

A BIMETALLIC CATALYST THAT HELPS TURN PLANTS INTO PLASTIC

Petroleum does more than fuel our vehicles. Many of the chemicals that supply industrial processes are also derived from petroleum, a limited resource that will likely become more expensive over time. In preparation for that cost increase, scientists are developing new sources for the chemicals typically provided by petroleum. One option is to extract valuable chemicals from biomass, such as plants or microbes, and convert these precursors into useful end-products. Biomass chemicals, however, have significantly more oxygen than petroleum-derived chemicals and require extensive, and expensive, processing. To ease the complex conversions of biomass precursors, catalysts are being developed that include an oxophilic (“oxygen loving”) metal alongside a hydrogenation metal (a metal that has been treated with hydrogen). These bimetallic catalysts are promising, but little is known about how they work. In this study, researchers used APS x-rays to unravel the catalytic mechanism. Their discoveries may help make biomass a viable chemical source

The researchers, from the University of Wisconsin–Madison, Purdue University, and Argonne, were initially interested in the reaction that converts 2-hydroxymethyl-tetrahydropyran into 1,6 hexanediol, a 6-carbon chain with two hydroxyl groups at opposite ends. This highly-sought after compound is used in the production of polymers and is typically sourced from petroleum. While it can be produced from biomass, the problem is conversion reactions often result in the improper placement of hydroxyl groups.

In a previous study, a catalyst made from a carbon support, rhenium, an oxophilic promoter, and rhodium, a reducible metal, selectively produced 1,6 hexanediol from 2-hydroxymethyl-tetrahydropyran (Fig. 1). They hypothesized that this specificity stems from the two metals working in concert. The rhenium helps open the ring of 2-hydroxymethyl-tetrahydropyran at the C-O bond, then, the rhodium does its work, avoiding the production of unwanted side products while hydrogenating the opened ring. Questions remained, however, as to the bimetallic catalyst’s mechanism, but these could be answered at the APS.

The MR-CAT 10-BM-A,B and 10-

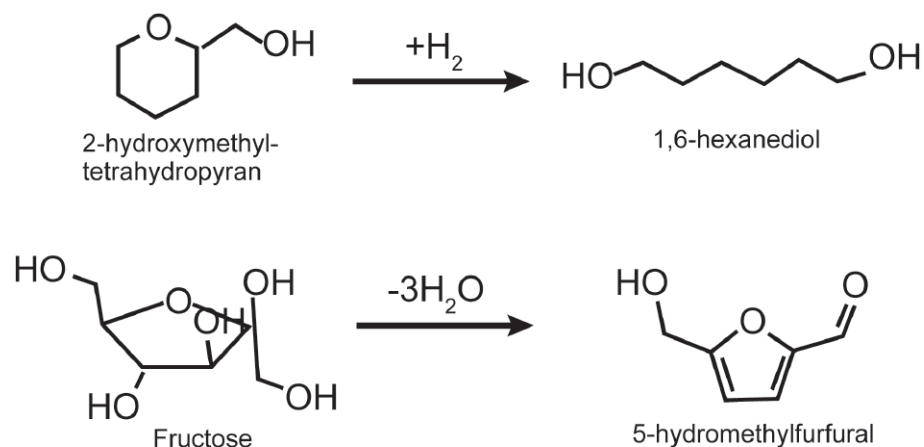


Fig. 1. Researchers studied the catalytic mechanism of two model reactions at the APS: the hydrogenolysis of 2-hydroxymethyl-tetrahydropyran to 1,6-hexanediol and the dehydration of fructose to 5-hydroxymethylfurfural. The reactants can be derived from plant biomass sources and the products, usually obtained from petroleum, have commercial value.

ID-B beamlines at the APS, where these studies were carried out, include custom equipment that allowed the research team the unique opportunity to study the catalyst *operando*, that is, during the reaction. The researchers performed x-ray absorption spectroscopy (XAS), which detects bonds between atoms in the catalyst. They observed that rhenium had fewer bonds

on average, suggesting that the metal mostly occupied the nanoparticle surface. They interpreted this and other data as evidence that rhenium likely interacts strongly with oxygen in the surrounding water molecules, such that the hydrogen part of the water molecule acts like an acid. The researchers therefore suspected that the bimetallic catalyst may catalyze reactions by be-

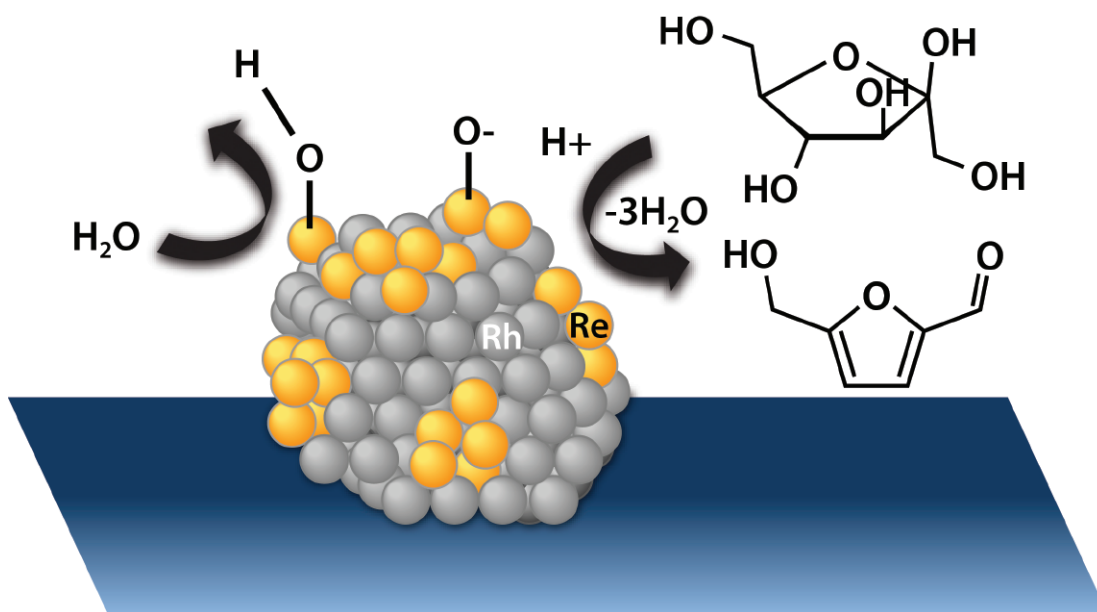


Fig. 2. An increase in reduction temperature results in a decrease in activity of a RhRe/C catalyst for C-O hydrogenolysis and fructose dehydration. XAS measurements and other data indicate that an increase in pretreatment temperature results in a decrease in surface Re on particles with an Rh core. Re atoms on the surface of Rh particles likely activate water, thereby promoting an acid catalysis mechanism.

having like a solid acid. This mechanism was supported by experiments showing that the reaction failed to work without water.

To further test the acid catalysis hypothesis, the researchers studied a second reaction: the conversion of fructose — another chemical that is derived from plant biomass — to 5-hydroxymethyl furfural, which is a chemical way station for several important end products (Fig. 1). This reaction can only be catalyzed by an acid-catalyzed mechanism. They found that 30% of the fructose was converted by the bimetallic catalyst to the desired product, with 50% selectivity, similar to what is achieved with other solid acid catalysts at those conditions.

In additional experiments, the researchers began to study factors that affect catalytic activity, such as pretreatment temperature. Tests on a series of catalysts revealed that higher pretreatment temperatures resulted in lower catalytic activity. Based on XAS data, the researchers found that higher pretreatment temperatures caused rhenium

atoms to migrate into the core of nanoparticles (Fig. 2). This may explain the lower activity, as the acid-based catalytic mechanism requires that the rhenium be on the nanoparticle surface, exposed to water.

In future studies, the researchers will continue to test various factors in an attempt produce better catalysts, bringing the dream of biomass-derived polymers and other materials closer to reality. — *Erika Gebel Berg*

See: Mei Chia¹, Brandon J. O'Neill¹, Ricardo Alamillo¹, Paul J. Dietrich², Fabio H. Ribeiro², Jeffrey T. Miller³, James A. Dumesic^{1*}, "Bimetallic RhRe/C catalysts for the production of biomass-derived chemicals," *J. Catal.* **308** (2013) 226. DOI:10.1016/j.jcat.2013.08.008

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X-ray adsorption spectroscopy studies were supported by the Institute for Atom-efficient

Chemical Transformations (IACT), an Energy Frontier Research Center funded by the U.S. Department of Energy Office of Science, Basic Energy Sciences. The research was also supported by the National Science Foundation under Award No. EEC-0813570. R.A. acknowledges support from the National Science Foundation Graduate Research Fellowship Program under Grant No. -DGE-0718123. MR-CAT operations are supported by the Department of Energy and the MRCAT member institutions. Use of the Advanced Photon Source at Argonne National Laboratory was supported by the U.S. Department of Energy Office of Science under Contract No. DE-AC02-06CH11357.

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