimeter site of the Au/TiO2 catalyst. The acetate, which adsorbs on TiO2 , undergoes dehydrogenation (oxidation) and the deoxygenation to form ketenylidene on the gold. Credit: *J. Am. Chem. Soc.*, 2012, 134 (33), pp 13569−13572. DOI: 10.1021/ja305911e

Researchers from the University of Virginia used computer simulations and laboratory experiments to discover a reaction site on gold-titanium oxides that is responsible for high rates of catalysis relevant to biofuel and fuel cell reactions. The findings help scientists understand the principle of the catalysis and choose the right catalysts for certain reactions.

In a well-known fairy tale, Rumpelstiltskin used magic to weave straw into gold. Today, scientists are reversing that formula—using gold to turn straw (and other forms of biomass) into today's global currency: energy.

The magic involves a special nanocatalyst, in which minute particles of gold dot the surface of titanium-oxide. The forces that emerge from the combination of these two materials are strong enough to breaks the O-O bond of oxygen molecules and the C-O bond of acetic acid, a byproduct of biomass conversion that, when combined with hydrogen, forms ethanol, an important precursor for fuel.

Because of its ability to split strongly bonded molecules, the gold titanium-oxide nanocatalyst is becoming a leading candidate for industrial applications that use biomass or fuel cells to create clean energy.

"Metal nanoparticles supported on oxide surface are very popular because they have high activity towards a variety of reactions, especially oxidation reactions," said Wenjie Tang, a research associate in the department of chemical engineering at the University of Virginia and a member of the Neurock group there. "People know they're active, but how they work and the real mechanism of their active sites was not quite understood."

Combining computer simulations and laboratory experiments, Tang and others from the University of Virginia discovered a reaction site on the perimeter of the gold-titanium complex that does much of the work of catalysis.

"Previously, researchers thought it might be only the gold that was active in the reaction; they didn't think the oxide surface had any influence," Tang said. "But recently we realized that the oxides play an important role in modifying the metals above them. They create this a special site at the perimeter which is really the important site for the reaction."

The researchers initial findings were reported in the August 2011 edition of *Science*. Further results of the study were published in the June 2012

edition of *JACS*. In August 2012, the scientists reported in the *Journal of the American Chemical Society* (*JACS*) the first catalytic oxidation of acetic acid to ketenylidene (CCO) over a gold titanium-oxide catalyst. (Oxidation is the loss of electrons by a molecule—an important process for catalysis.) The researchers think the discovery of this intermediate product, ketenylidene, will lead to the creation of valuable hydrocarbon fuels via reactions such as Fischer-Tropsch process. Further results of these studies are forthcoming.

Many analysts believe energy from oil will only grow more expensive over time. Biomass conversion has the potential to power a significant portion of the world's energy needs, however, scientists must find new ways to produce biofuels less expensively. Better catalysts are one important way to do so.

Catalysts speed up chemical reactions by altering the activation energy required for a reaction to proceed. Without a catalyst, two solvents may meet without a reaction. In the presence of a catalyst, those same molecules will be utterly transformed.

Catalytic reactions happen fast and the intermediate structures that form are not always apparent in the process. Computer simulations allow scientists to slow down the reactions in order to uncover and visualize the forces acting on molecules at the atomic level. The researchers used the Ranger supercomputer at the Texas Advanced Computing Center to explore aspects of the material reaction at the nanoscale that could not be investigated in the laboratory.

"Experiments can show many things, but they cannot reveal how the reactions take place," Tang said. "For example, we know there should be ketenylidene formation, but we were not sure whether it was on the gold or on the titanium. We also didn't know which site is the most active for turning acetic acid into ketenylidene."

Using density functional theory, a quantum mechanical modeling method used in physics and chemistry to investigate the electronic structure of molecules, the researchers calculated the interactions of more than 200 atoms using Ranger. The simulations helped the group identify the presence of an intermediate chemical in the reaction and determined that it was in fact ketenylidene.

The acetic acid-to-ketenylidene path combines dehydrogenation (oxidation) and the deoxygenation of the acetate, "which are crucial steps for biomass conversion into more valuable industrial chemicals," the authors wrote.

For Tang, the results proved the increasing usefulness of computer simulations to support physical experiment and to suggest new, more specific chemical reaction paths.

"I wouldn't have imagined calculating such a system five or 10 years ago," Tang said. "We didn't have the computing resources."

According to Jose Rodriguez from Brookhaven National Laboratory, the use of computational simulations in studies of surface catalysis is leading to new levels of understanding.

"[These are] excellent theoretical studies that help to understand the details for the mechanism of CO oxidation on Au/TiO2 surfaces," he said.

By generating gases from grasses and improving the capacity of fuel cells to separate hydrogen and oxygen, new catalysts are expected to alter fundamental energy-generating processes, promising cheaper and more sustainable fuels.

"Right now we're just trying to understand the principle of the catalysis,"

Tang said. "Hopefully, this will help other people when they try to choose a catalyst for certain reactions."

Provided by University of Texas at Austin