of Amsterdam researchers G. Rothenberg, E.A.B. de Graaf, and A. Bliek have developed a cerium tungsten oxide catalyst that is able to cleanly and selectively oxidize hydrogen while maintaining excellent thermal stability. Moreover, the catalyst can be readily regenerated with oxygen and serve as an oxygen "reservoir."

As reported in the July 28 issue of *Angewandte Chemie*, Rothenberg and coworkers doped ceria with Bi, La, In, Mo, Pb, Sn, V, W, Y, and Zr to make 10 ceria-based bimetallic oxides by using a parallel synthesis technique based on boiling molten mixtures of nitrate precursors followed by calcination. The extent of substitution of Ce ions was limited to 10% so as to retain the cubic fluorite crystal structure. As the redox chemistry of substituted ceria is sensitive to induced structural defects and stresses in the crystal lattice, the researchers expected to see varied oxygen mobility, which would produce different levels of catalytic activity and thermal stability in these systems.

Rothenberg said, "We had an idea that similar cations will create 'small holes' in the fluorite lattice, without causing too much disturbance. This way, you keep the oxygen-exchange properties of the ceria, but also, hopefully, tune the selectivity so that the new material will oxidize hydrogen selectively."

The catalysts were screened in cyclic redox experiments with a gas mixture that simulates the effluents from an ethane dehydrogenation process. While the lanthanum-, indium-, and zirconium-doped systems showed the highest activity, the tungsten-doped system showed >97% selectivity toward hydrogen. Moreover, this system showed excellent stability under sintering as well as negligible coke formation, properties that are of significance in commercial oxidative dehydrogenation reactions.

The mechanism of the hydrogen selectivity remains to be determined. Rothenberg thinks that the small hydrogen molecules may diffuse into the lattice, reacting with labile oxygen atoms that are unavailable to the bulky hydrocarbon molecules.

SARBAJIT BANERJEE

Titanium Nanotubes Serve as Hydrogen Sensors

Titanium nanotubes used as hydrogen sensors is an example of materials properties changing dramatically when crossing the border between real-world sizes and nanoscopic dimensions. Craig A. Grimes, associate professor of electrical engineering and materials science and engineering at The Pennsylvania State University, and colleagues have found that hydrogen entering an array of titanium nanotubes flows around all the surfaces, but also splits into individually charged atoms and permeates the surface of the nanotubes. These hydrogen ions provide electrons for conductivity. The change in conductance signals that hydrogen is present at a concentration above the background level.

The researchers report in the August 1 issue of *Sensors and Actuators B: Chemical* and an earlier issue of *Advanced Materials* (April 2003) that because the nanotubes are in close contact with each other (see figure), the contact points become highly conductive relative to the rest of the nanotube.

https://doi.org/10.1557/mrs2003.203 Published online by Cambridge University Press

The researchers said, "For a bulk conductivity constant with nanotube diameter, the greater the number of contact points, the greater will be the resistance change upon exposure to hydrogen. Therefore, the smaller-diameter tubes, with thinner walls and a greater number of contact points, will exhibit higher sensitivities than their larger-diameter counterparts."

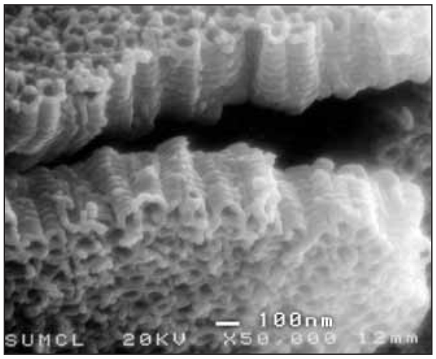

Figure. Vertical cross section of titanium nanotubes used for sensing hydrogen. Credit: Penn State, Craig A. Grimes.

The researchers studied titanium nanotubes of 22 nm and 76 nm diameters, which differed in surface area by a factor of two. They found that the response to hydrogen of the smaller tubes is 200× more sensitive than that of the 76-nm-diameter tubes. The researchers suggested that the hydrogen molecules become dissociated at the titanium surface, diffusing into the titania lattice, and act as electron donors, and that this mechanism makes the nanotubes sensitive to hydrogen.

Grimes said results show that titanium nanotube sensors can monitor hydrogen levels from 1 ppm to 4%. Furthermore, the material is not "used up" when sensing hydrogen, but once the gas clears from the tubes, can be used again. The researchers tested the titanium nanotubes with carbon dioxide, carbon monoxide, ammonia, and oxygen, finding little interference.

"Many researchers have tried to use carbon nanotubes as gas sensors, but they do not work very well," said Grimes. "Titania has really great sensitivity and a nice response."

Highly Ordered Merocyanine Dye Assemblies Reminiscent of Chlorophyll Dye Rods

Photosynthesis relies on highly organized dye assemblies for electron transfer. An orderly arrangement of dyes is also thought to be critical for organic materials in electronic and photonic applications. Typically, however, stacking of π-bonded systems results in one-dimensional dye assemblies, although two-dimensional brickwork and tubular aggregates of cyanine dyes have been discovered serendipitously. F. Würthner and S. Yao of Universität Würzburg, Germany, and U. Beginn of RWTH Aachen, Germany, have recently applied concepts of supramolecular polymerization and hierarchical self-organization to fabricate, in a controlled manner, highly ordered merocyanine dye assemblies.

As reported in the July 21 issue of *Angewandte Chemie*, Würthner and coworkers attached nonpolar tridodecyloxybenzyl substituents to highly polar merocyanine and bis(merocyanine) dyes, which made them soluble in low-polarity

https://doi.org/10.1557/mrs2003.203 Published online by Cambridge University Press