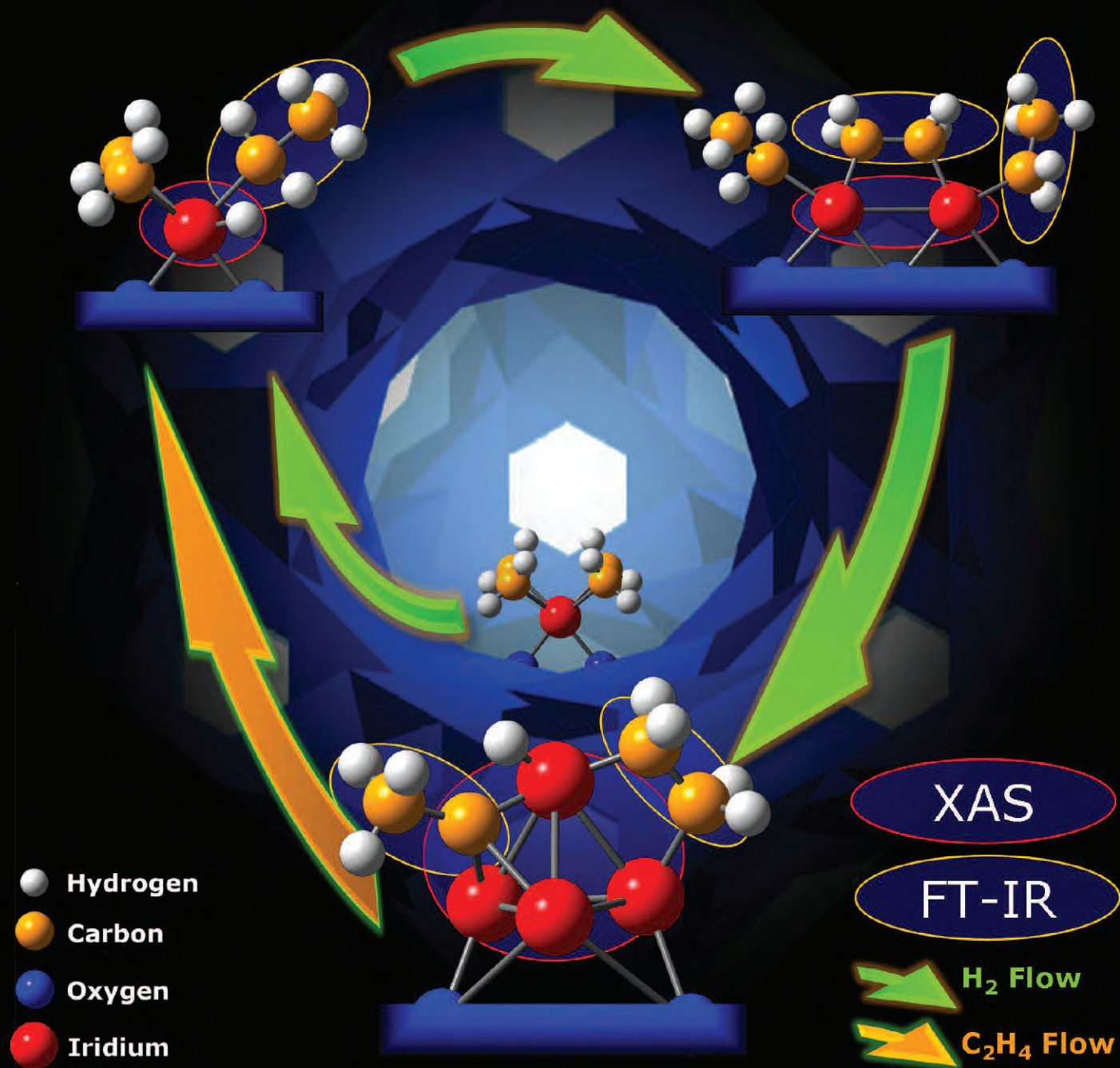


SHIP-IN-A-BOTTLE CATALYSTS



Reversible formation and breakup of iridium clusters in a zeolite.
Illustration courtesy of Alper Uzun and Bruce Gates, UC Davis.

High-intensity x-rays from the APS are helping researchers from the University of California, Davis (UC Davis) investigate the properties of tiny clusters of metal that are constructed, ship-in-a-bottle-like, within the nanoscale pores of certain crystalline solids. This work is providing new information about the nature of the interface between metal clusters and a support material, and how this interface can be controlled and modified to improve industrial catalysts.

The researchers used compounds that contain both an organic and a metal component—organometallic precursors—to make structurally simple metal-oxide-supported and zeolite-supported metals, including single-metal-atom complexes, metal carbonyl clusters, and metal clusters.

They have shown that some of these compounds have catalytic properties for speeding up industrial chemical reactions. Like other solid catalysts, these offer the advantages of ease of separation from products of the reactions and lack of corrosion. Because they have uniform structures, they offer the prospect of selective conversions, with the added advantage of reducing the side products and overall energy demands of the chemical conversion.

The UC Davis team has experimented with so-called rhenium subcarbonyls supported on magnesium oxide, and with clusters containing 4 or 6 iridium atoms or 15 platinum atoms supported on alumina and in zeolites (crystalline aluminosilicates). The process of studying catalysts dissolved in liquids is usually obscured by the presence of solvent molecules, which bond to the metals and hide the details of their chemistry. When the metals are bonded to a support, they can be investigated in the absence of solvents, and the simplicity of the structures allows new insights into the structures and the chemistry. The understanding emerges from probing the structures with infrared spectroscopy and other techniques.

The researchers recently showed how to create well-defined clusters of the metal iridium, containing just four atoms of iridium in each cluster. They began by reacting an organometallic precursor containing iridium with the surface of the zeolite from which some

of the aluminum had been removed. The dealumination process provided a set of isolated sites within the zeolite pores with which the precursor could react.

They used infrared spectroscopy to reveal the exact nature of the reaction between this precursor, $[\text{Ir}(\text{C}_2\text{H}_4)_2(\text{acac})]$, and the zeolite. The spectra show that the zeolite's hydroxy (OH) groups are partially lost from the interior surface of the pores and the acac group (acetylacetonone) splits off from the precursor. This dissociation process paves the way for the iridium atoms to anchor to the exposed reactive sites in the zeolite. The researchers used extended x-ray absorption fine structure (EXAFS) data, recorded at the MR-CAT 10-ID beamline at the APS, to show that, at this stage, only single, site-isolated iridium units were present in the zeolite pores.

The next step on the road to creating the well-defined iridium clusters was to initiate cluster formation by removing the ethylene groups that remained π -bonded to the iridium atoms by reaction with hydrogen gas; as a result, the bonds anchoring the iridium atoms to the zeolite were disrupted. The team followed the changes by continually checking via infrared spectroscopy and EXAFS spectroscopy. After just minutes, the spectral peaks associated with the attached ethylene ligands began to shrink and new peaks associated with ethyl groups replaced them; these peaks, in turn, disappeared as ethane gas formed and flowed out of the zeolite.

More critically, however, new weak spectroscopic bands indicative of a different type of group formed from ethylene emerged, bands that could only exist if more than two metal atoms were close together, thus hinting at the

onset of iridium cluster formation. At this stage, EXAFS was unable to see these sparse fledgling clusters.

Heating the material in a flow of hydrogen gas and monitoring with x-ray absorption near edge spectroscopy and EXAFS spectroscopy proved that Ir-Ir bonds were forming. This process involved continuous breaking of bonds between carbon atoms and iridium, and the migration of individual iridium atoms within the pores of the zeolite.

The researchers emphasize that, strictly speaking, the notion of a ship-in-a-bottle catalyst remains unexplained. What is known is that the zeolite pores are like tiny cages linked by windows. The team's clusters formed within the cages and when they became larger than the diameter of the windows, they could no longer escape and were potentially stabilized like ships in bottles.

This work is leading to new insights about the nature of the interface between metal clusters and a support material, and how this interface can be controlled and modified to improve catalysts. — *David Bradley*

See: Alper Uzun and Bruce C. Gates*, "Real-Time Characterization of Formation and Breakup of Iridium Clusters in Highly Dealuminated Zeolite Y," *Angew. Chem. Int. Ed.* 2008 **47**, 9245 (2008).

DOI: 10.1002/anie.200802140

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This work was supported by the U.S. Department of Energy Grant FG02-04ER15600. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

10-ID • MR-CAT • Materials science, environmental science, chemistry • Microfluorescence (hard x-ray), x-ray absorption fine structure (XAFS), diffraction anomalous fine structure, micro-XAFS • 3.3-cm undulator A • Accepting general users