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Author

Somorjai, Gabor A.

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The 13th International Symposium on Relations between Homogeneous and Heterogeneous Catalysis — An Introduction

Gabor A. Somorjai

Department of Chemistry, University of California, Berkeley, CA 94720

*Materials Sciences Division and Chemical Sciences Division, Lawrence Berkeley
National Laboratory, Berkeley, CA 94720*

Abstract

Over forty years, there have been major efforts to aim at understanding the properties of surfaces, structure, composition, dynamics on the molecular level and at developing the surface science of heterogeneous and homogeneous catalysis. Since most catalysts (heterogeneous, enzyme and homogeneous) are nanoparticles, colloid synthesis methods were developed to produce monodispersed metal nanoparticles in the 1-10 nm range and controlled shapes to use them as new model catalyst systems in two-dimensional thin film form or deposited in mesoporous three-dimensional oxides. Studies of reaction selectivity in multipath reactions (hydrogenation of benzene, cyclohexene and crotonaldehyde) showed that reaction selectivity depends on both nanoparticle size and shape. The oxide-metal nanoparticle interface was found to be an important catalytic site because of the hot electron flow induced by exothermic reactions like carbon monoxide oxidation.

To whom correspondence should be addressed. E-mail:somorjai@berkeley.edu

Short title: The nanoscience of Catalysis

Key words : Catalytic Selectivity, Colloid nanoparticles, Oxide-metal interfaces

This series of international symposia focuses on catalysis. The field of catalysis is like an onion (Figures 1a and 1b), the outer shell represents technology, process control and reactor design; the layer in the middle where synthesis and fabrication of catalysts and the techniques and instrumentation to characterize catalysts^[1, 2] are located along with studies of deactivation and regeneration and of course macroscopic kinetics. In the core of this onion are molecular studies to understand the molecular mechanisms of structure bonding and dynamics^[3-5], how the three types of catalyst systems (enzyme, heterogeneous and homogeneous) work. It is this molecular core that I aim to address in this Symposium.

The common property of all three catalyst systems that is most apparent is that they are all nanoparticles. For example, Cytochrome C, which is one of the over 3000 enzymes that functions in the human body (Figure 2a) is 4 nm in size with its protein shell wrapped around it, and its molecular weight is 12,000 daltons^[6]. The size of its active site is 1.4 nm. A typical homogeneous catalyst used for olefin polymerization is a so-called single site catalyst with an active site that is a titanium ion surrounded by ligands (Figure 2b), which is 1.6 nm in size. This nanosize molecule produces a million C-C bonds as it makes polypropylene^[7]. The heterogeneous catalysts such as platinum nanoparticles (Figure 2c) are between 1-10 nm in size^[8, 9]. In the figure we show a method to synthesize these nanodispersed nanoparticles with the desired size and shape that may be cubic or cuboctahedra^[10].

The 21st Century challenge for catalysis is to achieve the highest possible reaction selectivity for catalyst-based chemical processes ^[11-13]. We have to understand for multipath reactions where several reaction channels to produce different molecules are all thermodynamically possible, to make only the desired molecule instead of a mixture of the products ^[14]. Although the molecular mechanisms for reactions that form only one product (for example ammonia synthesis or ethylene hydrogenation) are quite well understood, the small changes in potential barrier height, that control which product molecule forms in multipath reactions, is not well understood.

In heterogeneous catalysis we know of four molecular ingredients that control catalytic activity and selectivity ^[15]; 1) reaction intermediates that form and determine which way the reaction is going; 2) surface mobility of adsorbate and substrate during the reaction; 3) surface structure and 4) charge transport. Sum frequency generation vibrational spectroscopy ^[16, 17] shows the reaction intermediates detected during ethylene hydrogenation and cyclohexene hydrogenation and dehydrogenation (Figure 3). There are three species (ethylidyne, di- σ -bonded-ethylene and π -bonded ethylene) that are visible on the platinum surface ^[18]. Out of the three, π -bonded ethylene is the most weakly adsorbed, and that is the one that turns over, the other two species are stagnant spectators during the reaction turnover. For cyclohexene hydrogenation/dehydrogenation it is 1,3-cyclohexadiene, 1,4-cyclohexadiene and π -allyl c-C₆H₉ that are all visible in various temperature regimes ^[19]. The mobility of the adsorbed species during catalytic turnover can be shown with the high pressure scanning tunneling microscopy technique (Figure 4) ^[20]. Under high turnover conditions the adsorbed species are invisible to the

scanning tunneling microscope that scans the surface at a speed of about 100 Å per millisecond. The species on the surface of the active catalyst are moving too fast to be detectable by high pressure STM ^[21, 22]. When we poison the reaction, for example by adsorbing carbon monoxide, we see ordered structures, which are readily imaged by STM, but the catalytic turnover stopped. In several reactions that we have studied the adsorbate mobility on the catalytically active surface is an important ingredient of catalytic activity, while the lack of mobility stops the catalytic reaction. The catalyst surface under high pressure conditions rapidly restructures as is shown in Figure 5. The (110) surface restructures differently when hydrogen or oxygen or carbon monoxide are adsorbed ^[23] indicating that the surface chemistry also controls the surface structure of the substrate catalyst that is stable under reaction conditions.

Our research in this field moved from platinum single crystal surfaces as model catalysts to nanoparticles in two dimensions or in three dimensional arrays ^[1] (Figure 6). In two-dimensional catalytic systems we use a Langmuir-Blodgett technique to disperse the nanoparticles and grow on a vapor of oxide support a two-dimensional higher or lower density nanoparticle assembly ^[10, 24] (Figure 7). If we want to place the nanoparticles into a mesoporous three-dimensional framework we use sonication or synthesize the mesoporous solid around the nanoparticles in solution ^[25, 26].

For two-dimensional platinum nanoparticle films, which are assembled using the Langmuir-Blodgett technique, we find that cubic platinum nanoparticles behave like the single crystal (100) crystal face, and form only one product, cyclohexane by benzene

hydrogenation (Figure 8) ^[13]. If we have hexagonal platinum nanoparticles we produce both cyclohexane and cyclohexene, just like the single crystal (111) crystal face. If we use platinum nanoparticles at different sizes in a three-dimensional framework of mesoporous silica, we find that the formation of cyclohexene by hydrogenation of cyclohexene and the dehydrogenation to benzene are particle size dependent, as shown in Figure 9 ^[26]. The reason for this is that the activation energy of dehydrogenation of cyclohexene to benzene is increasing with particle size. Similar correlation is found for crotonaldehyde selective hydrogenation to either crotyl alcohol or butyraldehyde (Figure 10), where the selectivity of both of these products is particle size sensitive. Finally, we find that the oxide-metal interfaces, that formed as metal nanoparticles are deposited on oxide supports, are also important active sites^[27, 28]. The reason for this is that during exothermic surface reactions hot electrons are produced in the metal that have enough mean free path to make their way to the oxide interfaces. We have studied CO oxidation for this purpose^[29-32]. The hot electrons can be collected after passing the Schottky barrier that is present at the metal-oxide interface^[33-36]. Figure 11 shows the chemical reaction induced current (chemicurrent) has the same activation energy as the turnover rate of CO oxidation, indicating that the chemicurrent and the turnover rates are correlated^[30, 32]. That is, the charge transport occurring at oxide-metal interfaces competes in producing chemistry with the reactions that occur only on metal surfaces.

There are major advances in single molecule enzyme chemistry that permits detection of molecular motion of the enzyme (conformational dynamics). We heard the talk of Professor Sunny Xie on this subject at this Symposium^[37]. Homogeneous catalyst

can be anchored to solid supports (talk by Professor Jones) without change of the chemical activity as compared to in solution as long as they exhibit mobility that is not inhibited in the molecules that are tethered to silica.

In order to directly compare the three fields of catalysis at the molecular level we have to design experiments that investigate the three types of catalysts under the same experimental condition. I suggest studies of catalysis at 300 K and in water. These conditions are the natural habitat of enzymes while we should be able to probe heterogeneous catalysts that are usually employed at higher temperatures and also homogeneous catalysts that are utilized in organic solvents under enzyme-friendly experimental conditions.

Molecular studies of catalysts promises to be exciting for many decades to come to produce selective chemistry, perhaps using hybrid systems that share the desirable features of enzyme, heterogeneous and homogeneous catalyst systems.

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Figure Captions

- Figure 1
- a) Layers of catalysis, from technologies to molecular science;
 - b) The molecular core of catalysis science
- Figure 2
- a) The Cytochrome C molecule
 - b) Titanium-based single site homogeneous polymerization catalyst
 - c) Platinum nanoparticle monodispersed catalysts of 1-8 nm size and well-controlled cubic or cuboctahedra shapes
- Figure 3
- Reaction intermediates detected by sum frequency generation (SFG) vibrational spectroscopy during ethylene hydrogenation and cyclohexene hydrogenation/dehydrogenation under catalytic reaction conditions on the Pt(111) surface.
- Figure 4
- STM pictures during cyclohexene hydrogenation/dehydrogenation exhibiting adsorbate mobility that is faster than the scanning speed of the STM tip. When the catalytic reaction is poisoned the STM image is ordered indicating lack of mobility.
- Figure 5
- Scanning tunneling microscopy (STM) pictures of the reconstructed (110) crystal face of platinum when exposed to hydrogen, oxygen or carbon monoxide at high pressures.

- Figure 6 Transition from catalytic studies on model surfaces of metal single crystals to metal nanoparticles that are deposited as two-dimensional films or dispersed on three-dimensional mesoporous supports.
- Figure 7 a) Deposition of two-dimensional nanoparticle films by the Langmuir-Blodgett technique.
b) Nanoparticles encapsulated by mesoporous silica (SBA-15) support that grows around the platinum nanoparticles in solution.
- Figure 8 Benzene hydrogenation over cubic and hexagonal shaped platinum nanoparticles and (100) and (111) crystal faces of platinum. Both the nanoparticles and the crystal faces form two products (cyclohexene and cyclohexane) over the hexagonal faces and only one product (cyclohexane) over cubic faces.
- Figure 9 Platinum nanoparticle size dependence of selectivity of cyclohexene hydrogenation/dehydrogenation.
- Figure 10 Platinum nanoparticle size dependence of selectivity of crotonaldehyde hydrogenation.

Figure 11

Hot electron charge transport at oxide-metal interfaces by simultaneous detection of turnover rate and electron current during carbon monoxide oxidation using a Pt/TiO₂ catalytic nanodiode.

Catalysis

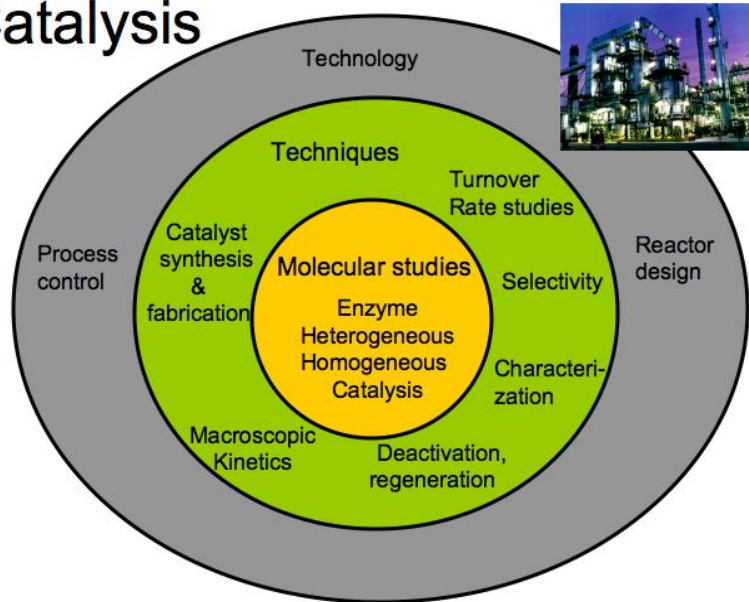


Figure 1a

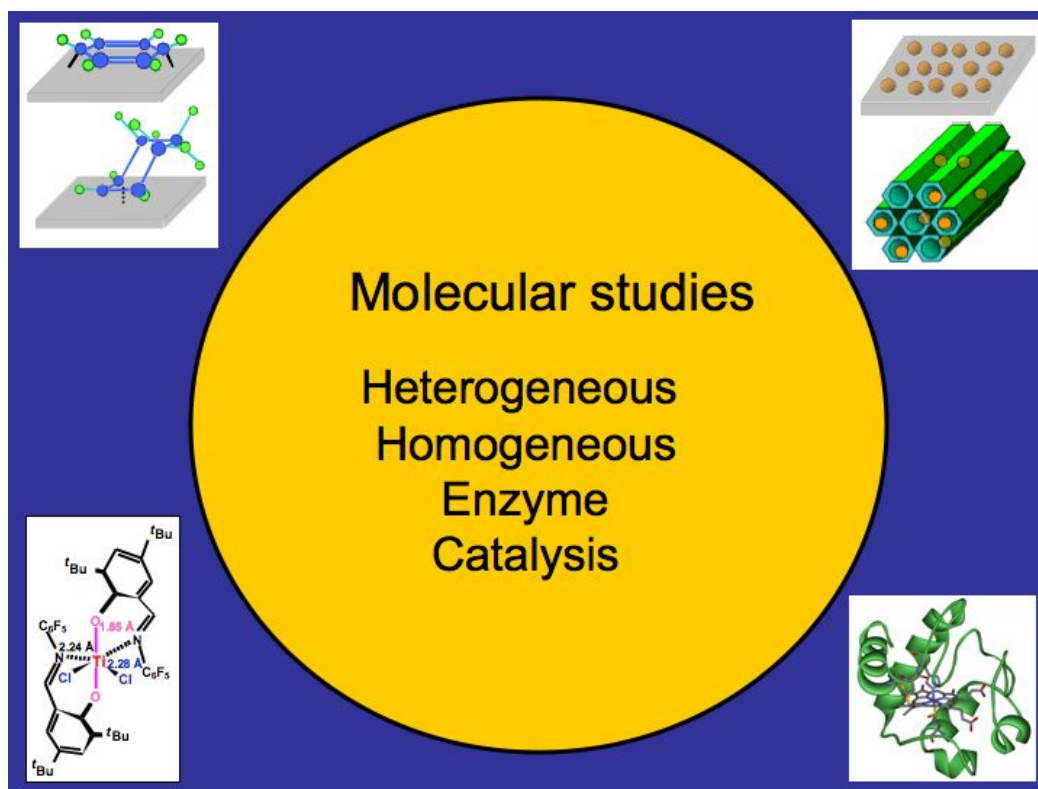
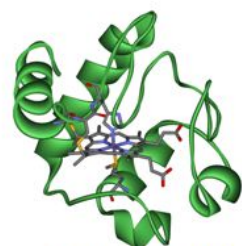
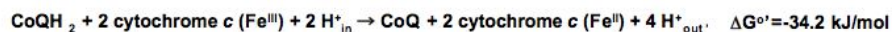


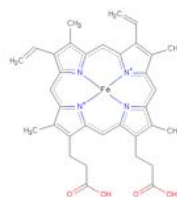
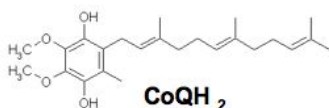
Figure 1b

Cytochrome C



Cytochrome C
100 amino acids
Molecular weight: ~12,000 daltons

Size: ~ 4 nm



Heme

Size: ~ 1.4 nm

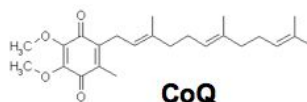
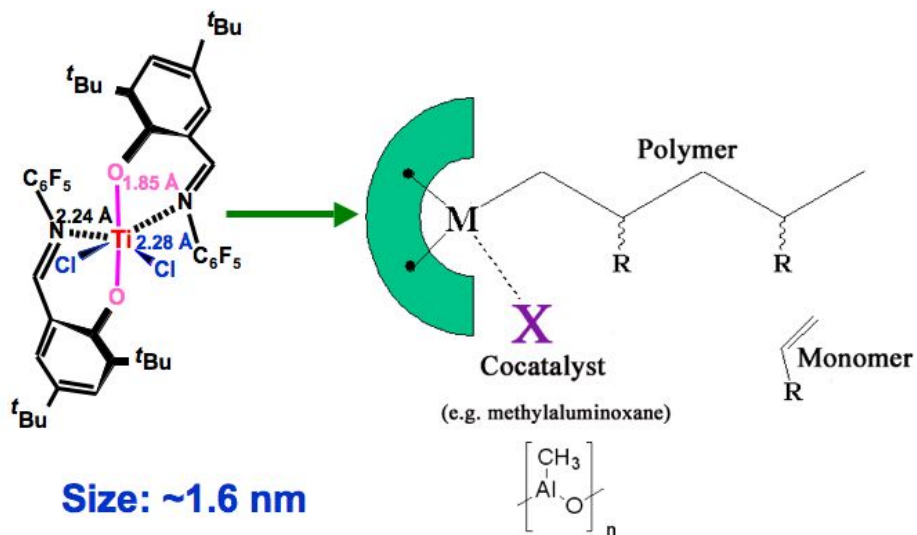


Figure 2a

Single-Site Olefin Polymerization Catalyst

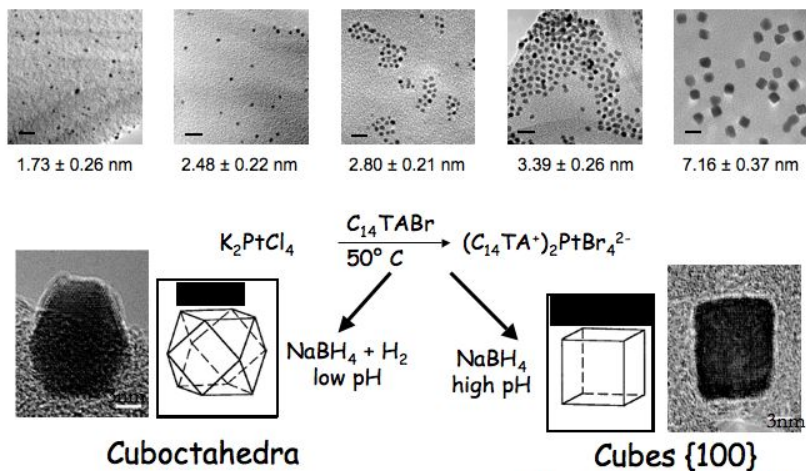


Coates et. al. *J. Am. Chem. Soc.* **2001**, *123*, 5134

Figure 2b

Control of Size and Shape of Pt Nanoparticles

- PVP: Poly(vinylpyrrolidone), surface regulating polymer
- Particle size control in the range of 1.7 ~ 7.1 nm



Lee, H. et al., *Angewandte Chemie*, 2006, 45, 7824.

Figures 2c

Reaction Intermediates

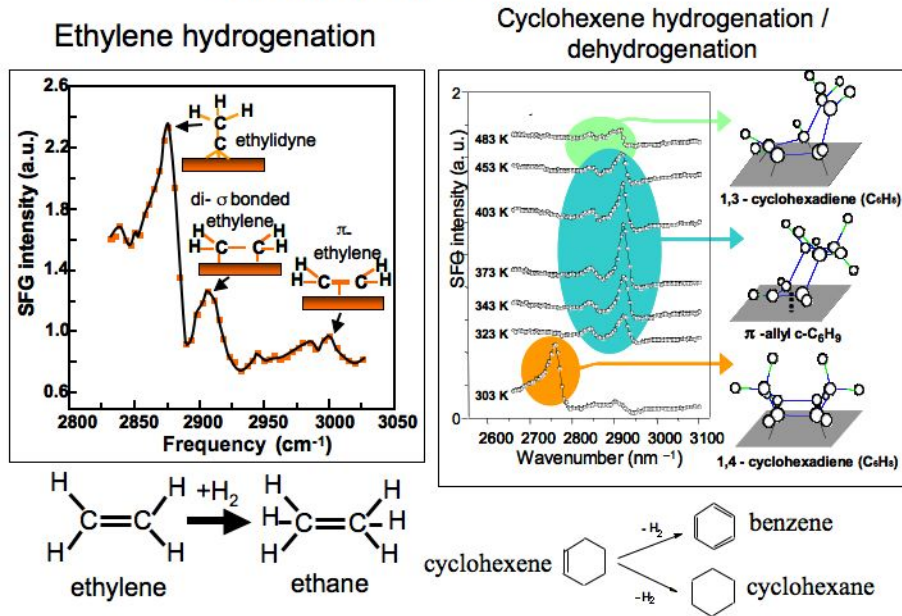


Figure 3

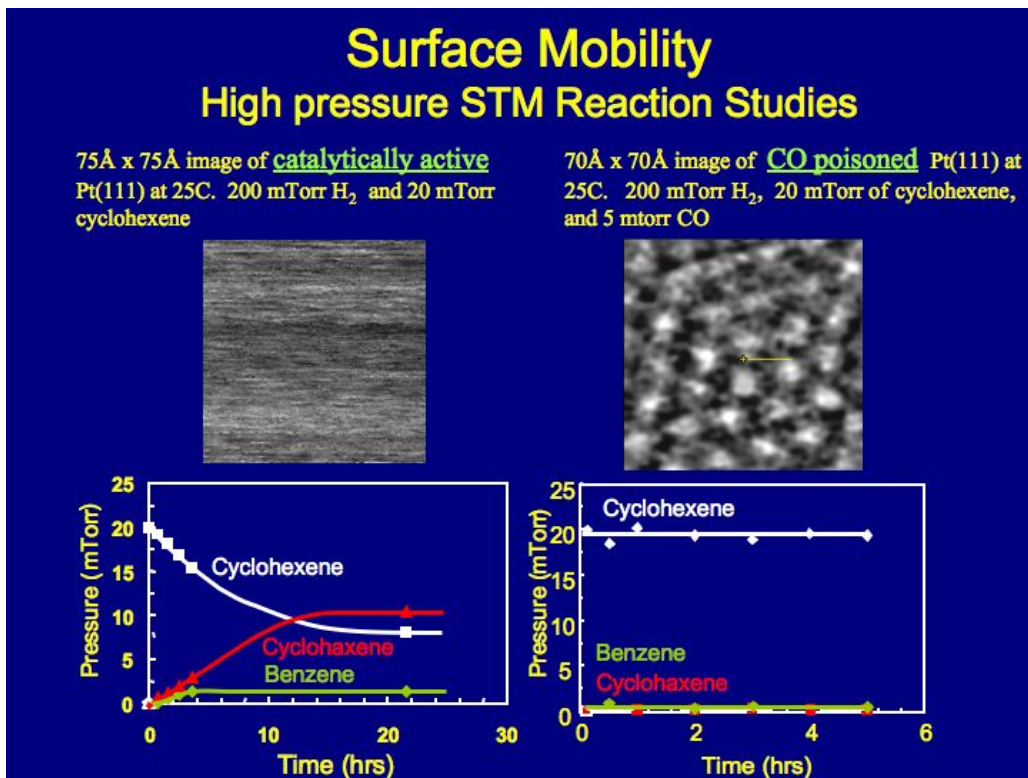


Figure 4

Adsorbate-induced restructuring of Pt(110) Surface

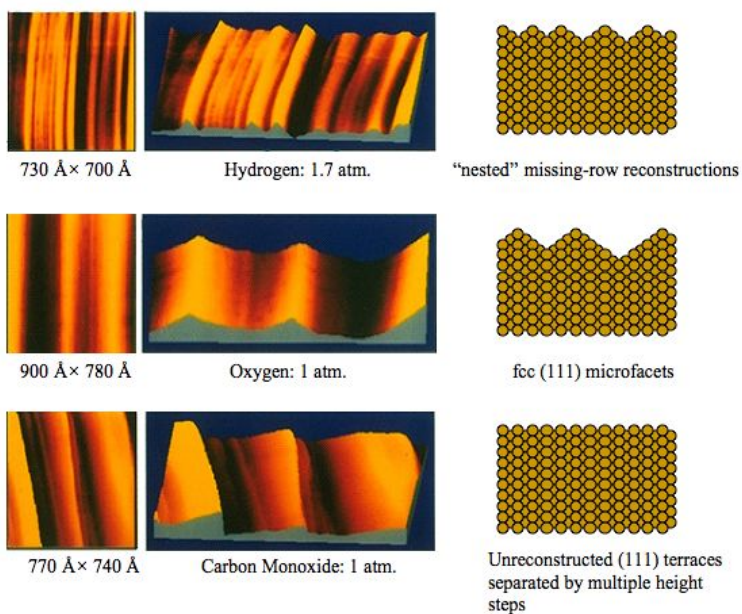


Figure 5

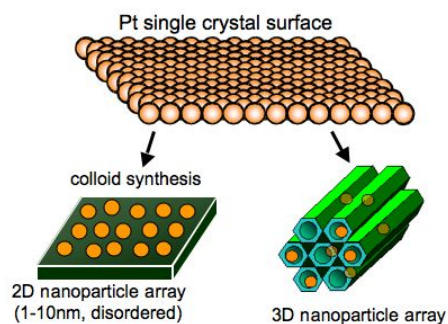
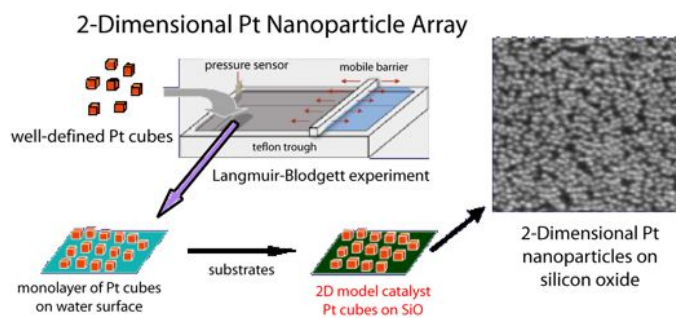


Figure 6

(a) 2-D and 3-D Nanoparticle Catalytic Systems



(b) 3-Dimensional Encapsulated Nanoparticles

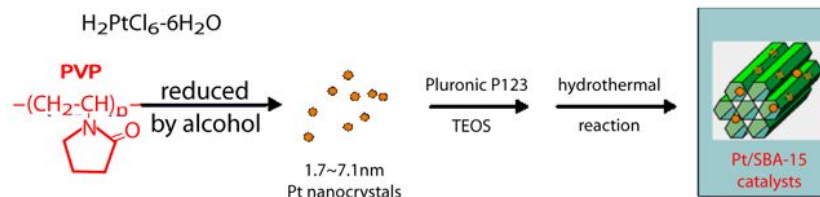


Figure 7 a and 7 b

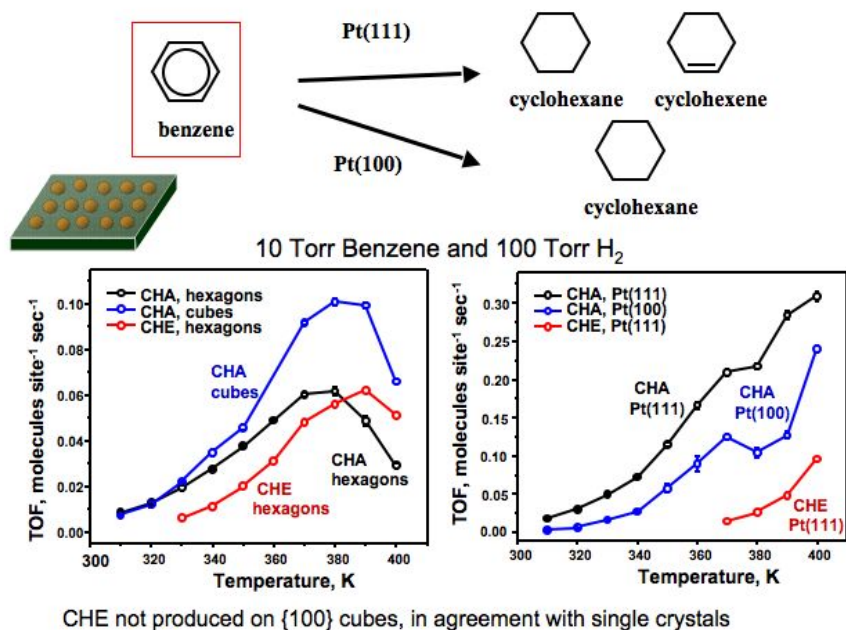


Figure 8

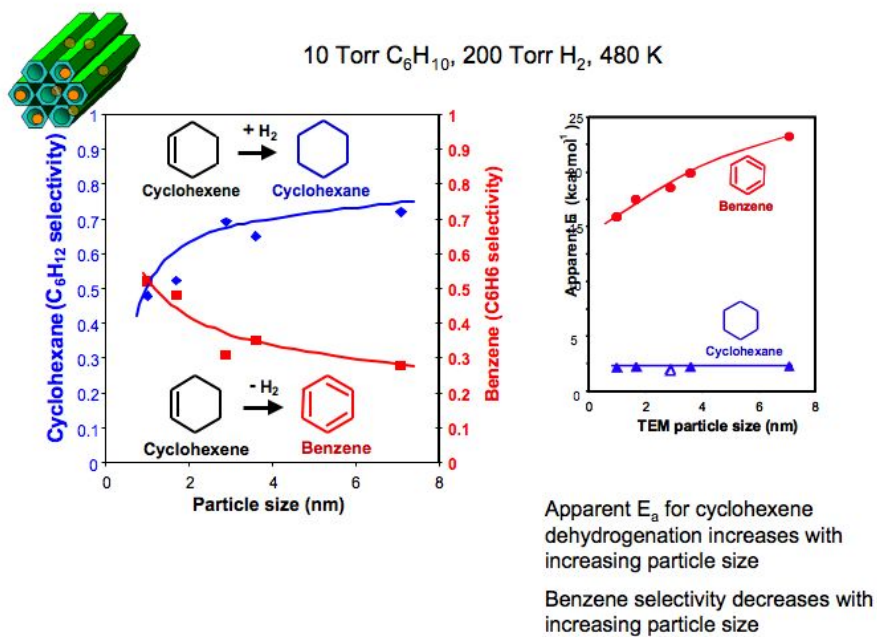
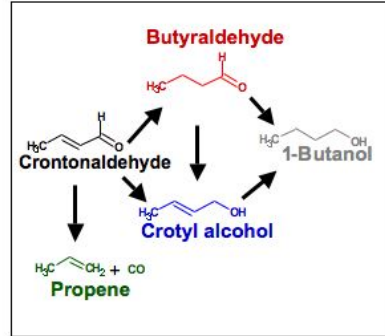
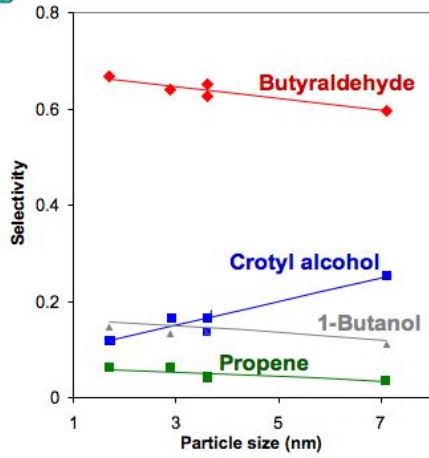


Figure 9



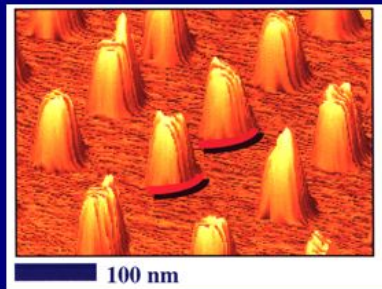
Platinum Nanoparticles



16 Torr C₄H₆O, 315 Torr H₂, 393 K

Figure 10

Charge Transport - Catalytic Nanodiode



Activation energy of Pt/TiO₂ nanodiode

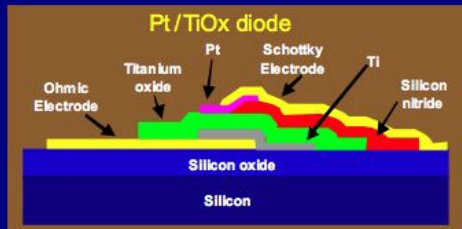
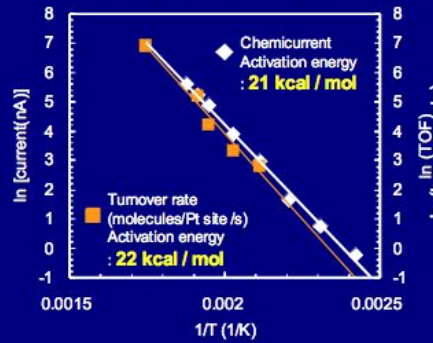


Figure 11

