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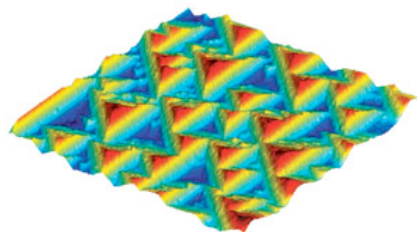
ACS Meeting News

San Francisco Surface Science

Potpourri of surface studies ranges from model systems to complex reactions

Mitch Jacoby

Films measuring just a few molecules in thickness hardly seem substantial enough to alter the properties of a big chunk of material. But they are. In catalysis, electronics, and other areas, the topmost atomic layers of a solid often control chemical reactivity or device performance, and for that reason those layers are often scrutinized in detail.



Courtesy of Ivan Ermanoski & Theodore. E. Madey

Facet-Nating! Treatment with oxygen and heat causes restructuring of an iridium surface, leaving the crystal decorated with nanometer-sized and catalytically active pyramidal facets.

At last month's American Chemical Society national meeting in San Francisco, surface science was a unifying theme in a number of symposia and divisions. Presentations ranged in topic from fundamental studies of the structures and properties of model systems to surface interactions of chiral molecules and the mechanisms of stereoselective surface reactions.

Surface scientists don't often stage popularity contests for their favorite crystals. But if they did, titania would win a prize. In the 30-odd years since TiO_2 was discovered to be a photocatalyst capable of splitting water into hydrogen and oxygen, TiO_2 's surface properties (especially those of the rutile phase of the material) have been studied extensively. As [Ulrike Diebold](#) pointed out, the high level of interest has led to the development of a variety of applications including self-cleaning and self-disinfecting coatings and purification systems that rid air and water of organic pollutants.

Diebold, who is a physics professor at Tulane University, in New Orleans, spoke at a symposium that addressed the fundamentals of metal oxide catalysis. The event was cosponsored by the Divisions of Physical Chemistry and Colloid & Surface Chemistry.

For all the interest in titania, the oxide's surface has been analyzed rather selectively. "Literally hundreds of studies have been conducted on TiO_2 (110)," thereby establishing that particular crystal face, which happens to be the most stable thermodynamically, as a classic oxide surface, Diebold remarked. But other crystal faces, such as TiO_2 (011), are also quite stable and prevalent in typical titania samples, yet they remain largely unexplored. So that's where Diebold's research group has been focusing its efforts lately.

Facets on a crystal, such as the ones on a polished gemstone, consist of the same types of atoms and may all look alike on the macroscopic scale. Yet sometimes they exhibit distinct properties, perhaps due to subtle differences in lattice structure or composition.

As a case in point, Diebold reviewed work by researchers in Japan who treated titania crystals with a solution of PtCl_6 and exposed the samples to light. Then they treated the products with a lead solution and again exposed the samples to light. The group found that platinum particles precipitated selectively on the (110) facets and that PbO_2 particles accumulated primarily on the (011) faces.

Searching for atomic-scale differences between the two crystal faces and sources for face-dependent behavior, Diebold and postdoc Olga Dulub probed the surfaces with scanning tunneling microscopy (STM) methods. Then they teamed up with Princeton University chemistry professor Annabella Selloni and postdoc Cristiana Di Valentin to develop a model that pinpoints the locations of the atoms in the (011) crystal face.

As it turns out, after just some of the work was completed, Diebold's group was forced to take what she referred to as "an emergency sabbatical" as a result of Hurricane Katrina. The group moved to Rutgers University temporarily and managed to continue its experiments in the lab of chemistry and physics professor [Theodore E. Madey](#), with whom Diebold had once served as a postdoc ([C&EN, Nov. 21, 2005, page 15](#)).



Mitch Jacoby/C&EN

Collaborators (Photo at left) Hurricane Katrina gave Tulane's Diebold (right) and her research group a chance to take "an emergency sabbatical" with Madey at Rutgers; (Photo at right) Laval Chemists Lavoie (left) and McBreen study enantioselective surface reactions.

Eventually, the study revealed a couple of key differences between the two TiO_2 surfaces. For example, on the (110) face, lattice oxygen vacancies, which are likely sites for surface reactions, are always isolated from one another. In contrast, on the (011) face, the lattice defects show up in pairs, trios, and other groupings, Diebold reported. She also noted that water generally bonds to the (110) face in molecular (undissociated) form, whereas on the (011) face, water forms layers with a mix of molecular and dissociated species, which may have implications for water-splitting catalysis (*Surf. Sci.* **2006**, 600, 4407).

Back at Rutgers, crystal facets and the processes through which they form on metallic surfaces have been recent research thrusts in Madey's group. The New Jersey scientist presented some of his group's findings at a symposium honoring [Gabor A. Somorjai](#), a surface science pioneer and chemistry professor at the University of California, Berkeley. The session was cosponsored by the Physical and Colloid Divisions and by the Catalysis & Surface Science Secretariat.

"Our work is driven by an interest in surface sensitivity and nanoscale size effects in catalytic reactions," Madey said by way of introduction. That motivation has led the team to study the way in which the surface layers of some metals undergo rearrangement to form facets in response to various chemical treatments.

In the case of iridium, for example, Madey's group found that exposing a particular crystal face to oxygen and then heating it to roughly 600 K causes the surface to grow three-sided pyramidal facets. They also found that the nanometer-scale dimensions of the facets could be controlled by adjusting the temperature.

With a method in hand for preparing model catalysts, Madey, research associate Wenhua Chen, and graduate student Ivan Ermanoski prepared a series of crystals with a range of facet sizes and then compared the samples' catalytic behavior in the ammonia decomposition reaction. That process is being studied in alternative-fuels circles as a method for producing hydrogen.

On the basis of thermal desorption spectroscopy, the team concluded that NH_3 decomposition pathways and temperatures on the iridium crystals depend on the size of the facets (*J. Am. Chem. Soc.* **2005**, 127, 5014).

In related work, Madey and graduate student Elena Loginova found that oxygen and heat treatments also induce restructuring of a nickel-aluminum alloy surface. Specifically, they observed that repeated oxidation and heating cycles form dendritic-like facets that have a spinel composition (NiAl_2O_4) and stand a few hundred nanometers tall.



Mitch Jacoby/C&EN

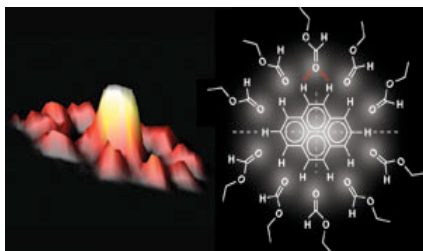
Ribeiro

"Our hope is to use the faceted surface as a template for the deposition and growth of nanometer-scale clusters of platinum, palladium, or other metals," Madey said. The goal is to develop a tunable method for preparing model metal-cluster catalysts and use them in studies of catalytic selectivity.

Other speakers at that symposium reported on applied catalysis studies. [Fabio H. Ribeiro](#), a chemical engineering professor at Purdue University, discussed his research group's work on surface oxidation of nitric oxide, which the team investigates as part of a research program in automobile emissions catalysis.

Today's automobiles are fitted with catalytic converters that feature three-way catalysts, so named because of their ability to facilitate three pollution-abatement reactions: oxidation of hydrocarbons, oxidation of carbon monoxide, and reduction of nitrogen oxides (NO_x).

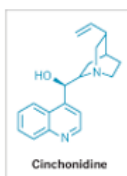
Ribeiro remarked that the catalyst technology works well but requires that engines be operated in a narrow air-to-fuel-ratio window, which limits fuel efficiency. Greater fuel efficiency can be derived from engines designed to run in a fuel-lean and oxygen-rich atmosphere, but under those conditions, NO_x is not readily reduced, Ribeiro said. So researchers have been trying to develop effective NO_x traps that oxidize NO on platinum, store the products, and later release the products and reduce them to nitrogen. According to Ribeiro, the slowest step in the process is NO oxidation, so that's where his group has focused its attention.



Courtesy of Marc-André Laliberté and Stéphane Lavoie

Ring of Fire The geometry and stability of 10:1 complexes of ethyl formate surrounding pyrene—as deduced from STM images such as these (shown at left above)—have been presented as evidence for the importance of H-bonding (red dashes) in enantioselective surface reactions.

The Purdue researcher described a number of experiments that shed light on reaction kinetics and mechanisms, catalyst deactivation processes, and particle size dependence. One of the key findings of the study thus far is that tiny platinum particles—less than roughly 3 nm in diameter—are ineffective NO oxidation catalysts, Ribeiro stressed. Catalyst manufacturers generally aim to minimize particle size in order to maximize the surface area of precious metals such as platinum. Just the same, Ribeiro cautions against making the particles too small.



Meanwhile, at a symposium addressing chirality and enantioselectivity at surfaces, sponsored by the Division of Colloid & Surface Chemistry, [Peter McBreen](#), a chemistry professor at Laval University, in Quebec, reported on investigations of enantioselective surface reactions.

By and large, stereoselective reactions are carried out in solution using liquid-phase reagents and catalysts. One exception is hydrogenation of α -ketoesters, such as ethyl pyruvate, on the surface of alumina-supported platinum catalysts that have been treated with a chiral alkaloid modifier, typically cinchonidine. The reaction can yield (*R*)-ethyl lactate with an enantiomeric excess of more than 95%.

Following experiments based on vibrational spectroscopy and other methods, McBreen and graduate student Stéphane Lavoie proposed that the basis of the reaction's enantioselectivity is a mechanism involving formation of various hydrogen bonds that anchor the reactant to the modifier in a specific configuration. According to McBreen, a key piece of the mechanism—formation of a hydrogen bond between the pyruvate's ketone carbonyl group and cinchonidine's aromatic unit—was considered somewhat speculative and not necessarily accepted by other researchers.

"We needed a killer experiment—a smoking gun" to establish that C-H \cdots O bonds can form readily between adsorbed carbonyl groups and aromatic rings, McBreen said. In a series of STM experiments, the team found what they were looking for and presented it in San Francisco.

The Laval group's micrographs show that when platinum-bound pyrene (a polybenzenoid hydrocarbon) is exposed to ethyl formate, 10 formate molecules form a crown around pyrene, which has 10 aromatic C-H bonds. According to McBreen, analysis of the data reveals that each molecule is aligned with its C=O group positioned between a pair of pyrene C-H bonds. That configuration suggests the formates are anchored in place through a pair of hydrogen bonds, McBreen said. He went on to show that methyl pyruvate and pyrene form similar 10:1 complexes that are stable at room temperature and argued that the results support the proposal of hydrogen bonding between pyruvate carbonyl groups and cinchonidine aromatic units. Results of the Laval group's study have just been accepted for publication in *Angewandte Chemie*.

From model systems of adsorbate-free crystals to catalyst surfaces that facilitate complex reactions, surface science remains a thriving area for chemistry research. The subjects under study vary by chemical nature and application but are linked by the origin of their properties, which often amounts to a skin no more than a few molecules thick.