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Scientists learn to control reactions with the shape of a rare-earth catalyst

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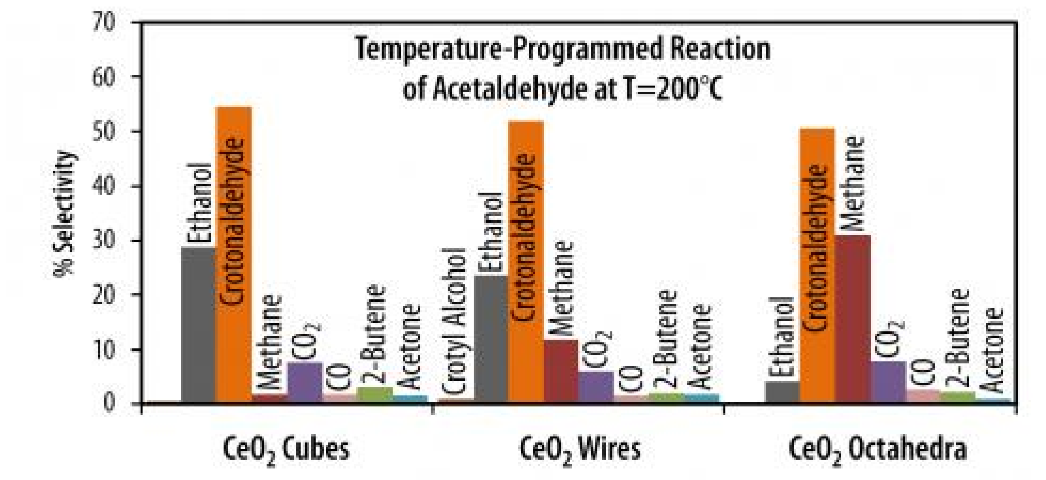

Cerium oxide nanocrystals of different shapes catalyze chemical reactions leading to different product types and yields.

(Phys.org) —Scientists at the Department of Energy's Oak Ridge National Laboratory have discovered they can control chemical reactions in a new way by creating different shapes of cerium oxide, a rare-earth-based catalyst. Their finding holds potential for refining fuels, decreasing vehicle emissions, producing commodity chemicals and advancing fuel cells and chemical sensors.

The researchers synthesized crystals of cerium oxide billionths of a meter wide, shaped as cubes, wires or octahedrons. The form of the catalytic surface dictated the pathways of chemical reactions that begin when cerium oxide binds with acetaldehyde, an oxygenated hydrocarbon common to diverse chemical reactions in both nature and industry. Different shapes of cerium oxide led to pronounced differences in reaction products and yields.

The findings, published in the American Chemical Society journal *ACS Catalysis*, could have wide impact because acetaldehyde, due to its ability to easily couple to other molecules, serves as an important building block for assembling into larger molecules, a process that could have implications for upgrading fuel. In this study, the cerium oxide catalysts coupled two acetaldehyde molecules to produce a dimer (a two-unit chemical chain).

"Many people know that catalysts speed up reactions. But in most chemical reactions, there can be multiple reaction pathways, and the catalyst may speed up a different reaction than the one you're interested in," said study leader Steve Overbury, who worked with first author and ORNL postdoctoral fellow Amanda Mann, ORNL spectroscopist Zili Wu and former ORNL postdoctoral fellow Florencia Calaza (now at the Fritz Haber Institute).

Improving selectivity, or the ability to make desired products while avoiding undesirable byproducts, is an important goal of catalytic chemists. Catalyts are critical means of arriving at desired ends."For example, methane would be a very good precursor for formation of alcohols, but when you try to oxidize methane to alcohol, you tend to get complete combustion of the methane. That's not what you want," Overbury said. "You can speed up methane oxidation easily with almost any catalyst or even just lighting a match, but to selectively convert it into methanol is a catalytic challenge."

In the current study, the researchers used the shape of the catalyst to guide reactions to desired products. They showed, for example, if nanocatalysts guiding acetaldehyde reactions were shaped as cubes, ethanol production was favored. But if the catalysts were shaped as octahedrons, methane yield increased. "This is the first time that this structural sensitivity has been clearly exhibited in reactions of this type," Overbury said.

Versatile catalyst

"Cerium oxide stores oxygen and can release it too," Overbury explained. That versatility is the reason it is the primary promoter of chemical reaction in the catalytic converters used in most gasoline-burning cars. "If the fuel-to-air mixture swings lean and there's too much oxygen, cerium oxide can absorb oxygen. And if it goes rich so that there's not enough oxygen, then it can release oxygen," he said. "In that way it can smooth out the catalytic cycle to better control both hydrocarbon and nitrogen oxide emissions from fuel combustion."

A carbon double-bonded to oxygen, a carbonyl, is a major component of oxygenates. The scientists were interested in understanding how it behaves in the catalyst. In a previous publication, Overbury's team observed the catalyst converted alcohol into acetaldehyde. "Because this catalyst is good at both oxidations and reductions, we're interested in the correlations between alcohol chemistry and carbonyl chemistry."

The researchers also learned the catalyst is good at coupling acetaldehyde molecules to form longer-chain molecules. They used it to create hydrocarbons and oxygenates containing two, four, and six carbons (C2, C4, and C6 compounds).

The work shows that, by taking away some oxygens and linking fragments, cerium oxide can turn oxygenates into longer-chain-length hydrocarbons that compose gasoline. "If you put two C6s together and get a C12, you're getting close to diesel fuel," Overbury said.

What's next?

Next the researchers will explore other aspects of cerium oxide chemistry. "We want to understand why you get these differences in selectivity," said Overbury, who will study how the rates of intermediate reaction steps depend upon the shapes of the catalysts.

Overbury is working with Ariana Beste of the Joint Institute for Computational Sciences (a partnership of ORNL and the University of Tennessee) on computations to understand how the orientation of a molecule on the catalyst's surface affects bond-breaking and subsequent reaction pathways.

Further, this spring Zili Wu, Eugene Mamontov and Overbury used the Spallation Neutron Source, a DOE Office of Science User Facility, to explore the dynamics of methanol adsorption on cerium oxide. This work explored commercially available cerium oxide using SNS's BASIS instrument for quasi-elastic neutron scattering measurements to gain knowledge about molecular dynamics.

For cerium oxide to catalyze reactions for fuel and polymer production, it must be plentiful. While cerium is a rare-earth element, it is the most common of the rare earths and in fact is more abundant than some non-rare-earth elements, such as cobalt. "Miners extract a lot of cerium to get the more precious rare earths, like europium and dysprosium, that have high-tech applications as phosphors in television screens, permanent magnets and lighting," Overbury said. As a result, miners have more cerium than they know what to do with. In fact, Overbury and colleagues are engaged in a project to find uses for cerium. It is funded through the Critical Materials Institute, a DOE Energy Innovation Hub led by Ames National Laboratory to address shortages of key compounds.

More information: Mann, A.K.P., Wu, Z., Calaza, F.C., and Overbury, S.H." Adsorption and Reaction of Acetaldehyde on Shape-Controlled CeO2 Nanocrystals: Elucidation of Structure–Function Relationships." *ACS Catal*. 2014, 4, 2437–2448

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