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The impact of surface science on the commercialization of chemical processes

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Surface science developed instruments for atomic- and molecular-scale studies of catalyst surfaces, their composition and structure, both in a vacuum and at high pressures, under reaction conditions (bridging the pressure gap). Surfaces ranging from single crystals, nanoparticles and thin films to porous high surface area catalytic materials have been studied. Classes of surface structure sensitive and insensitive reactions have been identified by surface science studies, including ammonia synthesis, hydrodesulfurization, reforming, combustion and hydrogenation. Rates of reactions often vary by orders of magnitude between using the right and the wrong surface structures. The roles of many promoters that modify the catalyst surface structures and bonding of adsorbates have been verified. Surface reaction intermediates could be identified and the mobility of adsorbates and the adsorbate induced reconstruction of the catalysts attest to the dynamic nature of the catalytic systems during the reaction turnover. The important active sites for catalysis include the low coordination surface step, kink, oxygen and chloride ion vacancies sites and sites at oxide-metal interfaces. Uncovering the molecular ingredients of heterogeneous catalysts will have a major impact on the understanding of reaction selectivity to help the evolution of green chemistry and selective reaction of many types.

KEY WORDS: surface science in catalysis; surface catalysis in chemical processes.

1. Introduction

Most chemical processes use surfaces as catalysts toward the production of desired chemicals, while selectively eliminating unwanted byproducts. Over the last 40 years, surface science has developed *instruments* that permit atomic and molecular level studies of the structure, composition, thermodynamics and dynamics of all those surfaces that are utilized in chemical process developments to correlate these data with the turnover rates and selectivity to deliver the desired chemical properties [1,2]. Surface science evolved so that using the instrumentation for surface analysis could be used in a vacuum, at high pressures and at solid-liquid interfaces (*bridging the pressure gap*) under realistic conditions where the chemical processes operate [3–5]. Surface science also developed new catalytic materials that operate at increased rates and selectivity [6–8]; through molecular scale studies *new concepts* were developed to understand how catalysts work on the molecular scale [9–11].

Below, we first show how surface studies elucidated the roles of catalyst surface structure in controlling reaction rates and reaction selectivity. Most of these studies were carried out using metal single crystal surfaces. Figure 1 shows the (111), (100) surfaces and (557) stepped surface in an unreconstructed structure of platinum as well as the hexagonal reconstruction of the (100) surface of platinum. We then show how we could detect reaction intermediates *in-situ*, with the instruments that were developed to operate at high reaction pressures [12,13]. Figure 2 shows the instruments that we most frequently use to study the molecular ingredients of catalytic reactions on single crystal surfaces. The high pressure/low pressure reactor that was developed first in our laboratory permits us to shuttle the low surface area (1 cm^2) sample between ultra high vacuum for studies of surface composition and surface structure, and high pressures under which condition we can monitor the rates of catalytic turnover. Figure 2a shows the high-pressure cell in both the open (top) and closed (bottom) positions. Figure 2b and 2c show schematics of scanning tunneling microscopy (STM) and sum frequency generation (SFG) vibration spectroscopy under high pressure. We found that the metal continually restructures during the catalytic turnover and the adsorbed molecules are mobile on catalytically active surfaces [14–16]. Finally, new catalyst nanoparticles could be synthesized using colloid science techniques that promise to be more selective than the present day catalysts employed in commercial processes [17–21].

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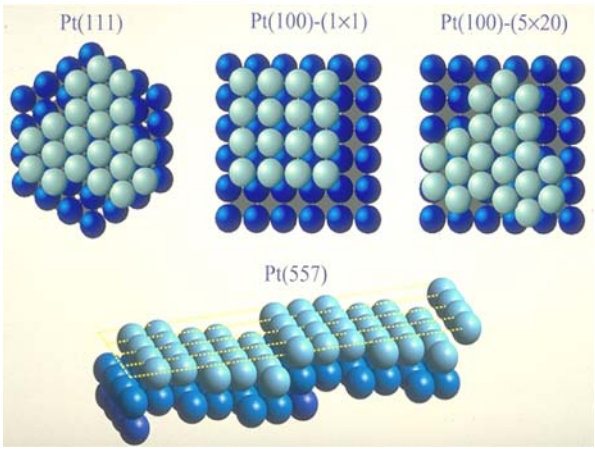

Figure 1. The (111), (100), and (577) stepped single crystal surface of platinum, as well as the hexagonal reconstruction of the (100) surface of platinum.

2. Surface structure sensitive—insensitive catalytic reactions

When a molecule impinges on a certain surface site the reaction probability varies with the nature of the site. Hydrogen dissociates with unity reaction probability on every collision on a stepped platinum surface, while the reaction probability is below the detection limit of 10^{-3} on a terrace of the metal of (111) orientation, which exposes a hexagonal surface structure [22,23]. Nevertheless, hydrogenation reactions that start with dissociation of the hydrogen molecules on the metal surface have relatively high reaction probability on many surface sites: top site, bridge site and step sites. For this reason, hydrogenation reactions are usually structure insensitive because they can be carried out in many different arrangements of surface atoms. Carbon–hydrogen bond breaking, however, such as the decomposition of methane, CH_4 to carbon and hydrogen, has a reaction probability of less than 1:100 million on collisions of methane molecules with the platinum surface [24]. In such circumstances, we have to have at least the Torr range of pressures and wait about 60 s to reach that reaction probability and monitor the accumulation of carbon on the metal surface [24]. In this circumstance, there are sites, which are uniquely active for C–H, C = O and N ≡ N bond breaking and give much higher reaction probability than other sites. We see structure sensitivity where a certain surface structure can be orders of magnitude more active for breaking of a particular chemical bond or bond rearrangement reaction than other sites. Below, we show examples of these structure sensitive reactions that include ammonia synthesis, thiophene hydrodesulfurization, the rearrangement of hydrocarbon molecules in reforming reactions to produce high-octane gasoline and the ignition reaction during CO oxidation.

2.1. Ammonia synthesis

The ammonia synthesis catalyst used in industry is "doubly promoted." In addition to iron, which is the

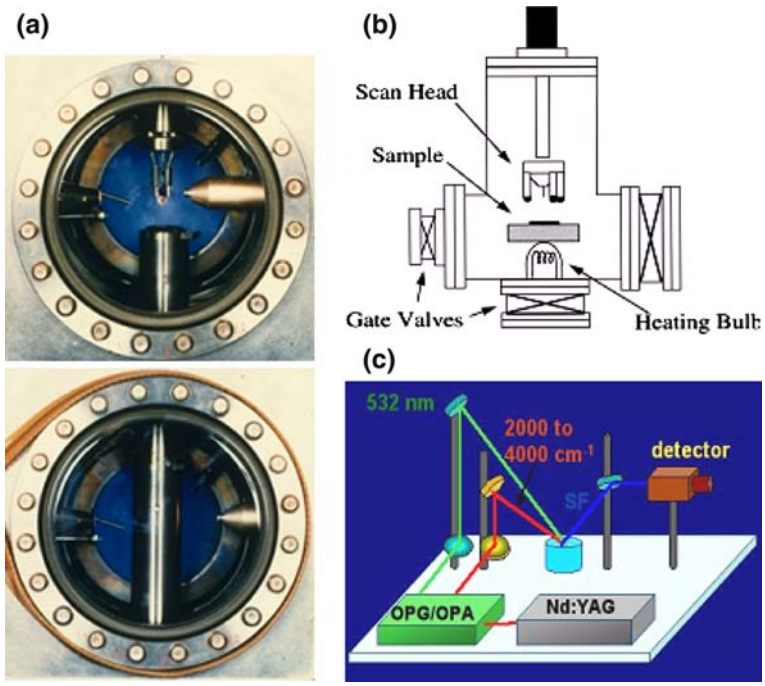

Figure 2. (a) Photograph of UHV high-pressure cell apparatus. (b) schematic of high-pressure scanning tunneling microscopy (STM) and (c) high-pressure sum frequency generation (SFG) vibration spectroscopy.

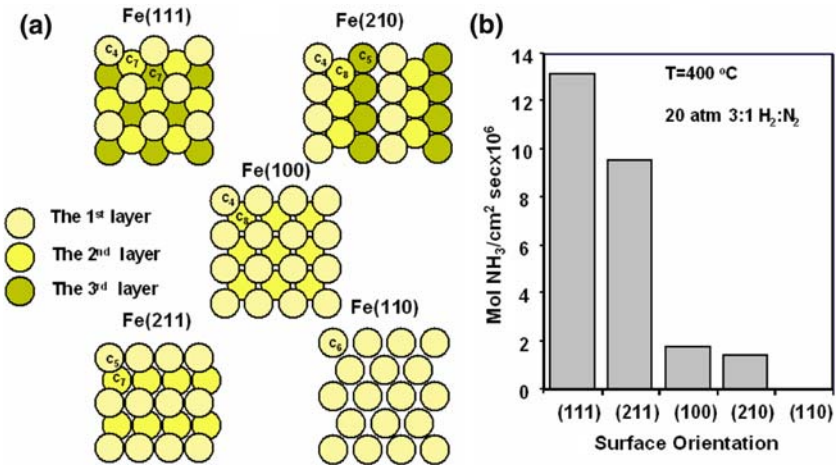

Figure 3. Ammonia synthesis as studied on various single-crystal surfaces of iron (a) schematic of various surfaces of Fe single crystal. (b) The (111) and (211) surfaces of iron are orders of magnitude higher activity than the other crystal faces.

most popular active metal used in this reaction, aluminum oxide and potassium oxide are used as structural and bonding modifiers [25–27]. The high pressure/low pressure reactor (figure 2a) was used in studies of ammonia synthesis on iron and rhenium single crystal surfaces. Figure 3 shows the structure sensitivity of ammonia synthesis, where the rate determining reaction is the breaking of the nitrogen–nitrogen triple bond to produce atomic nitrogen [25–27]. The (111) and (211) surfaces of iron are orders of magnitude higher activity than the other crystal faces, while the lowest free energy high atomic density (110) surface is virtually unreactive for dissociating dinitrogen. The presence of seven iron atom coordinated sites that are present in both (111) and (211) surfaces are implicated as the most active sites for dissociating the nitrogen molecule. The alumina promoter has the effect, through the formation of an iron aluminate compound intermediate, to restructure the iron surfaces to either the (111) or (211) orientation crystal faces, thereby optimizing the concentration of the most active surface structure for dinitrogen dissociation. Potassium is an electron donor (even in its oxide form) to the metal surfaces and ammonia, the product molecule, is also an electron donor. The donor–donor repulsive interaction lowers the heat of adsorption of ammonia by about 2.5 kcal/mol [28]. In this circumstance, at high ammonia pressures near equilibrium, the presence of potassium reduces the surface concentration of ammonia and thereby product poisoning is minimized, giving rise to a much higher concentration of ammonia in the gas phase [25,27,29]. Potassium also shifts the ammonia pressure dependence to have a smaller negative exponent, −0.35 in the case potassium promoted iron, while it is −6 without promotion by potassium.

2.2. *Hydrodesulfurization of thiophene*

The hydrodesulfurization (HDS) reaction to remove sulfur from naphta can be carried out on several transition metal surfaces. The most popular one, molybdenum, shows structure insensitivity. That is, the HDS reaction can occur on many, or most, surface sites on molybdenum [30,31]. However, on rhenium the reaction shows structure sensitivity, indicating that certain sites are much more active for this reaction than others (figure 4) [32].

2.3. *Reforming with platinum catalysts*

The prototype model reforming reaction is a conversion of *n*-hexene or *n*-heptane to other molecules (shown in figure 5) of high octane number, while the reactants have zero octane number. Platinum single crystal surface studies indicate that the hexagonal (111) surface produces benzene as a dominant reaction in *n*-hexene conversion, while the (100) faces prefers to catalyze isomerization reactions [33–35]. The kink sites on the platinum surface break carbon–carbon bonds, which is an undesirable reaction, and thereby a poison is added to the reactant mixture in the form of H_2S that blocks the kink sites by strong adsorption. Poisoning of certain active sites to inhibit undesirable reaction is one of the strategies for developing selective catalysts for particular reactions.

When gold is added to platinum, the gold preferentially blocks the high coordination three-fold sites in a hexagonal surface, where benzene forms, called dehydrocyclization [36]. The addition of gold converts benzene-producing platinum catalysts to branched isomer-producing catalysts—a marked change of selectivity. Bimetallic catalysts are almost exclusively used for this reforming reaction in the form of platinum tin, platinum

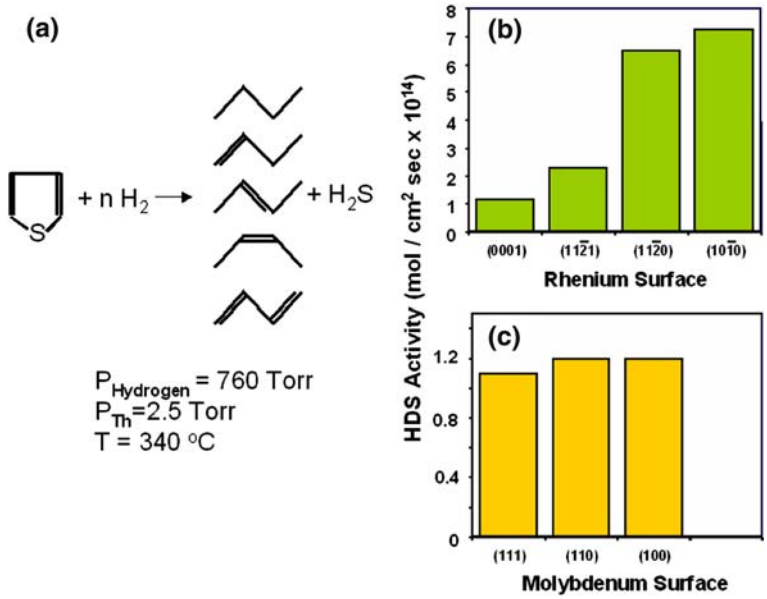

Figure 4. The hydrodesulfurization of thiophene as studied on single-crystal surfaces of molybdenum and rhenium (a) Schematic showing hydrodesulfurization of thiophene (b) The reaction is structure sensitive over rhenium (c) and structure insensitive over molybdenum surfaces.

iridium or platinum rhenium. All these catalysts have unique functions that are provided by the second metal component, which has been studied exhaustively and verified by modern surface science.

2.4. CO oxidation ignition

When carbon monoxide is adsorbed on various platinum surfaces, a new technique, sum frequency generation vibrational spectroscopy (shown in figure 2c), which is monolayer sensitive, can monitor the dissociation of this molecule [13,37,38]. It was found that on the (111) and stepped surfaces, CO dissociation, which produces carbon deposition on the metal surface, occurs at higher temperatures than on the (100) platinum surface (figure 6). When ignition occurs, there is a sudden jump, about 200°, in temperature, indicating a sudden increase in the heat produced by the reaction. This marked increase in temperature coincides with the deposition of carbon on the various platinum surfaces. The reaction below ignition is the oxidation of molecular CO. At the ignition point, the carbon that deposited can also be oxidized by molecular oxygen to CO_2 and this reaction is even more exothermic than the oxidation of molecular CO. The combination of these two reactions, both exothermic, causes ignition. The two reaction channels

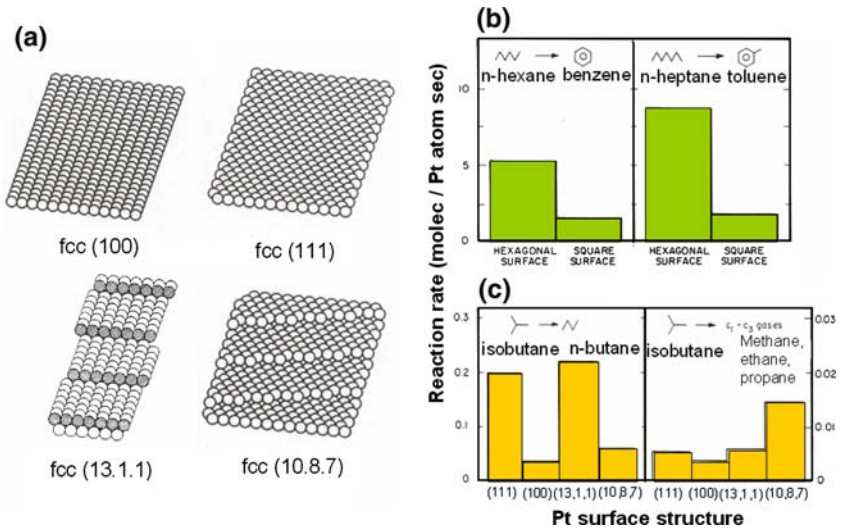

Figure 5. The hydrocarbon conversion as studied on Pt single crystal surfaces. (a) Schematics of various Pt surfaces. (b) Structural sensitivity of alkane aromatization and (c) light alkane skeletal rearrangements are revealed.

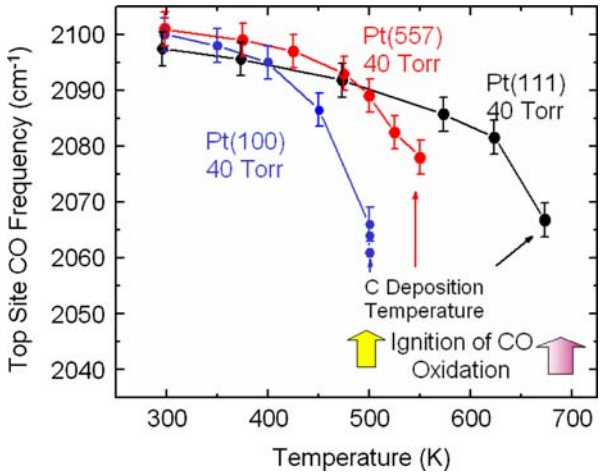

Figure 6. Top site CO frequency measured as a function of the temperature during CO oxidation. Structure sensitivity of CO dissociation and ignition of CO oxidation are shown on Pt(100), Pt(111), and Pt(577) surfaces.

provide much more heat above ignition than the one reaction channel, molecular CO oxidation, below ignition.

3. Detection of reaction intermediates leading to molecular mechanisms of catalytic turnover

3.1. Ethylene hydrogenation

One of the great advances in the use of modern molecular surface science for studies of catalytic reactions is the identification of reaction intermediates on the surface that are responsible for the high catalytic turnover of a particular catalytic reaction. One of the simplest of these reactions is ethylene hydrogenation, which yields one product, ethane [16,39–41]. Ethylene adsorption on the platinum (111) surfaces causes restructuring of the metal surface, which is shown in figure 7 [42]. The surface becomes covered with ethylidyne C_2H_3 and its structure and the restructuring of the metal surface as the strong bond between ethylidyne and platinum forms are indicated [40,41,43]. However, ethylidyne does not turn over and become hydrogenated. It is so strongly bound that it is a permanent unreacted fixture of the metal surface. When the carbon is labeled by a carbon isotope, it was shown that the turnover of the ethylidyne is about a million times smaller than the turnover of ethylene hydrogenation, which is a facile reaction with a rate at room temperature of about 10 molecules of ethane per metal site per second. When sum frequency generation vibrational spectroscopy is used to identify the surface species during the catalytic turnover, there were three: ethylidyne, di-σ-ethylene, and π-bonded ethylene, the last of which, π-bonded ethylene, is weakly bound [41,44,45]. This is the molecule, which turns over while occupying only 4% of the metal sites. The picture that emerges is that the ethylidyne, while strongly adsorbed on the metal, is mobile on the surface with an activation energy of about .1 eV at room temperature. While it is mobile, incoming ethylene molecules that can occupy weakly π-bonded sites on the

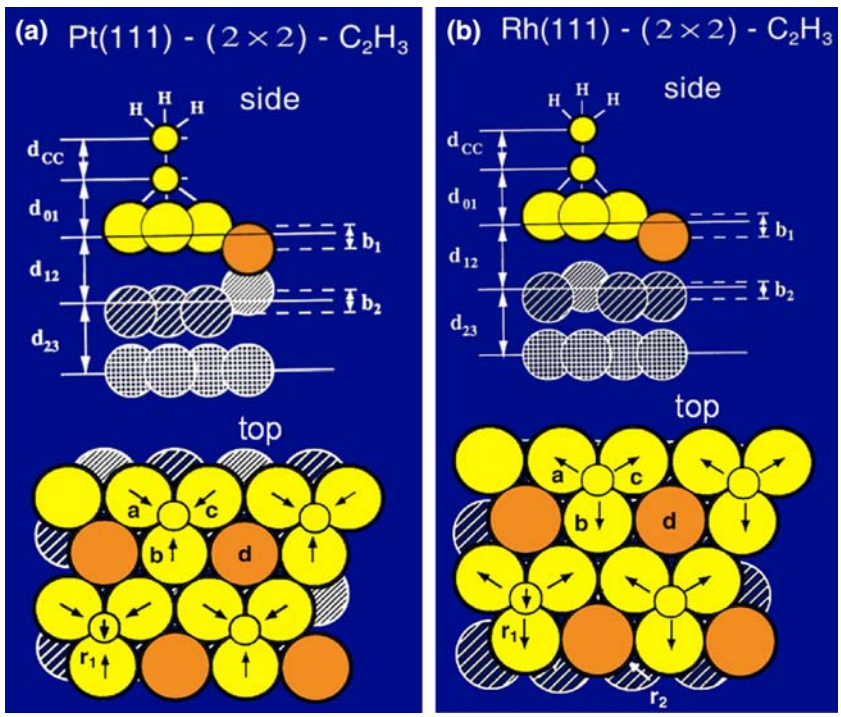

Figure 7. (a) Side and top views of Pt(111) + (2 × 2) − C_2H_3. The interlayer spacings dij involving metal layers are measured between average atomic positions within the layers. Lateral metal displacements are labeled ri for layer i. (b) Side and top view of Rh (111) + (2 × 2) − C_2H_3.

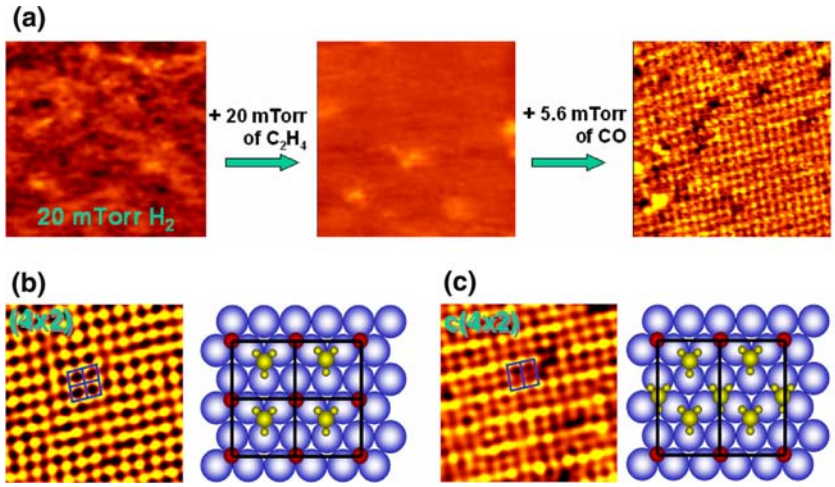

Figure 8. (a) 10 nm × 10 nm STM images of a Pt (111) surface after the subsequent addition of 20 mTorr H2, 20 mTorr of C2H4, and 5.6 mtorr of CO. (b) 5 nm × 5 nm STM images revealing (4 × 2)–CO + C_2H_3 and (c) c(4 × 2) – CO + C_2H_3 structure formed at 20 mTorr H_2, 20 mTorr of C_2H_4, and 5.6 mtorr of CO on Rh (111). Schematics show the proposed structures of the corresponding unit cell as indicated in the image.

surface can pick up rapidly two hydrogen atoms sequentially to form ethyl, C_2H_5 then ethane, C_2H_6 and desorb. These weakly bound reaction intermediates, while available in very small concentrations, are responsible for the catalytic turnover.

High pressure scanning tunneling microscope is another technique that we use often and is shown in figure 2c. This technique allows the detection of molecular mobility by scanning the surface at about 100 Å per millisecond. If the molecules move faster than this speed they cannot be imaged by STM, however if they are slower than the scanning rate of the STM an ordered structure can be seen. Under reaction conditions of catalytic turnover, the hydrogen and ethylene are mobile species on the surface, and there is no well-resolved scanning tunneling microscope image, while the reaction turns over in a steady state (figure 8). However, when we poison the reaction by the addition of carbon monoxide, the reaction stops and an ordered surface structure is observed. The carbon monoxide poisons the mobility of ethylidyne and therefore new sites where adsorption of weakly bound π-bonded ethylene can occur are no longer available. This was observed on various metal surfaces for not only ethylene hydrogenation but other hydrocarbon conversion reactions. There is one more hydrocarbon conversion that I would like to describe, which is somewhat more complex but still showing the same molecular features as ethylene hydrogenation – and that is cyclohexene hydrogenation and dehydrogenation.

3.2. *Cyclohexene hydrogenation and dehydrogenation*

This reaction yields two product molecules, cyclohexane and benzene [15,46]. SFG vibrational spectroscopy detects three reaction intermediates on the surface: 1,3-cyclohexadiene,1,4-cyclohexadiene and an allyl intermediate, the structures of which are indicated in the figure 9 [46–48]. On the platinum (111) surface, the dehydrogenation reaction to benzene has a considerably lower rate than on the (100) surface. The SFG spectra shows that while on the (111) face, there are two reaction intermediates present (1,3- and 1,4- cyclohexadiene), while on the (100) surface there is only one (1,3-cyclohexadiene). It appears that there are two reaction channels involving the two cyclohexadiene intermediates, one of them slower than the other. Both of these reaction channels are operating on the (111) surface. On the (100) surfaces, however, only the reaction channel, which is faster through the 1,3-cyclohexadiene intermediate, is operating. Therefore, this surface has a higher turnover rate for dehydrogenation to benzene.

Similarly, STM studies show that while the reaction turns over and cyclohexene reacts to form the products, the STM picture is diffuse, the molecules are moving too fast on the surface for us to image them [15]. However, when the reaction is poisoned by the coadsorption of carbon monoxide, the catalytic turnover stops and an ordered surface structure forms. It appears that reaction turnover can only occur on adsorbed molecules in a dynamic state when they are mobile on the catalyst's surface. The adsorbed molecules also restructure the metal catalyst's surface. As shown in figure 10 for hydrogen, the oxygen and carbon monoxide restructure the platinum (110) face differently by forming thermodynamically stable structures in the presence of these adsorbed gas atoms or molecules. This phenomenon, called adsorbate-induced restructuring, indicates that under reaction conditions both the adsorbed surface species that may be reaction intermediates and the metal surface are continually mobile.

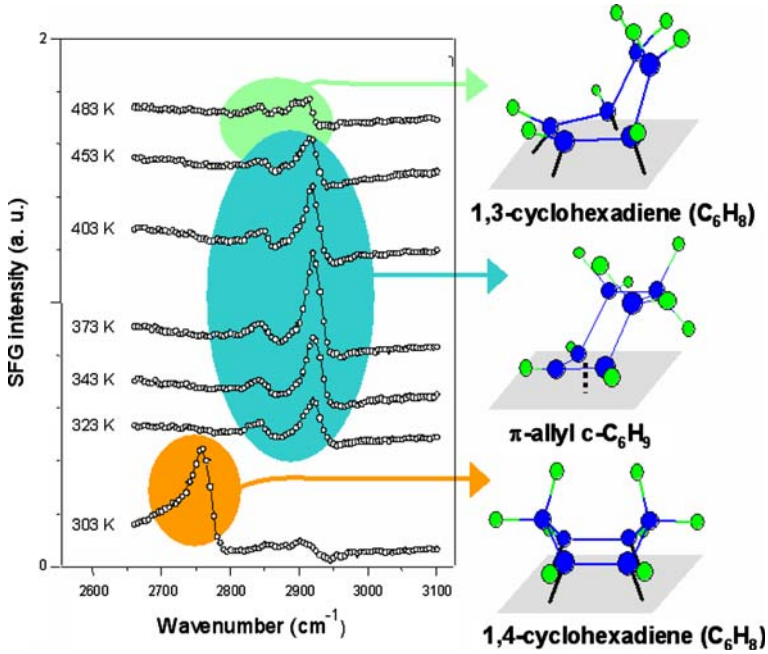

Figure 9. SFG spectrum of the Pt (111) surface during cyclohexene hydrogenation revealing reaction intermediates, 1,4-, 1,3-cyclohexadienes and p-allyl c-C_6H_9.

4. Bridging the materials gap

Catalysts used in commercial chemical processes are nanoparticles, usually in the 1–10 nm size regime in size. We have undertaken research to use nanoparticles of this size instead of single crystal surfaces, and this is schematically shown in the next figure 11 [8]. The use of nanoparticles as model catalysts requires making them all the same size and shape because the surface structure is a key ingredient for selectivity [7,49]. This is demanded by the change of emphasis in catalyst technology from producing more products by the development of higher activity catalysts to producing more selective products, eliminating byproducts as much as possible by

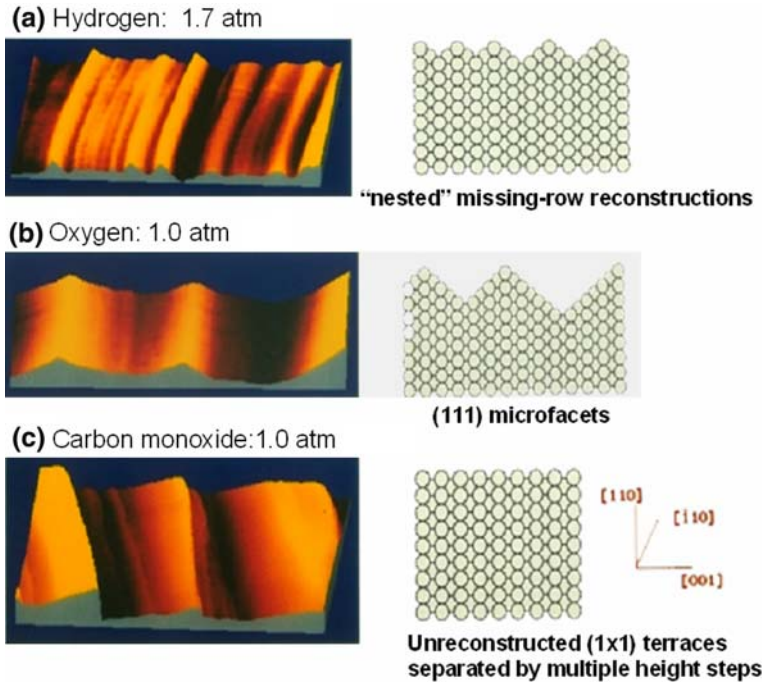

Figure 10. STM topographical images of adsorbate-induced surface reconstructions of Pt (110) surface in (a)1.7 atm hydrogen (73 nm × 70 nm), (b) 1.0 atm oxygen (90 nm × 78 nm) and (c) 1.0 atm carbon monoxide (77 m × 74 nm).

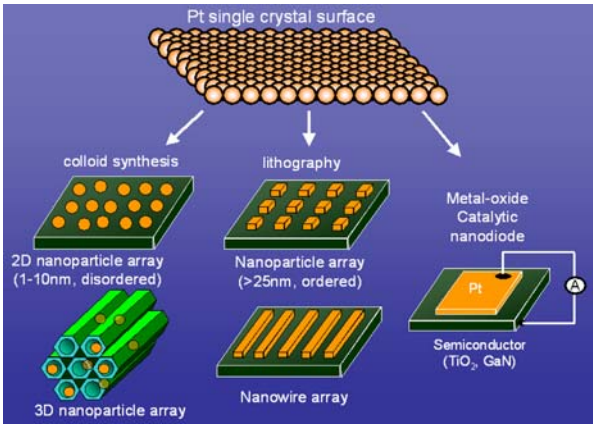

Figure 11. Schematic showing the evolution of the catalyst model system from the single crystal metal surface to the 2D and 3D nanoparticle arrays that are colloid synthesized, and to nanowire arrays and nanodiodes that are fabricated with lithography.

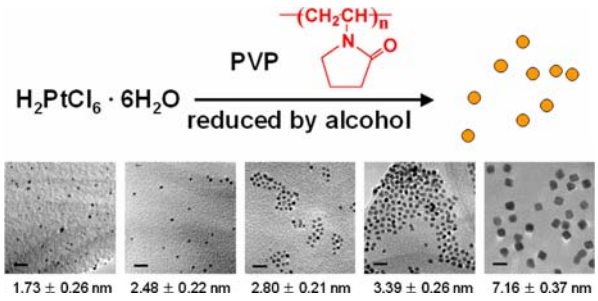

Figure 12. TEM images of Pt nanoparticles with various sizes capped with PVP poly (vinylpyrrolidone). Size of nanoparticles can be controlled in the range of 1.7 ~ 7.1 nm.

use of selective catalysts. This is called "green chemistry" and it is a major challenge to commercial catalysis-based chemical processes because our understanding of the molecular ingredients of selectivity is much poorer than that of catalytic activity. Selectivity is controlled by very small differences in potential energy barriers which separate the formation of one molecule compared to the molecules of other types (all thermodynamically feasible) and minor changes of structure, composition, temperature or pressure lower one of the potential barriers as compared to the other. By using colloid science in solution, we can prepare platinum, rhodium and other metal nanoparticles in the 1–10 nm regime, as shown for platinum in figure 12 [17,18,20]. These particles are polymer capped to avoid aggregation of the metal particles in the solution where this reaction occurs. We find also that by suitable arrangement of conditions to produce these nanoparticles, we can control the shape of the nanoparticles as shown in figure 13 where platinum has been prepared in either cubic or hexagonal shape. We can take these nanoparticles and place them in a Langmuir-Blodgett trough which we can use surface pressure to create different particle densities as shown in the figure 14 [20]. By collecting these nanoparticle aggregates onto an oxide wafer, we can produce thin films of nanoparticle deposits, which can be used as model catalysts. Alternatively, these nanoparticles, which are monodispersed, can be deposited on a mesoporous support by sonication or by direct encapsulation by synthesizing the mesoporous support around the nanoparticles. This way, we can deposit the nanoparticles in a three-dimensional support, which can be more readily employed in commercial chemical processes. Such model nanoparticle deposits show particle size sensitivity of reaction selectivity as shown by the particle size dependence of the cyclohexene hydrogenation/dehydrogenation reaction (figure 15). As the particles become larger, less benzene forms. The reason for this is that the activation energy for dehydrogenation increases the particle size, while the hydrogenation reaction activation energy to produce cyclohexane remains constant. Another model reaction to probe selectivity is hydrogenation of crotonaldehyde to either butyraldehyde or crotyl alcohol. As shown in the figure 16, with increasing particle size, we form more crotyl alcohol and less butyraldehyde.

A reaction with great structure sensitivity is ethane hydrogenolysis which shows two orders of magnitude decrease in the formation of methane with increasing particle size. Through the synthesis, characterization and reaction studies of monodispersed metal nanoparticles of well-defined surface structure, the field of

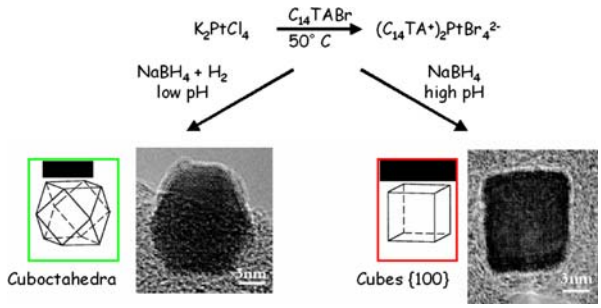

Figure 13. TEM images of Pt nanoparticles capped with C14TAB (tetradecyltrimethylammonium bromide).

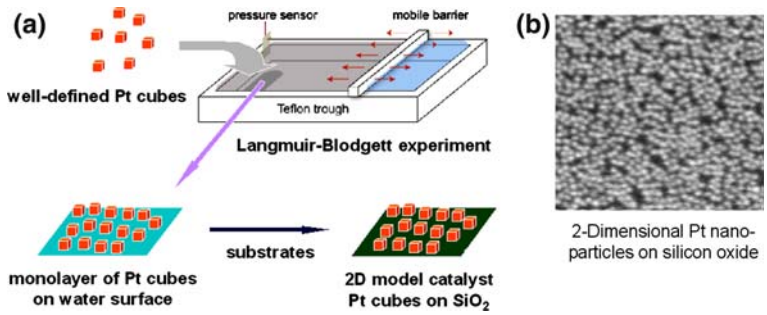

Figure 14. (a) schematic of Langmuir-Blodgett method (b) SEM image of 2-dimensional Pt nanoparticles arrays on silicon oxide.

nanocatalysis has been created. We can explore the molecular ingredients of selectivity for nanoparticles in this manner and it is likely that many other molecular features that give rise to selectivity will be discovered.

5. Active sites in catalysis

Studies over the decades have shown that defects sites on surfaces such as atomic steps and oxygen and chloride ion vacancies are important sites of higher reaction probability [50] and these sites are available in large concentrations on nanoparticles. It may well be that reactions of nanoparticles with size-dependent rates are influenced by the change in concentration on these sites. However, there is another site of equal importance for active production of selective reaction, and these are *the oxide metal interface sites* as shown in figure 17 Schwab, in the late 1950's, documented that when non-reactive oxides were deposited on reactive metals, the metal activity increased by 10 fold or more, and this he called "inverse catalysis" [51,52]. Over the last 15 years, the field of hot electron generation on metal surfaces provided evidence for the mechanisms of operation of such important oxide metal active sites in catalytic reactions [53,54]. When either vibrationally excited molecules or photons inpinge on metal surfaces within 20–30 femtoseconds, the energy deposited converted to the excitation of hot electrons, which carry most, if not all, of the energy of light or excited molecules [55]. This has been studied and proven on metal surfaces, while on insulator surfaces, in the absence of free electrons, this process does not occur. By careful studies, the electron mean free path in the metal was determined to be in the 3–7 nm regime. In my laboratory, we constructed a so called catalytic nanodiode, which is composed of a metal of thickness smaller than the mean free path of hot electrons, deposited on a semiconductor surface

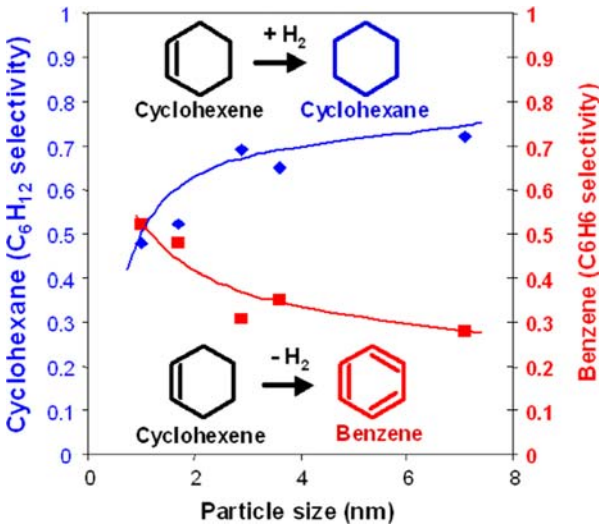

Figure 15. Size dependence of Pt nanoparticles on selectivity of cyclohexene hydrogenation/dehydrogenation.

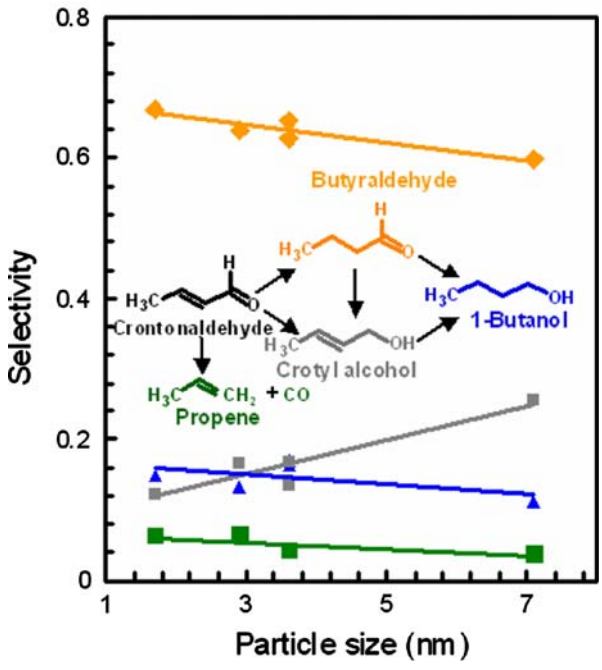

Figure 16. Size dependence of Pt nanoparticles on selectivity of the hydrogenation of crotonaldehyde.

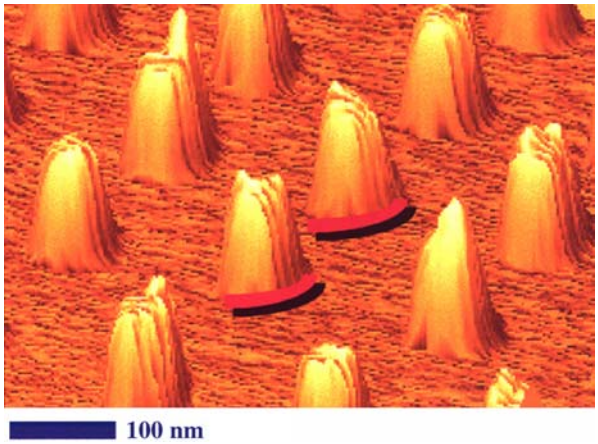

Figure 17. AFM images of 28 nm Pt nanoparticle arrays on silicon surface fabricated with nanoimprint lithography.

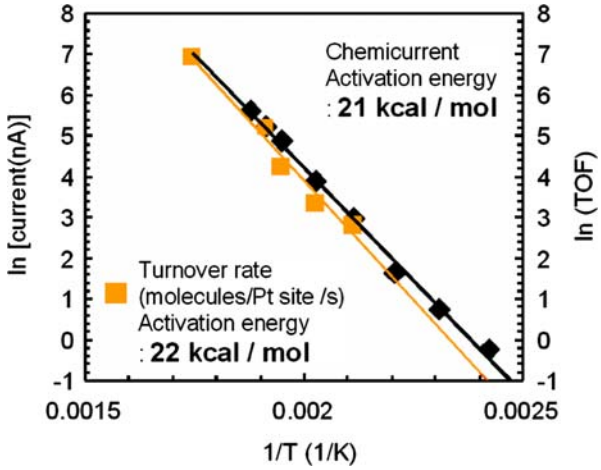

Figure 19. Plot of chemicurrent and turnover rate as a function the temperature during CO oxidation (40 Torr CO and 100 Torr O2).

[10,56–60]. When exothermic catalytic chemical reaction occurs, we find that the heat deposited converted to hot electron flow and that can pass through the metal film, which is thinner than the electron mean free path, into the semiconductor which has a Schottky barrier, which allows the passing of energetic electrons in one direction but not in the reverse direction [61]. Figure 18 shows two types of diodes and their diode characteristics. We place the diode into a catalytic reactor and we measure simultaneously the hot electron current, which is often called ''chemicurrent'', and the turnover rate. Figure 19 shows that the turnover rate and the chemicurrent are correlated as a function of temperature [10]. They have the same activation energy and obtained roughly one electron per 1000 CO_2 molecules in the CO oxidation reaction [59]. We tried several reactions with success, including the hydrogen/oxygen reaction and cyclohexene hydrogenation and dehydrogenation. There is another interesting finding in these studies. By applying a potential that opposes the flow of hot electrons, we can reduce the turnover rate in CO oxidation by 20%. This indicates that it may be possible to control the turnover rate, and perhaps the selectivity, by applying potential in the right direction in the right circumstance.

6. Conclusion

Figure 20 shows the evolution of surface science over the years, from ultra-high vacuum surface science, where techniques had to be used under low pressure conditions to study model surfaces, to surface science where new techniques could be used to study surfaces at high pressures. By bridging the pressure gap, reaction studies

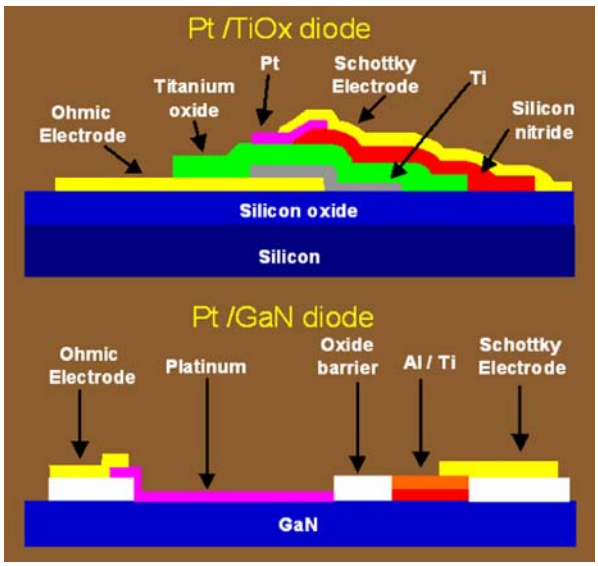

Figure 18. Schematic of Pt/TiO2 and Pt/GaN catalytic nanodiodes.

Figure 20. Direction of surface science.

were possible under conditions where commercial chemical processes are carried out. In the meantime, nanosciences have permitted the closing of the materials gap and have changed single crystal model surfaces into nanoparticles that are monodispersed and of the same size and shape, and to use them as model systems in catalytic processes at high pressures. This bridging of the materials gap now positions surface science to have major impact on the understanding of reaction selectivity and help the evolution of green chemistry and selective catalytic reactions of many types. It is our hope that with the possibility of carrying out catalytic reactions at solid-high-pressure gas and solid-liquid interfaces other fields of catalysis, including homogeneous and enzyme catalysis, might show similar molecular features as heterogeneous catalysis, thereby the three fields of catalysis might merge over the next 20 years.

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