

# Richards Award Address

*Molecular Catalysis Science. The Development of Surface Science toward Integration of Heterogeneous, Homogeneous, and Enzyme Catalysis on the Nanoscale*



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My adventure into this field followed the transformation from investigating single crystal surfaces in vacuum and high pressures and at the liquid phase,<sup>1</sup> to the development of the molecular science in all three fields of catalysis, heterogeneous, homogeneous and enzyme that I am attempting to integrate.<sup>2</sup> Much of the surface science of catalysis started with metal single crystals, mostly platinum, which was the granddaddy of all catalysts, discovered in the beginning of the 19<sup>th</sup> Century. Low energy electron diffraction showed different types of single crystal surfaces of platinum; e.g., hexagonal, square, or stepped crystal surfaces with periodic steps and kinks.<sup>3</sup> Molecular beam scattering in the 1970s discovered that stepped surfaces can perform H<sub>2</sub>/D<sub>2</sub> exchange with high probability.<sup>4</sup> On the other hand, the defect-free flat surfaces do not break H-H bonds, where such bond breaking is below the detection limit.<sup>5</sup> More studies of bond breaking revealed not only

H-H chemical bonds but also C-H, O-O, C-O, and that C-C bonds can be broken at these low coordination sites at steps and kinks of surfaces.<sup>1</sup>

Making a big jump in chemistry to nanoparticles, it was found that most catalysts are in nanoparticle dimensions.

### **Metal Nanoparticles and Mesoporous Oxide Synthesis**

Colloidal synthesis of nanoparticles starting with ionic salts, surfactant solvents, and reducing agents can produce nanoparticles from 1-10 nm in size.<sup>6</sup> Oxide supports for the transition metal nanoparticles are frequently utilized. The mesoporous inorganic oxide shells enable high temperature catalytic oxidation studies.<sup>7</sup>

### **Metal Nanoparticles' Size Dependent Covalent Bond Catalysis**

Metal nanoparticles in the size range of 1 to 10 nm are produced with very well defined size control. The size and shape of metal nanoparticles affect most catalytic reaction rates and selectivities.<sup>6a</sup> Most reactions, including the hydrogenation reactions of benzene, cyclohexene, crotonaldehyde, pyrrole, pyrene, and furfural, are multi-path.<sup>8</sup> It was found that the turnover rates and selectivities are particle size dependent. For example, CO hydrogenation, commonly called Fischer-Tropsch synthesis, shows a 5-fold increase in turnover rates as the cobalt catalyst nanoparticle size changes from 3 to 11 nanometers.<sup>9</sup> Methylcyclopentane isomerization shows size and shape dependence of the nanoparticles.<sup>10</sup> The question that naturally arises is “why are the catalytic selectivity and turnover rates of metal nanoparticles size and shape sensitive?”

### **Atomic Level Characterization under Reaction Conditions**

In-situ surface techniques, mostly practiced using the synchrotron, can be used to identify the size and shape dependence of reaction rates and selectivities of catalytic reactions. Sum frequency generation vibrational spectroscopy, high pressure scanning tunneling microscopy, and synchrotron techniques, including ambient pressure X-Ray Photoelectron Spectroscopy (APXPS), extended X-ray absorption fine structure, and Infrared and X-ray microspectroscopy, reveal how the size and shape of catalysts control reaction rates and selectivities. Many bimetallic nanoparticles with various sizes and shapes show that a composition change is driven by a change in chemical and oxidizing environments of these nanoparticles.<sup>11</sup> High pressure scanning tunneling microscopy shows the adsorbate mobility under reaction conditions. The adsorbates restructure the metal surfaces, and this is enhanced at high reactant pressures.

## **Changing the Oxidation States of Nanoparticles with Decreasing Size — Conversion of Homogeneous to Heterogeneous Catalysis**

As the sizes of nanoparticles change from 2 nm toward 0.8 nm, the electronic structure and oxidation states of these nanoparticles change as well, as indicated by XPS studies.<sup>12</sup> Rhodium or platinum nanoparticles change their oxidation states from metallic to oxide rhodium 3+ or platinum 2+ and 4+ as the nanoparticle size is changed. Calculations by Norskov et al clearly indicate that when oxygen is adsorbed on gold or platinum nanoparticles, the oxygen removes electrons from the metal nanoclusters, which then become oxides.<sup>13</sup> When the small transition metal nanoparticles are encapsulated by dendrimers, the high oxidation state is maintained and these nanoparticles can carry out homogeneous catalytic reactions as shown in many examples by Toste and Somorjai.<sup>14</sup> Dendrimer-encapsulated nanoparticles with very small size carry out electrophilic reactions (e.g. hydroformylation and decarbonylation) in a solution phase, similar to transition metal ions. Transition metal nanoclusters can carry out single metal ion-like catalytic reactions.

### **Oxide-Metal Interfaces as Active Sites for Acid-Base Catalysis: Crotonaldehyde Hydrogenation as an Example**

When platinum is supported on SiO<sub>2</sub> or titanium oxide mesoporous support, the product distribution of crotonaldehyde hydrogenation dramatically changes. On titanium oxide many products from crotonaldehyde, including butanol, croton alcohol, butyl aldehyde, and propylene are formed; while on platinum supported in SiO<sub>2</sub> the only product is butyl aldehyde. This process, which changes the product distribution by changing the support, which alone does not carry out reactions, changes the catalytic activity of group VIII transition metals of iron, nickel, rhodium, palladium, and iridium. The supports that change the catalytic activity are titanium oxide, cerium oxide, and niobium oxide. This phenomenon, frequently called SMSI or strong metal support interaction, is related to the electron flow between the transition metal and the oxide support under reaction conditions.<sup>15</sup>

The fundamental reasons for this process have been studied, and it is caused by the electron flow between the transition metal and the oxide support. It is also called “hot electron flow.” The electrons in the transition metal are excited when an exothermic catalytic reaction or photons produce an electron flow, which is observed by carbon monoxide oxidation or hydrogen oxidation reactions.<sup>16</sup> When an oxide metal interface is constructed, often called a Schottky barrier, with a metal layer of a nanometer-range thickness on a transition metal oxide surface, the electrons flow from the metal to the

oxide. The electron flow ionizes the reacting molecules. In the case of CO oxidation  $\text{CO}_2^-$  forms, and in the case of hydrogen oxidation  $\text{H}_2\text{O}^-$  forms.<sup>17</sup> These are the electrons that can be detected by applying the potential between the metal and the oxide interface. These electron flows between an oxide and a metal interface ionizes molecules and they are commonly called acid-base catalysis phenomena. When the platinum is supported by various oxides, ranging from silica to zirconium oxide, the isomerization activity of n-hexane is controlled by the oxide metal interface charge flow.

### **Hybrid Systems. Hybridized Enzymes to Immobilize onto Glass**

Enzymes are able to maintain remarkably high selectivity towards their substrates while still retaining high catalytic rates. By immobilizing enzymes onto surfaces we can heterogenize these biological catalysts, making it practical to study, use, and combine them in an easily controlled system. We have developed a platform that allows for the simple and oriented immobilization of proteins through DNA directed immobilization (DDI).<sup>18</sup> We use DDI to deposit enzymes onto glass slides. This is done through bottom-up assembly of two separate components. The first is coupling an aldolase DNA to aniline functionalized glass slides. In tandem, aldolase is modified at the N-terminus with a complimentary DNA strand, also substituted with the aminophenol coupling partner. The subsequent hybridization of the surface oligomer with the complementary oligomer-protein conjugate results in the oriented display of aldolase on the glass surface.<sup>18</sup> Taking advantage of the transparent nature of the glass surfaces used in these studies, we are also seeking to characterize these surfaces using alternative spectroscopic techniques, such as sum frequency generation and X-ray photoelectron spectroscopy, to gain information about the orientation and coverage of the protein. Similar studies are carried out by adsorbing on glass surfaces dehydrogenase enzymes that oxidize alcohol to aldehydes and aldehydes to acids, respectively.

### **Integration of the Three Fields of Catalysis (Heterogeneous, Homogeneous and Enzyme) — Future Promise**

In our attempt to focus on the chemical correlations between the three groups (heterogeneous, homogeneous and enzymatic) the future looks very promising for molecular catalysis science studies. Catalysis of heterogeneous, homogenous and enzymatic origin alike involve nano-sized materials. These nanocatalysts comprise organic and inorganic components. Charge, coordination, interatomic distance, bonding, and orientation of catalytically active atoms are molecular factors shared by all three fields of catalysis. By controlling the governing catalytic components and the molecular factors, catalytic processes of multichannel and multiproduct nature could be run in all

three catalytic platforms to create unique end products. This is the promise of molecularly unified catalytic scheme of the future.

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