Perspectives in Catalysis

Research in nanosciences – Great opportunity for catalysis science

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Catalysts represent the oldest commercial application of nanotechnology. It is suggested that the focus of catalysis research in the 21st century should be on achieving 100% selectivity for the desired product (clean manufacturing). The molecular ingredients of selectivity are not well understood. The electronic and atomic structures of nanoclusters should be investigated as a function of their size. Because of the facile restructuring of metal clusters under reaction conditions they have to be characterized *in situ*. New synthetic methods need to be developed to produce catalyst particles with the same size, structure and location on the support.

KEY WORDS: nanoparticle catalysts; 100% catalyst selectivity; electronic structure of catalysts; atomic surface structure; catalyst synthesis; catalysts characterization

Initiatives for large national programs in "nanosciences" have been proposed in many countries in Europe, Asia and North America. Some of these are initiated by the physics community to focus attention on the need to understand the behavior of more complex systems, beyond atoms and molecules. Others are proposed with the leadership of the surface science community that finds most devices based on surface technologies, the microelectronic circuit, magnetic information storage, hard coatings and others are becoming smaller and thinner as their properties continuously improve. However, their behavior on the nanoscale (electronic structure, atomic structure, mechanical properties) is poorly understood. Biological and medical sciences are increasingly utilizing bio-implants and bio-sensors and employ enzymes that frequently contain small metal clusters, and increasingly monitor complex phenomena on the molecular level. Most of the problems and challenges are being defined on the nanoscale.

Many heterogeneous catalysts utilize nanoparticles. Nanoparticles of metals, oxides and sulfides have been developed and used as catalysts for hydrocarbon conversion, partial oxidation and combustion reactions since the 1920's; as such they represent the oldest commercial application of nanotechnology.

In the development of catalyst-based technologies the catalysts were mostly optimized for activity all through the 20th century. That is, productivity per site per second. The higher the activity the faster the fuels and chemicals were produced. Good examples of high activity are the new generation of Ziegler–Natta heterogeneous polymerization catalysts that produce $\sim 10^6$ C–C bonds per site per second.

In the 21st century there is a further opportunity to increase the societal benefits of catalysis. Harnessing catalytic processes improves our quality of life, produces wealth, improves health and increases our life expectancy, and furthers energy independence of each country. *Catalysis research in the 21st century should focus on achieving 100% selectivity for the desired product in all catalyst-based processes*. This will enable "clean manufacturing" with no generation of wasteful or polluting byproducts. Focussing on catalyst nanoscience will help us to move more rapidly toward this goal.

The nanoscience of selectivity

Selectivity, that is, to produce one molecule out of many other thermodynamically feasible product molecules is much less understood than activity in catalyst-based reactions. It depends on several key factors that have been documented in catalyst research to date. One is the *atomic scale surface structure* of the catalyst; for example, in the reforming reaction that produces motor fuels, *n*-hexane or *n*-heptane are converted to aromatic molecules, branched isomers and cyclic hydrocarbons, the metal surface structure changes product selectivity [1]. Also on the atomic scale, it is well known that *selective site blocking* can inhibit undesirable sites where reactions occur that we wish to eliminate; for example, C–C bond breaking during reforming reactions occurs at kink sites on platinum surfaces. Blocking these sites with sulfur by adding H_2S to naphtha eliminates hydrogenolysis by selective poisoning of the active sites for this reaction [2,3]. On the nanometer scale, *bifunctional catalysis* has been documented as playing a major role in selectivity. On these catalysts reactant molecules undergo chemical change to produce intermediates. These reaction intermediates will then diffuse a certain distance to other sites where they undergo further rearrangements to produce the final product, which then desorbs. In this circumstance, selectivity changes markedly with conversion. One example would be the Fischer–Tropsch reaction that produces long chain hydrocarbons from CO and H_2 [4].

There are other factors that influence selectivity in high-surface area industrial catalysts. For example, the nanoarchitecture of zeolites [5] can enhance selectivity by controlling

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the diffusion rate of reactants or products according to their molecular shapes [6].

Thus, looking to the future of research in reaction selectivity, there are a number of basic questions:

- How many catalyst metal atoms are needed and optimal to make or break chemical bonds in the case of oxygen (O_2), hydrogen (H_2), nitrogen (N_2), carbon monoxide (CO), and other more complex molecules where C–H and C–C bond breaking also play important roles?
- What are the roles of surface structure, and the 3-D architecture of nanoparticle lattices?
- What are the roles of promoters and site blockers?
- What are the roles of secondary reactions that are likely to be diffusion controlled?

The electronic structure of nanoclusters and its alteration with size and shape

Kubo [7,8] and Friedel [9,10] were among the first to discuss the electronic structure of metal nanoclusters by considering that they are similar to molecules. The energy differences of successive energy levels are no longer small when compared to thermal energy, kT. In a particle with N number of atoms the average energy spacing, δ_N, is $\delta_N = E_f/N$ where E_f is the Fermi energy. For example, the energy spacing for electrons in an Al particle of <10 nm size have been measured [11]. The energy spacing is about 0.5 meV at a temperature of 0.32 K.

There are surface effects due to boundary conditions depending on the surface-to-volume ratio and the shape of the particles that also alter the spacing between electronic energy levels. There are differences in the electronic structure of small metal clusters depending on the presence of even or odd number of electrons (figure 1). Using molecular orbital calculations [12] the effects of cluster size on electronic structure were examined for naked metal clusters in the 2–79 atom range using a face centered cubic atomic packing. For ruthenium clusters a rather slow approach toward bulk electronic behavior with cluster size has been found. If electron donation or acceptance to and from reacting molecules is an important elementary step in a catalytic reaction, this process should be strongly dependent on metal particle size and shape. Small metal clusters also provide multielectron, often quasi-synchronous, transfer so necessary to carry out bond breaking under mild conditions (*e.g.*, nitrogenase, hydrogenase) [13,14]. It was found that ionization potential changes dramatically with cluster size for nickel and copper clusters [15,16]. Experimental molecular beam studies [17] that probed the reactivity of oxygen and methane with aluminum, platinum [18] and palladium [19] clusters as a function of particle size show marked size selectivity for reaction with both molecules. The bond breaking kinetics is not a monotonic function of particle size. Large metal carbonyl clusters are first synthesized by Chini so there is an opportunity to study their structure and chemistry as a function of particle size [20]. Although there are experimental difficulties in ensuring their structural integrity during catalytic reactions, they exhibit size dependent hydrogenation and carbonylation reaction rates and selectivities. The onset of metallic behavior begins for clusters of 100 atoms or larger.

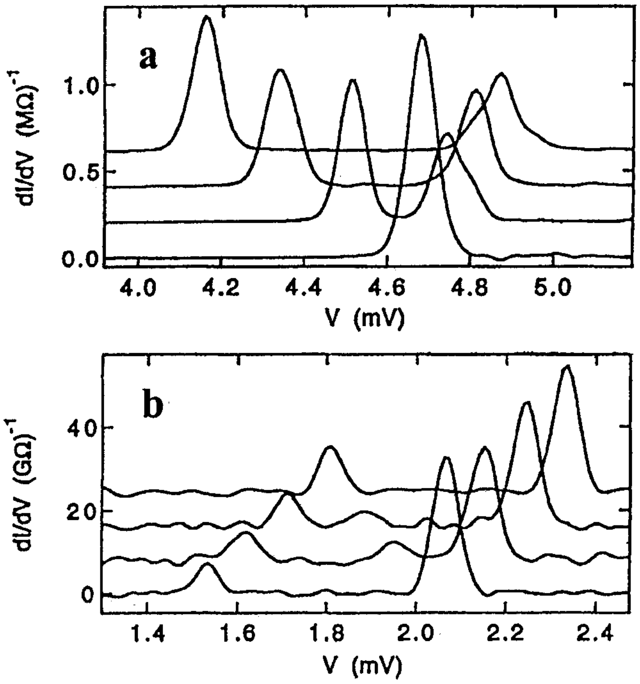

Figure 1. Effect of an applied magnetic field H on the dI/dV–V curve at 0.05 K and $H = 0.03$, 1, 2, 3 T from bottom to top, for two different Al particles [11]. (a) Because the first transition above the Coulomb-blockade threshold exhibits Zeeman splitting, this Al nanoparticle has an even number of electrons. (b) A sample in which the first transition does not exhibit splitting and hence is identified as having odd number of electrons.

The atomic structure and restructuring ability of nanoparticles

Recent electron microscopy studies revealed that small nanoparticles are highly ordered and bound by crystal faces of low Miller index (figure 2) [21,22]. This observation explains the great similarity of catalytic behavior of metal single crystal surfaces and nanoparticles. The synthesis of metallic nanoparticles with well-defined crystal faces opens the door to the utilization of a greater body of data on catalysis on metal single crystal surfaces [1]. The reactivity of specific surfaces of single crystals can be used to guide the preparation of metallic nanoparticle catalysts with optimal crystal faces to produce highly selective heterogeneous catalysts. By this means one can avoid an unnecessary diversity of active sites with different reactivity that is one of the reasons of lesser selectivity of heterogeneous catalysts in comparison with homogeneous or enzyme catalysts.

Metal surfaces restructure when molecules chemisorb and during catalytic reactions [23–27]. Both single crystals and nanoparticles can readily restructure and have very similar surface structures. The difference is that single crystals and indeed large size clusters restructure only in the surface regions while small nanoparticles can restructure as a whole.

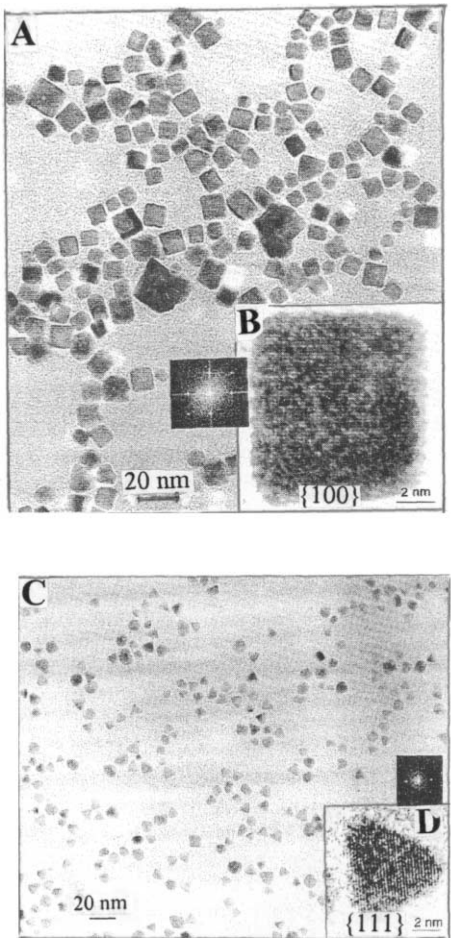

Figure 2. (a) Low-magnification TEM image of sample showing the size and shape distribution of the cubic particles. (b) High-resolution lattice image of cubic Pt oriented with [100] parallel to the incident beam; the Fourier transform of the lattice image gives the optical diffractogram of the particle (inset), which explicitly shows the presence of the {100} facet [21,22]. (c) Low-magnification TEM image of sample indicating the abundance of tetrahedra. (d) High-resolution image of tetrahedral particle; the Fourier transform of the lattice image gives the optical diffractogram of the particle (inset), which shows the presence of the {111} facet [21,22].

There is evidence that capped metal nanoparticles change their structures with small changes in temperature. Skeletal isomerization was observed for tetranuclear platinum and palladium clusters by NMR and X-ray studies [28,29] (figure 3). Small clusters are more flexible and can restructure more readily than larger clusters because of the lower coordination of its metal atoms. In this circumstance, several configurations have very similar free energies of formation. Also, the exothermic heat of adsorption of molecules on these clusters can compensate for the endothermic bond weakening of metal–metal bonds necessary for the structural reorganization as long as there are only a few. Restructuring is thought to be essential for bond breaking and molecular rearrangements and is an essential part of the catalytic cycle. This is why nature and the catalytic technologies utilize small nanoclusters instead of large particles. Enzymes restructure when reactants adsorb or desorb from the active sites [30–32].

The nanoscience of catalyst synthesis

Researchers have begun to use nanostructured catalysts in selectivity studies and have begun to investigate the influence of metric parameters (*i.e.*, size and shape) on the chemical behavior of the catalyst. The main hurdle to overcome is the development of reliable synthetic methods for the construction of nanostructured catalysts for which various metric parameters can be varied in a systematic way. The synthesis of monodispersed metal and semiconductor nanoclusters for this purpose is underway in several laboratories [33,34]. However, despite some notable successes along these lines, general methods for the predetermined synthesis of a given transition metal cluster or colloid with precisely defined dimensions, have not been developed.

For transition metal nanoclusters, five synthetic methods have been identified: (1) transition metal salt reduction, (2) thermal decomposition and photochemical methods, (3) ligand reduction and displacement from organometallics, (4) metal vapor synthesis, and (5) electrochemical synthesis [35–37]. "Monodispersed" nanoclusters prepared by these methods generally have size dispersities within ±15% in di-

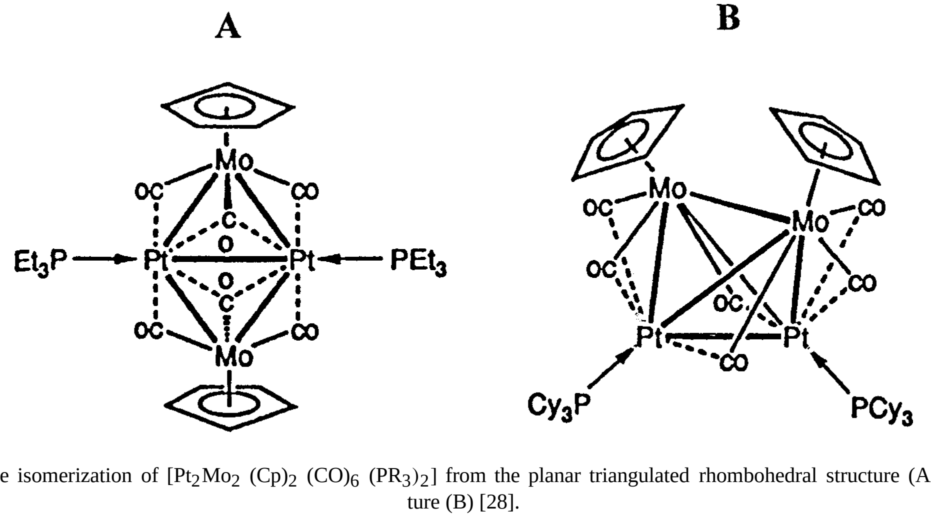

Figure 3. Cluster core isomerization of $[Pt_2Mo_2\ (Cp)_2\ (CO)_6\ (PR_3)_2]$ from the planar triangulated rhombohedral structure (A) to tetrahedral structure (B) [28].

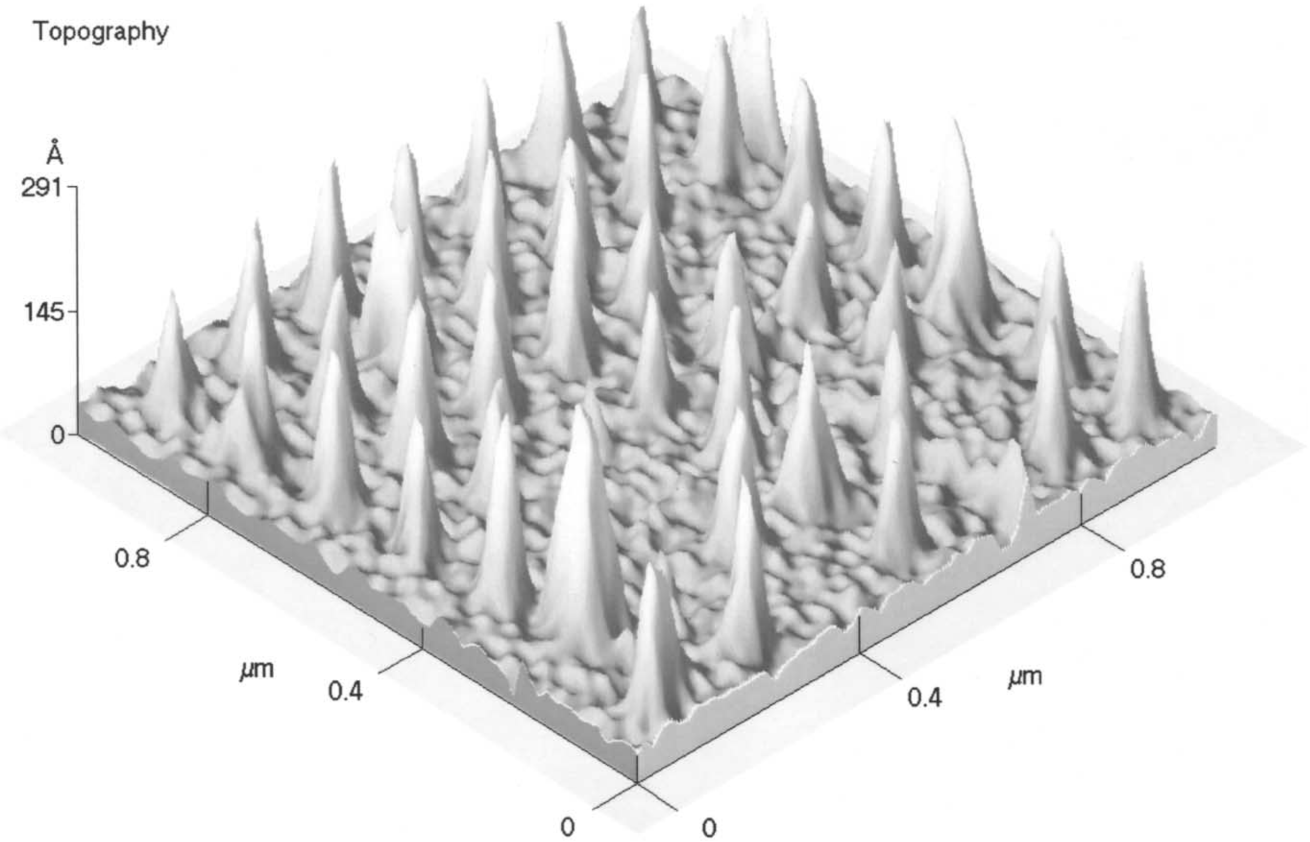

Figure 4. Atomic force microscopy (SFM) scan of platinum nanocluster arrays deposited on alumina by electron beam lithography. Pt particle diameter 20 nm and spacing between nanoclusters 150 nm.

ameter. Apparently, in only two cases, Moiseev's $Pd_{\sim 561}$ and Finke's polyoxoanion-stabilized Rh and Ir nanoclusters [38,39], has it been demonstrated that isolated transition metal nanoclusters are stable enough in solution to allow routine chemical manipulations. Thus, there are many key issues related to nanocluster synthesis that remain to be thoroughly addressed. The synthesis of bimetallic nanoclusters is of particular interest with respect to catalysis [40,41].

Fabrication of 2-D platinum and silver nanoparticle arrays by electron beam lithography has been reported to deposit single metal nanocluster arrays. The EBL fabrication process consists of several steps [42]: The oxide supports are prepared on a Si(100) wafer either by surface oxidation to form SiO_2 or by deposition of an alumina or titania film onto the Si substrate (both oxides were about 10 nm thick). The next step is to spin-coat an 80 nm thick electron sensitive polymethylmethacrylate (PMMA) onto the support surface. The desired pattern is subsequently "written" into the polymer layer by a highly collimated electron beam (4 nm sized 100 kV) produced by the nanowriter (Leica Corp.). This is followed by the selective dissolution of the polymer chains damaged by the electron exposure in methylisobutyl ketone/isopropyl alcohol. This procedure produces periodically-spaced holes in the PMMA layer. A thin film of metal is then deposited on this mask and, after the remaining polymer resist is removed completely by dissolution in acetone, metal nanoparticles of the prescribed pattern remain on the support (figure 4).

Platinum nanoparticle arrays have been used to study isomerization, dehydrogenation and hydrogenation reactions [43]. Precise control of nanocluster size, structure, thermal and chemical stability have been achieved.

Characterization of nanoparticle catalysts on the molecular scale under vacuum and under reaction conditions

It is critical to evaluate at the molecular level the structure and chemistry of the nanostructured catalysts that are fabricated. In addition to the characterization of model catalysts and of adsorbed molecules in UHV, we require information about the changes that occur on the catalyst surfaces under *in situ* reaction conditions at the solid–gas and solid–liquid interfaces. A number of *in situ* surface characterization techniques have been employed to study catalysts and detect reaction intermediates [44], and these are listed in table 1. As shown in the table, some of these are more appropriate for investigation of two-dimensional nanostructures while others are more suitable for studies of three-dimensional nanostructures under reaction conditions.

Increased investment and focus in nanosciences presents an opportunity for a renaissance in research in catalysis science. By focussing on the need to achieve 100% selectivity in catalyst-based chemical processes, research to under-

Table 1

System	Technique
2-D	High pressure scanning tunneling microscopy (STM) Sum frequency generation (SFG) vibrational spectroscopy Atomic force microscopy (AFM) X-ray photoelectron spectroscopy at high pressures (XPS) Near edge X-ray absorption fine structure (NEXAFS) Grazing incidence X-ray diffraction (GIXRD)
3-D	Ultraviolet (UV) Raman spectroscopy Time-resolved infrared spectroscopy (FTIR) X-ray diffraction (XRD) Nuclear magnetic resonance (NMR)

stand the molecular ingredients that control selectivity must be pursued. New methods of catalyst fabrication should be developed to achieve this goal. New methods of catalyst characterization under reaction conditions should be utilized or invented. Spatial resolution and time resolution are important frontiers for research in this field.

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