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A Catalyst in Action: Structure and Bonding of Supported Iridium Nanoclusters During Propene Hydrogenation Catalysis Determined by EXAFS and Infrared Spectroscopies

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The structures of catalysts – ranging from molecular complexes and enzymes to clusters dispersed on supports – depend on the conditions under which they are used. So, the most incisive determinations of catalyst structures require techniques characterizing functioning catalysts. Scientists at the University of California, Davis have used X-ray absorption spectroscopy in combination with infrared spectroscopy to investigate supported metal cluster catalysts as they functioned, revealing the structure of the catalyst, consisting of four iridium atoms (Ir_4), and the roles of the ligands, including the support. This is the first characterization of a solid catalyst, elucidating the interplay of the support and reactant-derived ligands through their bonding with Ir_4 .

Metals in catalysts used in petroleum refining or automobile exhaust conversion usually are in the form of clusters, each a few billionths of a meter in size, attached to a support. Because the clusters are so small, a large fraction of the atoms on the cluster surface is exposed, thus increasing the rates of chemical reactions. But such cluster-based catalysts are not well understood because they are made of particles of varying sizes. Scientists have developed structurally simple models, usually of single crystals, but such models do not provide information about the support's role in a chemical reaction.

We prepared nearly uniform metal nanoclusters on supports, identified the catalytic clusters and their interactions with the support by using extended x-ray absorption fine structure (EXAFS) spectroscopy, and identified the reactant-derived ligands by applying in-

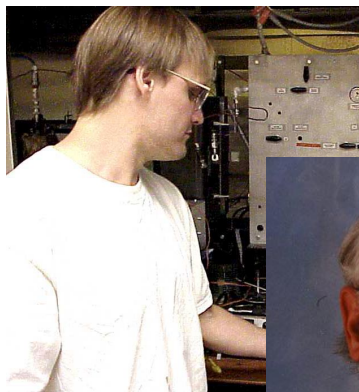
frared spectroscopy. The EXAFS spectroscopy techniques were developed at NSLS beamline X11A.

We investigated the reaction of propene with molecular hydrogen (H_2) to form propane, catalyzed by clusters consisting of four iridium atoms (Ir_4) dispersed on porous $\gamma\text{-Al}_2\text{O}_3$ or MgO . The catalytic ac-

tivity of Ir_4 depends on the support. Replacement of the MgO support with $\gamma\text{-Al}_2\text{O}_3$ boosts the catalytic activity tenfold.

When the catalyst attaches to propene or H_2 alone, we observed no significant changes in the iridium-iridium or iridium-oxygen distances. But during a catalytic reaction, the iridium-iridium and the longer, non-bonding iridium-oxygen distances exceeded the corresponding distances observed under non-catalytic conditions. We attribute the distance elongations to reaction intermediates bonded to Ir_4 .

The two supports have different characteristics that affect the electronic properties of the clusters, which in turn affect the interactions of the clusters with the ligands formed from the reactants. So, the support influences the reactivities of the reactant-de-



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rived ligands – determining which ones are observed during catalysis – and thus affects the rate of the catalytic reaction.

Our observations are consistent with the reaction mechanism shown schematically in **Figure 1**. In addition to electronic effects caused by the support, geometric properties of the clusters distin-

guish them from other metal catalysts. The smallness of the clusters limits the structures that can be bonded to them, thereby affecting the reactivity.

The electronic and geometric effects of the ligands are analogous to those known in molecular and enzymatic catalysis. Our results bolster theoretical cluster models

that incorporate the support, and indicate new opportunities for tuning the catalytic properties of small-supported clusters by changing the nature of the support. None of the understanding emerging from this work would have been possible without the use X-ray absorption spectroscopy and its application to working catalysts.

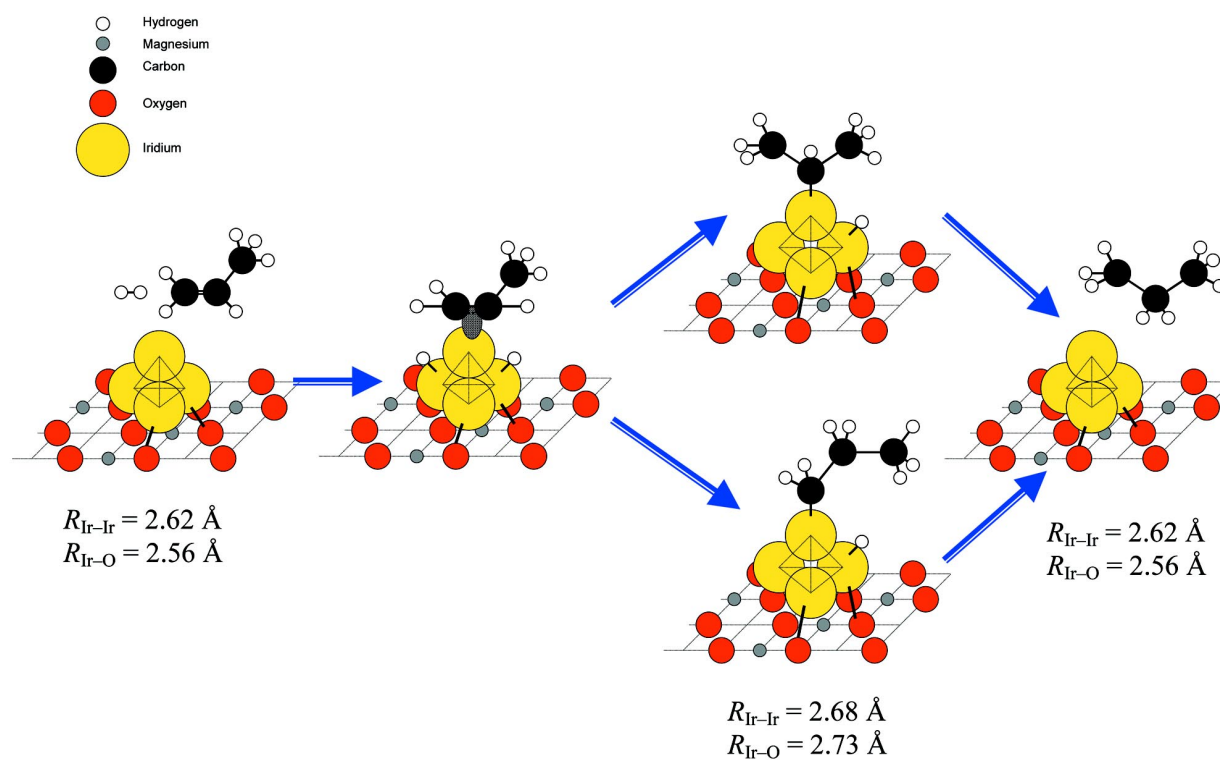


Figure 1. Schematic representation of the reaction of propene with hydrogen on MgO-supported Ir_4 catalyst. The structural changes shown were determined by extended x-ray absorption fine structure (EXAFS) spectroscopy of the working catalyst.