# WHY ZINC MAKES PLATINUM A BETTER CATALYST

Many industrial processes rely on chemical catalysts to increase the rate of a desired reaction and inhibit the formation of unwanted products. But how catalysts work and how they can be improved are often somewhat mysterious questions. Working at three x-ray beamlines at the APS, researchers have identified two distinct mechanisms by which the addition of a zinc "promoter" to a platinum catalyst increases both the selectivity of a catalytic reaction and the rate at which it works. The findings, backed up by theoretical calculations, should make it easier to design and refine catalysts in rational ways rather than relying on trial and error, which could pave the way for rational design of still better catalysts that would increase the economic value of ethane, propane, and other light alkanes in shale gas.

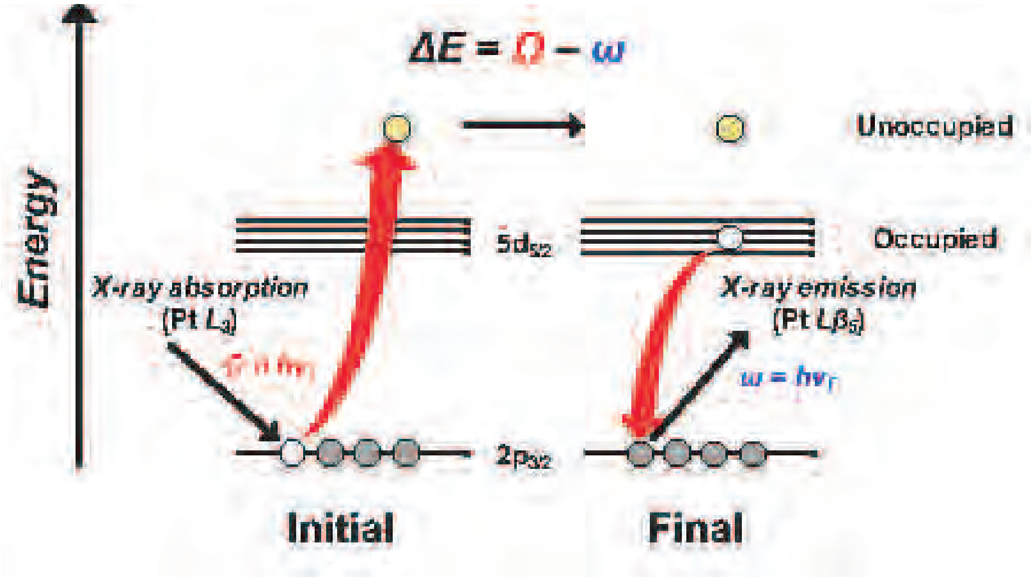

Fig 1. These RIXS planes for Pt and PtZn catalysts plot the incoming x ray energy against the corresponding energy transfer – the difference between the incoming and outgoing x ray energies, which measures the energy gap between occupied and unoccupied 5d valence states. That gap is larger for PtZn than for Pt alone, a crucial factor in its superior performance as a catalyst.

The development of horizontal drilling and hydraulic fracturing ("fracking") in recent years has greatly enhanced the production of natural gas in the United States from shale reserves. The major component of natural gas is methane, but significant amounts of ethane, propane, and heavier hydrocarbons are also produced. Ethane and propane can be converted, by catalyzed dehydrogenation, into ethylene and propylene, which are important feedstocks for polymer production. The quantity of these heavier hydrocarbons promises to exceed what the chemical industry requires, however, raising the possibility that further processing, also requiring catalysis, could convert ethylene and related compounds into still larger molecules that would serve as useful fuels.

Realizing these gains begins with simple reactions, notably the conversion of ethane ($C_2H_6$) into ethylene ($C_2H_4$). A team from Purdue University, Argonne National Laboratory, and the National Institute for Standards and Technology combined x-ray studies with theoretical calculations to understand how the atomic and electronic structure of zinc-promoted platinum catalysts influences their performance.

Platinum alone has an affinity for activating single C-H bonds that enables it to catalyze the ethane-ethylene reaction, but it can also convert ethane to unwanted smaller molecules. Adding zinc to platinum catalysts improves their selectivity (the propensity to create ethylene, but not other products) and their turnover rate (the rate of catalyzed reactions per surface platinum atom). How this promotion works has been unclear.

The researchers made Pt and PtZn catalysts on silica ($SiO_2$) substrates and characterized them in reactors under catalytic conditions at three different APS beamlines (the APS is an Office of Science user facility at Argonne). The team recorded initial selectivities for ethylene of 74% with the Pt-only catalyst and 100% for PtZn at about 40%

Cont'd. on the next page

conversion; the turnover rate for ethane-to-ethylene conversion was also six times higher for PtZn than Pt.

By means of x-ray absorption measurements at the MR-CAT beamline 10-BM-A,B, and x-ray diffraction at XSD beamline 11-ID-C, the researchers determined that in the Pt-only catalysts, the platinum atoms formed metallic nanoparticles, with a structure similar to that of bulk platinum. In the PtZn catalysts, the two metals combined in an ordered $Pt_1Zn_1$ intermetallic alloy to form nanoparticles with a 1:1 composition. Significantly, the surface platinum atoms on these nanoparticles were isolated, each with about seven zinc nearest neighbors on average, so that the closest Pt-Pt distance was much greater than for the pure platinum nanoparticles.

Next, the researchers turned to resonant inelastic x-ray spectroscopy (RIXS) studies, performed at MR-CAT beamline 10-ID-B. Incoming x-rays excite electrons from the 2p level of platinum to an unoccupied 5d valence state; the empty 2p state is then filled by an electron falling from an occupied 5d valence state, accompanied by the emission of a lower energy x-ray photon . Through a comparison of the absorbed and emitted x rays, RIXS revealed the energy structure of the valence states (Fig. 1). The researchers found that in the isolated platinum atoms of the PtZn nanoparticles, the gap between occupied and unoccupied 5d states increased by about 2 eV.

Researchers have suspected that the catalytic function of platinum derives from the interaction of these filled valence states with molecular species such as ethane. One proposed explanation for zinc's effect as a promoter is that it donates electrons to the unoccupied states of platinum. However, by analyzing the RIXS results with the help of density functional theory calculations that capture the interaction of the occupied 5d levels, the researchers concluded that it is the energy shift of those levels, as opposed to electron transfer, that amplifies their interaction with C-H bonds and thus increases the catalytic turnover rate. Moreover, the isolation of platinum atoms on the surface of the PtZn nanoparticles inhibits, for geometrical reasons, the interaction of the catalyst with C=C double bonds, thus inhibiting carbon deposition on the catalyst surface and improving the selectivity of PtZn to ethylene over side products.

Thus, the understanding of these two factors explain why PtZn is a better catalyst than Pt alone. *— David Lindley*

*See:* Viktor J. Cybulskis[1], Brandon C. Bukowski[1], Han-Ting Tseng[1], James R. Gallagher[2], Zhenwei Wu[1], Evan Wegener[1], A. Jeremy Kropf[2], Bruce Ravel[3], Fabio H. Ribeiro[1], Jeffrey Greeley[1]*, and Jeffrey T. Miller[1]**, "Zinc Promotion of Platinum for Catalytic Light Alkane Dehydrogenation: Insights into Geometric and Electronic Effects," ACS Catal. **7**, 4173 (2017).
DOI: 10.1021/acscatal.6b03603

*Author affiliations:* [1]Purdue University, [2]Argonne National Laboratory, [3]National Institute of Standards and Technology
*Correspondence:*
* jgreeley@purdue.edu,
** mill1194@purdue.edu

Materials Research Collaborative Access Team operations are supported by the U.S. Department of Energy (DOE) and the Materials Research Collaborative Access Team member institutions. Support for V.J.C. and H.-T.T. was provided by Qatar National Research Fund No. 13121024. J.G. and B.C.B. acknowledge support from the Designing Materials to Revolutionize and Engineer our Future program of the National Science Foundation (CBET1437219). This research used resources of the Advanced Photon Source, a U.S. DOE Office of Science user facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

10-BM-A,B • MR-CAT • Materials science, chemistry, environmental science, physics • X-ray absorption fine structure • 4-32 keV • On-site • Accepting general users •

10-ID-B • MR-CAT • Materials science, environmental science, chemistry • X-ray absorption fine structure, time-resolved x-ray absorption fine structure, microfluorescence (hard x-ray) • 4.3-27 keV, 4.8-32 keV, 15-65 keV • On-site • Accepting general users •

11-ID-C • XSD • Materials science, chemistry, physics • High-energy x-ray diffraction, diffuse x-ray scattering, pair distribution function • 105.6 keV • On-site • Accepting general users •

## A Word (or Two) about Platinum

Platinum is known as a "transition metal" because it is ductile, malleable, able to conduct electricity and heat, has a high freezing point, and expands upon heating. It is a part of the platinum group of metals, which all share similar properties. Other metals in this group are: ruthenium, rhodium, palladium, osmium, and iridium. Platinum does not oxidize in air and is often combined with other metals.

Originally called "platina," derived from plata, which is Spanish for silver, platinum has been found in ancient Egypt; specifically, the Casket of Thebes was found to be adorned with platinum, along with gold and silver. Platinum was a nuisance for Spanish conquistadors, as little platinum nuggets were mixed with the nuggets of gold they were finding, and were difficult to separate.

Platinum's credited discoverer was Antonio de Ulloa, who returned to Spain in 1746 with platinum samples. Platinum was not recognized as its own element until 1751, when it was successfully melted down. Until the 1820's, Colombia was the only major producer of platinum in the world, Platinum was discovered in the Ural Mountain gold fields in Russia, and in 1924, platinum was discovered in a riverbed in South Africa.

A cylindrical hunk of platinum and platinum alloy is used as the international standard for measuring a kilogram. In the 1880s, about 40 of these cylinders, which weigh about 2.2 lbs. or 1 kilogram, were distributed around the world.

Platinum is used in jewelry, catalytic converters, petroleum, the medical field, spark plugs, gasoline, hard-disk drives, anti-cancer drugs, fibre-optic cables, LCD displays, eyeglasses, paints, and pacemakers. Platinum is also the key catalyst in fuel cells.

It is estimated that today one-fifth of everything we use either contains platinum or requires platinum in its making. 50% of the platinum produced annually in all mines is used for industrial applications.

*Source: http://eochemistry.wikispaces.com/Platinum*