Scientists draw unified picture of alcohol's interactions with early transition metal oxide catalysts

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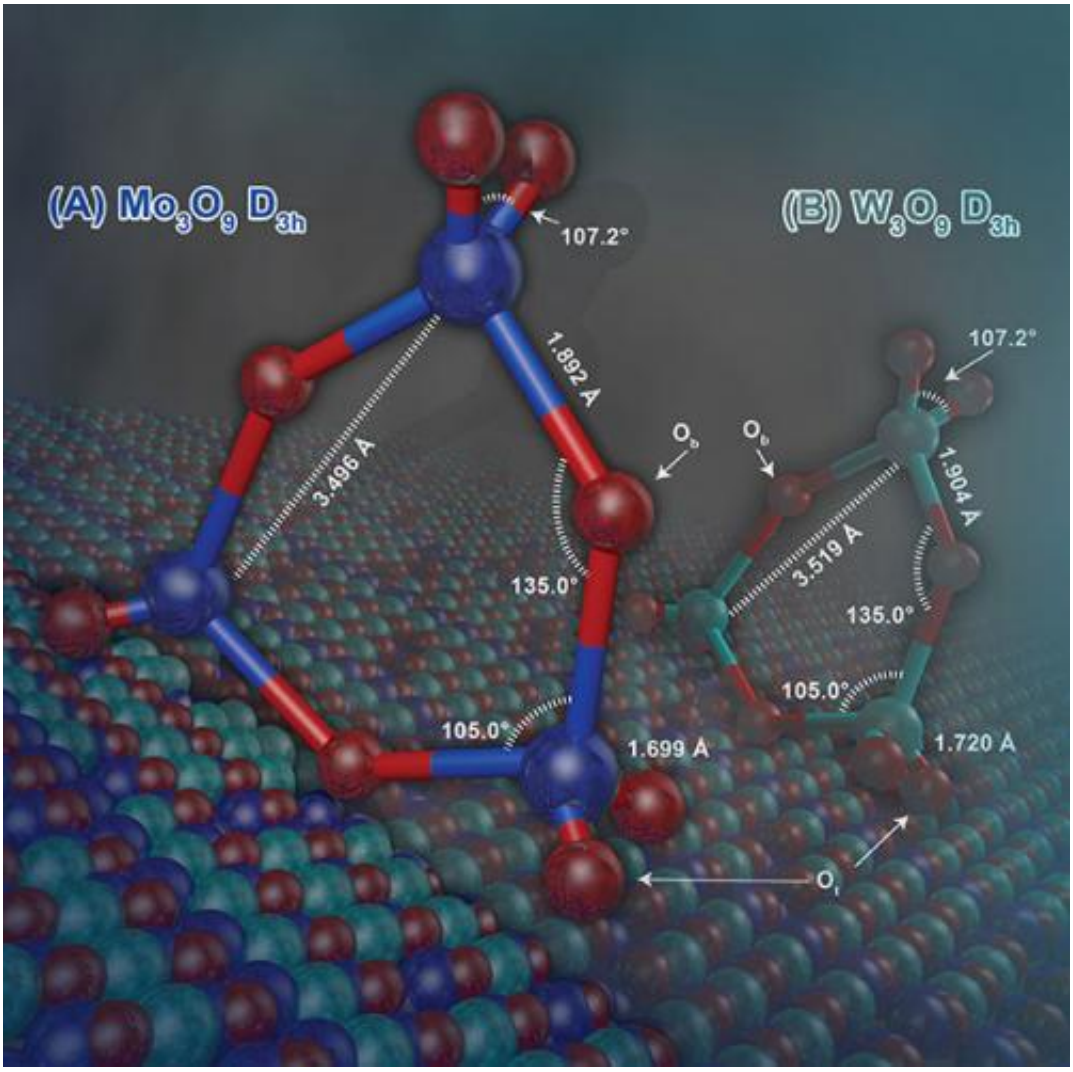

In their review article, the researchers discuss catalytic cyclic (WO3)3 and (MoO3)3 clusters and the surfaces on which they react.

(Phys.org) —Based on 8 years of study, scientists at Pacific Northwest National Laboratory (PNNL) and the University of Alabama described in exquisite detail how alcohols behave on two early transition metal catalysts, molybdenum trioxide and tungsten trioxide, in a 17-page article in *Chemical Society Reviews*. All the catalysts were prepared using an innovative method introduced at PNNL that allows for the preparation of monodispersed catalytic clusters of identical size and structure. Such model systems can be utilized by scientists needing a structurally well-known material. The review provides a detailed discussion of the reaction mechanisms of these prepared catalysts for dehydration, dehydrogenation, and condensation reactions of small aliphatic, or open chain, alcohols.

"I'm happy that we could summarize the research and publish it in a high-profile review journal," said Dr. Zdenek Dohnálek, a PNNL scientist who worked on the experimental research. "The only way we could afford to do this review and the underlying research was with long-term Basic Energy Sciences funding."

Catalysts drive countless reactions, such as converting alkenes and other petroleum-derived chemicals into plastics that are used in everyday items from carpets to capacitors. Replacing the petroleum in these reactions with alcohols derived from biomass demands a new catalyst. To build that catalyst, scientists need to understand how catalysts drive reactions that convert propanol, ethanol, and other alcohols into those same alkenes and other hydrocarbons. The team's research into molybdenum and tungsten trioxides and the resulting review article reveals important catalyst characteristics.

"We came up with a pretty simple picture of how these things work," said Dr. Roger Rousseau, a PNNL scientist who worked on the

computational simulations. "We found the small changes in the molecular structure that determine whether the molybdenum or tungsten oxide catalyst is good for a reaction."

Initially, the team's goal was to prepare catalytic metal oxide clusters supported on other oxides and determine how the clusters react. "You'd look in the literature in the past, and you would see all types of poorly defined clusters in the experiment, making it hard to determine anything," said Dohnálek.

The team devised a new method to obtain identical clusters. They evaporated the oxide into the gas phase, getting primarily cyclic trimers. The clusters could then be dispersed on different supporting materials. Now, this method is used by other scientists at other research institutes to study catalysts properties. Their work and that of PNNL's appears in the review article.

Using the monodispersed preparation method, the authors and their colleagues spent years studying the catalysts. "Frequently researchers focus only on the characteristics of the system or the chemistry, not both. Whatever we prepare as the model system, we understand the structure and understand how the reactions work, or don't," said Dohnálek.

Rousseau added, "Some of the reactions were very disappointing, although overall even the disappointing ones showed us what was important in the reactions."

Now, the team is focusing on how tungsten and molybdenum oxides catalyze deoxygenation of diols and other more complex molecules.

More information: Rousseau R, DA Dixon, BD Kay, and Z Dohnálek. 2014. "Dehydration, Dehydrogenation, and Condensation of Alcohols on

Supported Oxide Catalysts Based on Cyclic (WO3)3 and (MoO3)3 Clusters." *Chemical Society Review*. Advance Article. DOI: 10.1039/C3CS60445D