The Development of Molecular Surface Science and the Surface Science of Catalysis: The Berkeley Contribution†

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Received: October 1, 1999; In Final Form: January 11, 2000

Since the early 1960s, surface science has uncovered the atomic and electronic structures of surfaces and the nature of chemical bonding of adsorbed monolayers of atoms and molecules. Surface instrumentation was developed to carry out these studies as well as to monitor surface reactions, stoichiometric and catalytic. Metal, oxide, molecular crystal, and polymer surfaces have been investigated on the molecular scale. Studies in vacuum and at low pressures that used electrons, ions, and atoms as surface probes have been extended in recent years to high pressures and studies of solid−liquid interfaces by using photon scattering techniques and surface probe microscopes. My laboratory in Berkeley has participated in the development of molecular surface science and heterogeneous catalysis during the past 35 years. The following is a personal review of our contributions to the field.

The Beginning

I left Hungary in the late fall of 1956 after the defeat of the revolution and had the good luck to start graduate school in the College of Chemistry at Berkeley in February of 1957. After taking courses in physical chemistry, unit operations, and organic chemistry while on probation, I decided to continue my graduate work in physical chemistry, a switch from chemical engineering, which was my major at the Technical University in Budapest. At the end of the semester I was accepted as a chemistry graduate student and started the search for a research director. Catalysis and polymers were the two fields of chemistry that intrigued me, but there was no one on the College of Chemistry faculty who carried out research in either field. Luckily, Professor Richard Powell, an inorganic kineticist with very broad research interests was willing to suggest a research topic in catalysis. As a consequence, I spent the next 2 1/2 years doing small-angle X-ray scattering on platinum particles[1] that were dispersed on γ-alumina to unravel how the particle size distribution changes as a function of chemical and thermal treatments. I learned a lot, both inside and outside the laboratory. It became clear to me that modern physical chemistry was defined by molecular level studies of systems, by spectroscopy, or by diffraction to learn about structure and dynamics. If I were to pursue research at the frontiers of the discipline I would have to find techniques that permitted such studies.

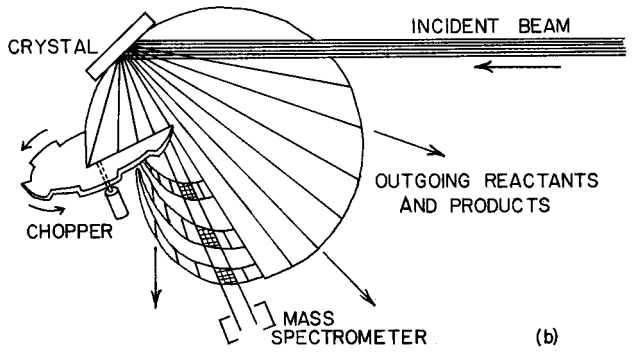


Figure 1. The molecular beam surface scattering apparatus used to study surface reactions at low pressures on metal single-crystal surfaces.

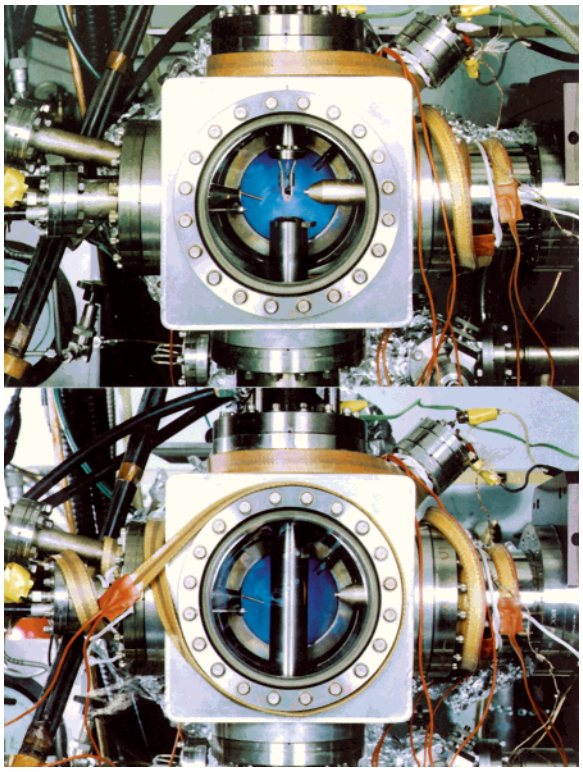


Figure 2. Photograph of the UHV high-pressure cell apparatus used in the experiments. The high-pressure cell is shown in both the open (top) and closed (bottom) positions.

My first job was with IBM Research in Poughkeepsie, NY, starting in January 1960, and then in Yorktown Heights, NY, with the opening of the research center there. There I learned solid-state chemistry and physics. IBM Research was one of the premier industrial laboratories. I learned about the necessity of fabricating pure materials and the need to characterize them on the atomic scale. I learned that interdisciplinary research carried out by physicists, materials scientists, chemists, and engineers is at the heart of most discoveries that lead to innovation and new products. I found out that I enjoyed doing research immensely and that I was good at it. I loved surfaces

† Part of the special issue "Gabor Somorjai Festschrift".

10.1021/jp993515p CCC: $19.00 © 2000 American Chemical Society
Published on Web 03/09/2000

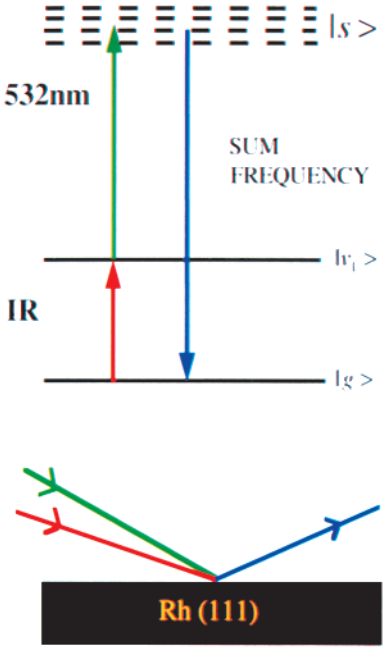


Figure 3. Schematic diagram describing the sum frequency generation (SFG) technique.

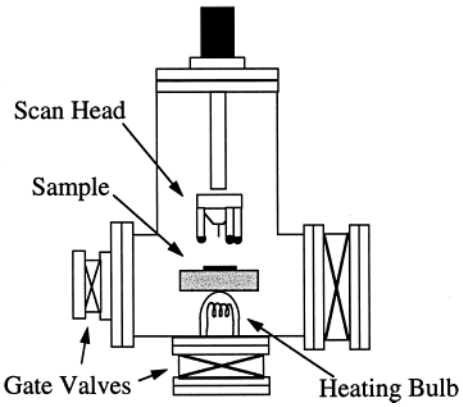


Figure 4. The high pressure−high temperature scanning tunneling microscope. Pressure range: 5×10^{-10} torr to 1 atm. Temperature range: 25 to 400 °C.

whose properties controlled the performance of most of the solid-state devices used in those days, such as transistors and photoconductors.[2] Around 1962, low energy electron diffraction (LEED) began to make its mark in the studies of the surface structures of semiconductors. Due to experimental innovations in Bell Laboratories and the economical availability of ultrahigh vacuum (-10^{-9} Torr) from space research and technology, the clean surfaces of silicon, germanium, and compound semiconductors could be studied by LEED along with the structures of monolayer adsorbates. I was certain that this technique could be my entry to the atomic and molecular level investigations of surfaces, so I persuaded IBM to purchase the first commercial instrument that became available from Varian Associates.

To pursue a long-term career in research and teaching, I started to look for a faculty position, and in July 1964 I moved to Berkeley to join the Department of Chemistry as an Assistant Professor. As soon as I arrived, I ordered my first ultrahigh vacuum LEED system, which was delivered in January 1965. This turned out to be the last complete vacuum system I purchased. We have constructed more than 25 vacuum systems and equipped them with the various techniques of surface science over the past 35 years using the outstanding machine

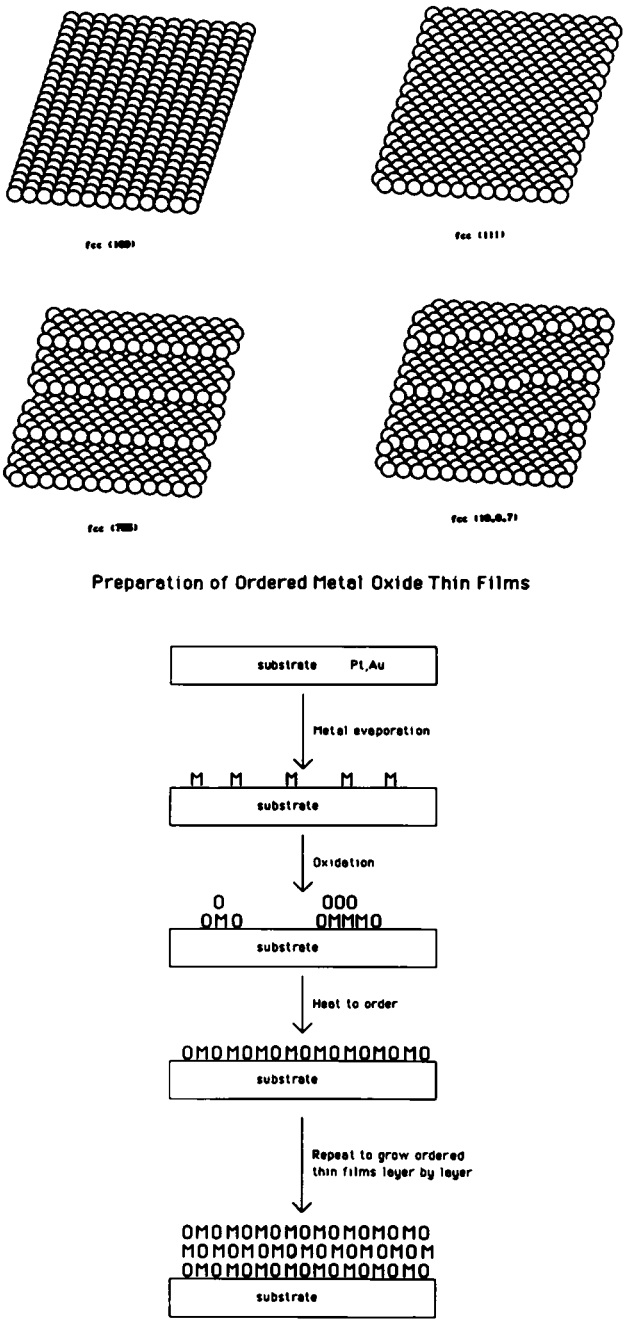


Figure 5. Schematic representation of model surfaces used in adsorption and catalytic surface reaction studies. Single-crystal surfaces cut in various crystallographic directions exhibiting hexagonal, square, stepped, and kinked topology and epitaxially grown thin films on metal single-crystal surfaces permit structural and catalytic studies of more complex multicomponent systems.

shop and electronic shop facilities in the College of Chemistry and the Lawrence Berkeley National Laboratory (LBNL). Building prototype instruments became a way of life for me and an education for the students who joined my group. I also became a Faculty Scientist in the Inorganic Materials Research Division of LBNL; that provided further opportunities for interdisciplinary research for the next 35 years.

Single-Crystal Surface Chemistry

I started my research in Berkeley by studying platinum single crystal surfaces, their structure, and their surface chemistry. Platinum is the grandfather of all catalysts and the most versatile.

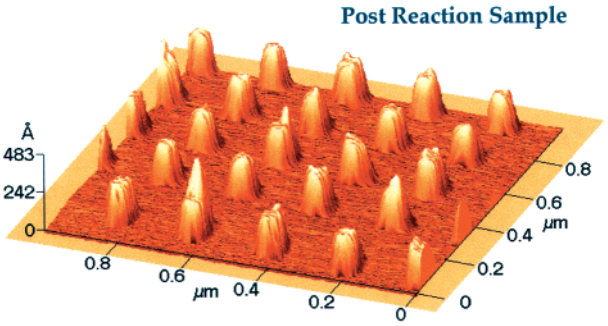


Figure 6. AFM image of Pt nanoparticles−SiO_2 fabricated using electron beam lithography: 50 nm particles, 200 nm interparticle distance.

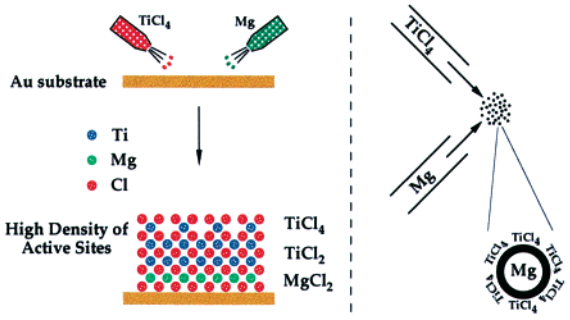


Figure 7. Fabrication of new Ziegler−Natta catalysts by $TiCl_4$−Mg metal co-deposition.

Its catalytic properties were discovered as early as 1823, and it is an excellent catalyst under both reducing and oxidizing conditions. The first platinum single-crystal surface with (100) orientation that we placed in the vacuum chamber after appropriate cleaning produced an unusual LEED pattern—we discovered the surface reconstruction of platinum and then gold.[3] We adsorbed small diatomic and organic molecules on platinum and watched them forming ordered structures that changed with coverage and temperature.[4] We carried out studies of mean displacement of surface metal atoms, surface melting, and liquid metal surfaces.[5] Auger electron spectroscopy (AES) made its debut in 1968 so that the surface chemical composition could be determined, helping to identify the origins of the various surface structures.[6] We built a molecular beam-surface scattering apparatus to measure first the angular distribution, later the translational energy and vibrational energy distributions of incident and scattered molecules from single crystal surfaces of metals.[7] Technology in the 60s, 70s, and 80s permitted the study of well characterized surfaces only at low pressures because most surface probes were electrons, ions, and atoms requiring large mean free paths for their applications. Surface

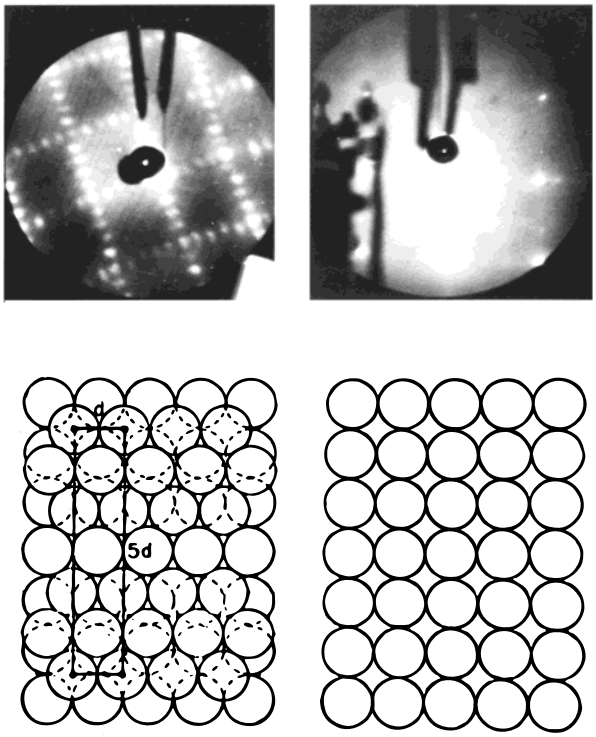


Figure 8. A low energy electron diffraction pattern and schematic diagram of the platinum (100) in its reconstructed and unreconstructed states.

reactions of molecular beams were my vehicle to explore surface reactivity of single crystals in low-pressure environments.[8] We found a surprising lack of reactivity of the low Miller Index (111) and (100) crystal faces of platinum even for the simplest of all surface reactions, H_2 exchange with D_2 to form HD. I remember well the amazement of the participants of the Catalysis Gordon Conference when I showed them that the (111) crystal face of platinum does not dissociate hydrogen molecules on a single scattering as studied by molecular beams. Platinum is known to dissociate hydrogen at liquid nitrogen temperatures in its dispersed particle form supported on oxide surfaces. The chemical inertness of smooth, low Miller Index platinum single-crystal surfaces at low ambient pressures, however, made them excellent substrates to study monolayers of organic molecules without fear of much fragmentation or decomposition at low pressures and at moderate temperatures (<400 K).[9] In fact, by lowering the temperature we could produce molecular single-crystal thin films of hydrocarbons whose structure could also be studied by LEED.[10] The epitaxial growth of single-crystal thin films on metal single-crystal surfaces turned out to be an

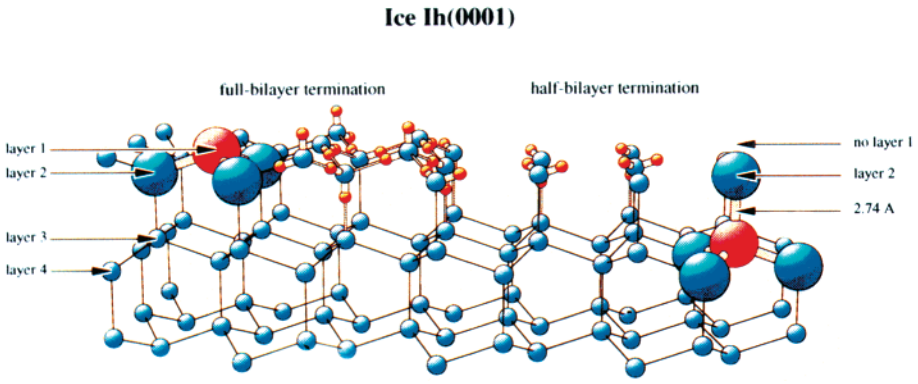


Figure 9. Surface structure of the ice (0001) crystal face as determined by low energy electron diffraction surface crystallography.

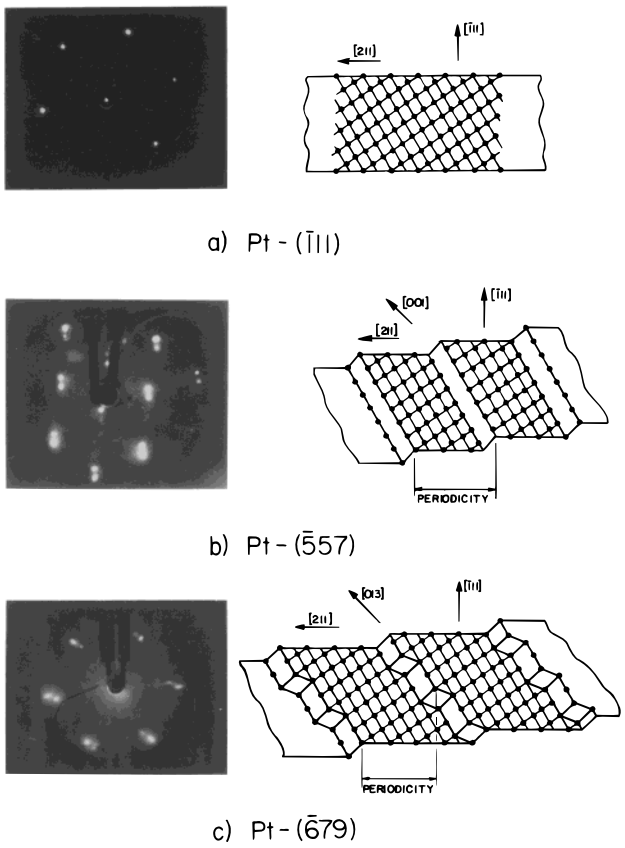


Figure 10. Low energy electron diffraction patterns and schematic representation of surface structures of platinum flat, stepped, and kinked crystal surfaces.

excellent means to study the surface structures of more complex solids: hydrocarbons, oxides, ice, and alkali halides.[11]

Reactivity of Surface Defects, Steps and Kinks, and the Low Pressure−High Pressure Apparatus

In search of the active sites of platinum that dissociate H_2, C−H, and C−C bonds, I began studies using high Miller Index, stepped and kinked surfaces of the metal.[12] The atomic height steps were ordered so they could be characterized by LEED. We discovered the active sites for breaking chemical bonds on platinum. Steps on platinum crystal surfaces could perform H_2−D_2 exchange with unity reaction probability on a single scattering of molecular beams of mixed H_2 and D_2. Stepped surfaces could also readily dehydrogenate organic molecules. We then constructed high pressure cells in the middle of ultrahigh vacuum chambers to carry out catalytic reactions on small surface area (~1 cm^2), single-crystal surfaces of platinum, rhodium, and iron at high pressures, close to experimental conditions used in chemical technology.[13] We monitored the rates of reactions and product distribution by gas chromatography or other sensitive techniques (ammonia formation by photoionization, for example). Still, we could prepare clean surfaces in UHV and characterize them in UHV before and after the high pressure catalytic reactions without ever exposing the crystal surfaces to air. This low pressure−high pressure instrumentation became our workhorse for studies of catalytic reactions of many types on single-crystal surfaces of transition metals Pt, Rh, Fe, Re, and Co. These reactions were CO hydrogenation on Rh and Fe, *n*-hexane (*n*-heptane) reforming on Pt, hydrogenation of olefins on Pt, Rh, ammonia synthesis on Fe and Re, and hydrodesulfurization of thiophene on Mo, Co, and Re.[14]

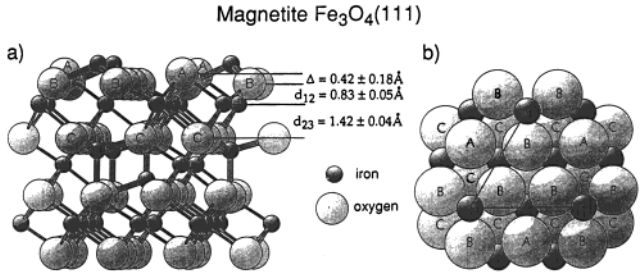


Figure 11. The restructured (111) crystal face of iron oxide Fe_3O_4 as determined by low energy electron diffraction surface crystallography.

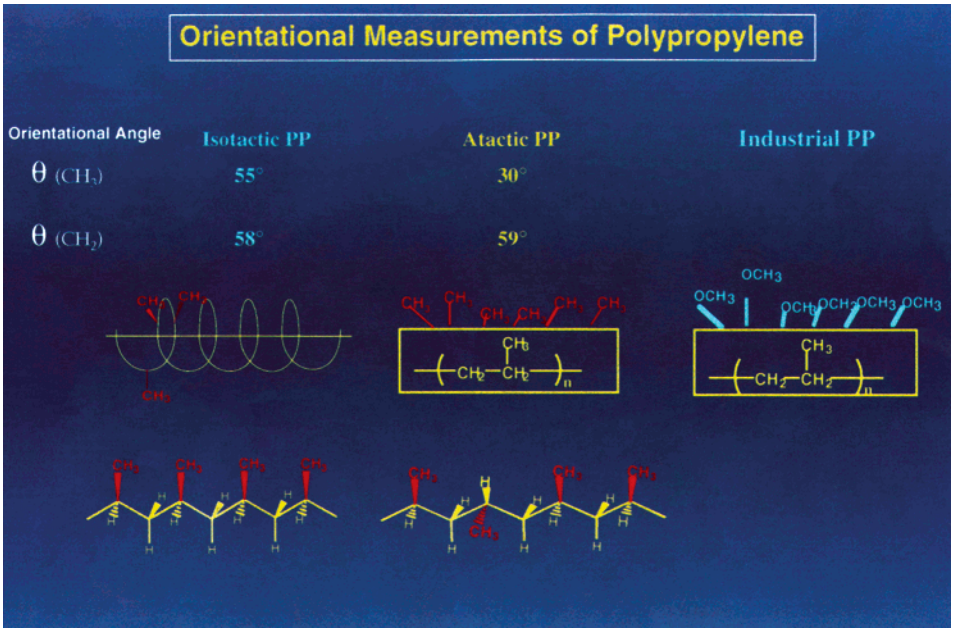


Figure 12. The surface structure of isotactic and atactic polypropylene as studied by sum frequency generation surface vibrational spectroscopy. The methyl group orientation is indicated.

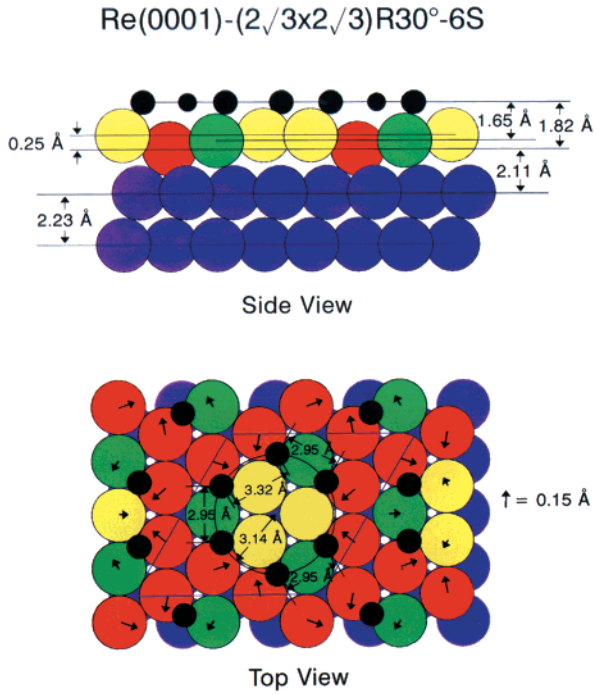


Figure 13. Sulfur adsorbate induced restructuring of the rhenium (001) crystal face as studied by low energy electron diffraction surface crystallography.

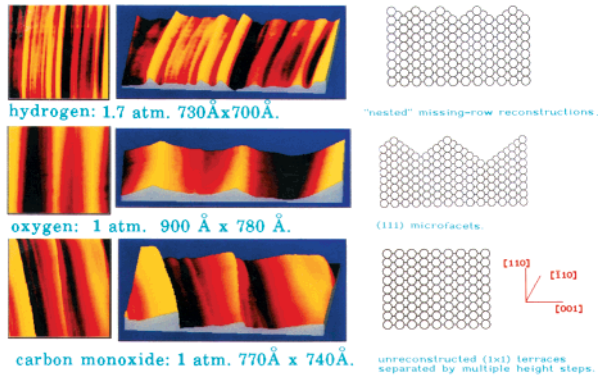


Figure 14. In situ high pressure STM. Adsorbate induced surface reconstructions of Pt(110) under atmospheric pressures of hydrogen, oxygen, and carbon monoxide.

The Structure and Chemical Bonding of Organic Monolayers on Metals

High resolution electron energy loss spectroscopy, pioneered by Harald Ibach, became one of the important new techniques in my laboratory for studies of molecular monolayers on transition metal surfaces.[15] We found that the vibrational spectra of small organic adsorbates on metals were very similar to the vibrational spectra of organometallic clusters, indicating a similarity of structure and bonding. This technique is also uniquely sensitive to adsorbed hydrogen atoms that showed a large number of binding states. Combined HREELS and LEED studies have been used to investigate coadsorbed monolayers. Organic molecules and alkali metals were coadsorbed with carbon monoxide. Because of electron donation to and from the transition metal and acceptor−donor interactions between different molecules in the adsorbate layer there can be enhanced ordering and in some cases bond dissociation when two molecules coadsorb.[16]

By the late 70s, LEED surface crystallography had developed to the point that we could determine the surface structure of

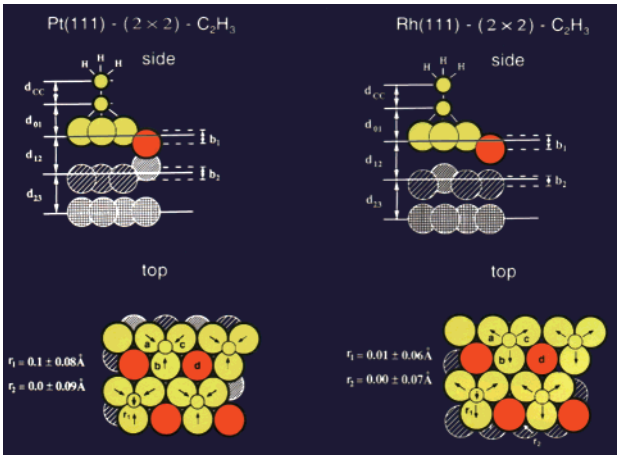


Figure 15. Ethylidyne surface structure and ethylidyne induced restructuring of the platinum (111) and rhodium (111) crystal faces as determined by low energy electron diffraction surface crystallography.

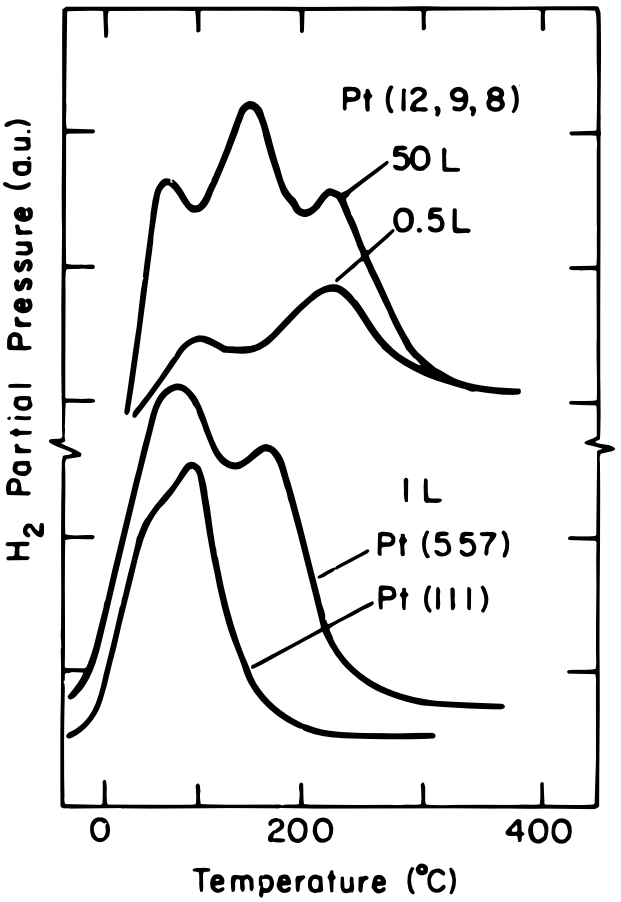


Figure 16. Thermal desorption of hydrogen from the flat (111), stepped (557), and kinked (1298) crystal faces of platinum indicating different binding energies of hydrogen at the different defect sites on the metal surface.

ethylene on Pt(111) that forms ethylidyne (≡CCH_3) at a 3-fold site.[17] This was the first surface structure for an adsorbed organic molecule—with many more to follow. The development of Tensor LEED in the 80s provided the means of rapid determination of surface structures of ever larger unit cells and more atoms per unit cell. The LEED−surface crystallography of adsorbed molecules produced a library of surface structures, the lion's share of which were determined in my laboratory in Berkeley.[18] A careful quantitative analysis of bond distances and bond angles of the adsorbate structures led to the discovery

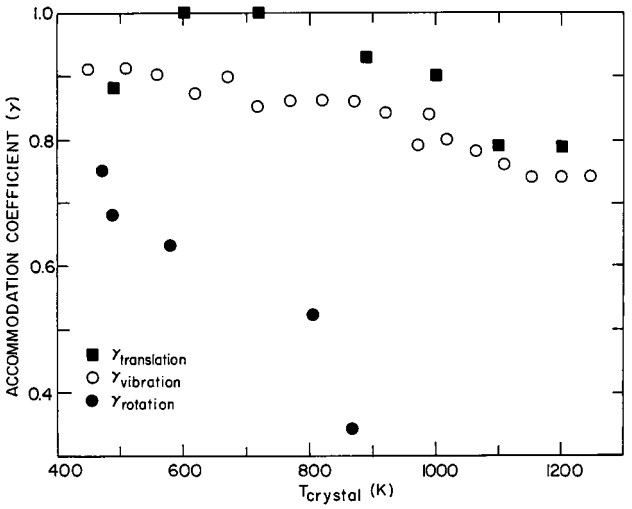


Figure 17. The translational vibrational and rotational energy accommodation coefficients of NO on the platinum (111) single-crystal surface as a function of crystal temperature as studied by molecular beam surface scattering.

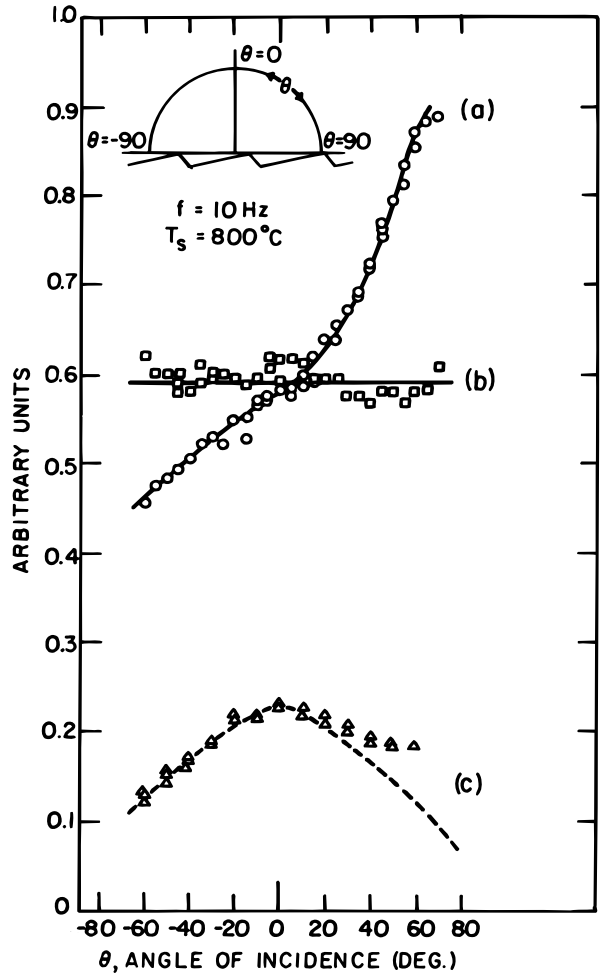
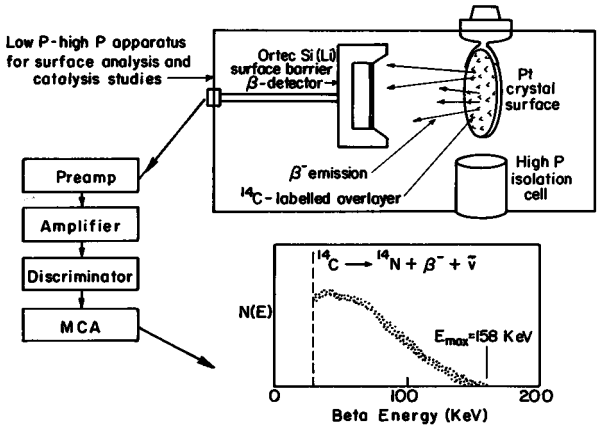


Figure 18. H_2/D_2 exchange on flat and stepped platinum single-crystal surfaces as studied by molecular beam surface scattering. The high reactivity of stepped surfaces is indicated by the near unity reaction probability while the flat surface is unreactive for hydrogen dissociation.

of *adsorbate-induced restructuring of metal surfaces*.[19] The act of adsorption, an exothermic process, leads to the weakening of metal−metal bonds so that metal atoms can relocate around the adsorption site to optimize the strength of the adsorbate−substrate bond. Adsorbate-induced restructuring explains why



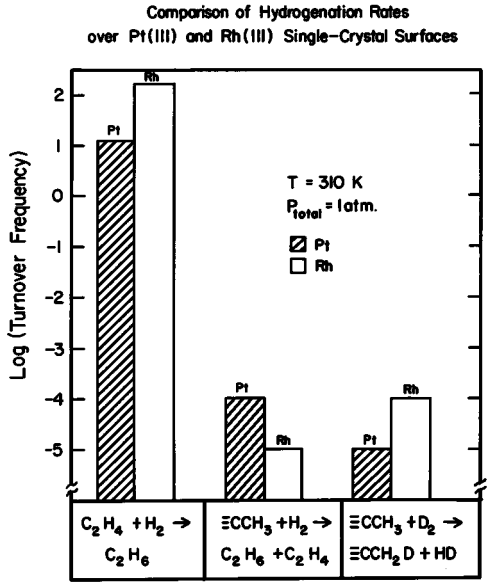


Figure 19. Ethylene hydrogenation as studied by carbon 14 labeling of adsorbed ethylene and measuring reaction turnover rates on single-crystal surfaces.

the structures of adsorbed molecules on metal surfaces are similar to the structures of organometallic cluster compounds. If adsorbate-induced surface restructuring is an important ingredient of surface chemical reactivity leading to bond breaking, it also explains the unique activity of lower coordination metal sites and steps and kinks; because of a lower number of nearest metal neighbors, those sites restructure more readily. This can be the reason why heterogeneous metal catalysts and other chemically active metal systems (metalloprotein enzymes, for example) are used in small cluster forms: they are more flexible to rearrange upon the adsorption of reactants to produce chemical change.

Surface Science and Molecular Catalysis at High Pressures

Two new surface science techniques emerged that promised to again revolutionize molecular surface chemistry. They were developed, as many of the earlier surface techniques were, in the solid-state physics domain. Sum frequency generation (SFG) surface vibrational spectroscopy provides the surface structure of molecules at the interface in a uniquely surface-sensitive way at both low and high pressures over a pressure range of 14 orders of magnitude.[20] Since it involves photon scattering, which has much smaller cross sections than electron or ion scattering, it can be used at high pressures and also at the buried interfaces,

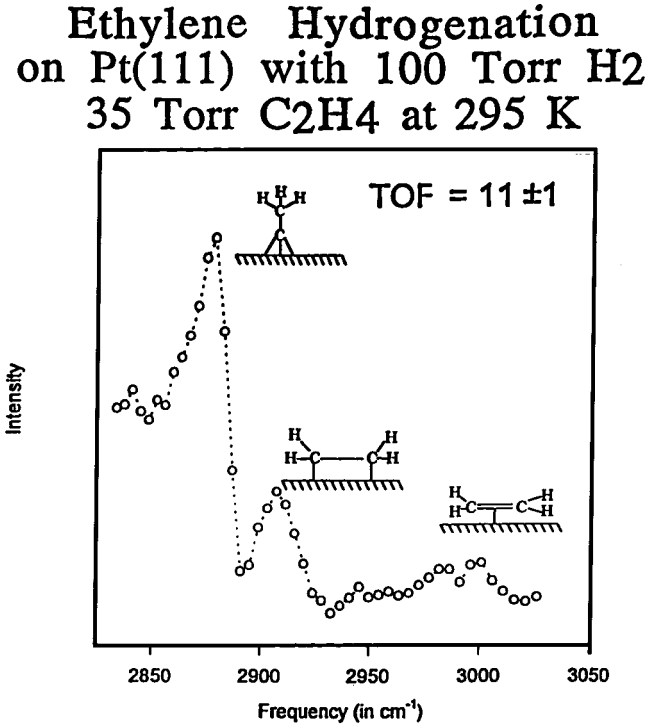


Figure 20. Ethylene hydrogenation as studied by sum frequency generation surface vibrational spectroscopy. Three species have been detected on platinum surfaces: ethylidyne, diσ-bonded ethylene and π-bonded ethylene; only π-bonded ethylene participates in the reaction turnover, while the other two species are strongly bound spectators during the reaction.

solid−liquid and solid−solid. The other technique is scanning tunneling microscopy (STM), also operable in a very broad pressure range.[21] For the first time we could monitor the surface on the molecular level at high pressures during the catalytic reactions. We studied the hydrogenation of olefins (ethylene, propylene, 1-butene, cyclohexene) and discovered that the strongly bound species that adsorb first (ethylidyne, for example) and restructure the surface are stagnant spectators and not reaction intermediates.[22] They do not turn over readily. Rather, the species that adsorb on the remaining surface sites and are only there at high pressures (they readily desorb as the reactant pressure is reduced) are the reaction intermediates (π-bonded olefins, for example). CO oxidation as well as cyclohexene hydrogenation and dehydrogenation have also been studied using SFG under reaction conditions. During CO oxidation at high pressures CO molecules that form an incommensurate overlayer are the reaction intermediates that turn over rapidly,[23] while the adsorbed top-site CO species are spectators that also block reaction sites. For cyclohexene, the reaction intermediates are cyclohexadienes that are not readily detectable at low pressures. The surface reaction mechanisms are complex, with many reaction channels that become operative or inactive with changing temperature, pressure, catalyst surface structure, and other reaction conditions.[24]

We built an STM into a high pressure reactor cell.[25] This technique can monitor the movement of metal atoms on single-crystal surfaces while SFG monitors the structure and residence time of adsorbed molecules, thereby providing complementary information. We found that metal atoms on platinum and rhodium surfaces have great mobility at 300 K at high ambient pressures (~1 atm), while their mobility is negligible in a vacuum or at low reactant pressures as detectable by STM. Again, the higher surface coverages at the high pressures provide large numbers of adsorbate−substrate bonds that weaken metal−

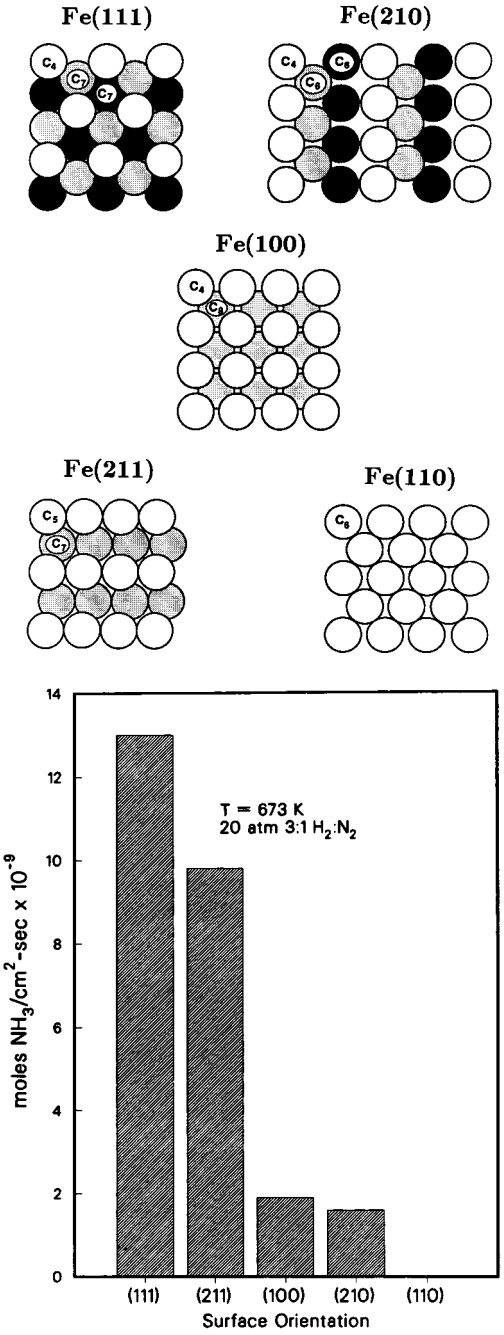


Figure 21. Ammonia synthesis as studied on various single-crystal surfaces of iron: the (111) and (211) surfaces are most reactive.

metal bonds to induce their surface mobility. The rapid movement of metal atoms under reaction conditions at high pressures has to be considered an important property of the catalytically active surface.

We also found that the platinum tip of STM catalyzes the hydrogenation or oxidation of carbonaceous deposits at 300 K during the scanning of the metal surface. The tip chemistry, whether it becomes oxidized or carbided or it carries out reactions in the surface layer it scans, is particularly important at high pressures.[26]

High pressure surface science was born by the application of techniques such as SFG and STM and others.[27] This way, molecular surface science is extended to studies of surfaces under conditions more likely to be encountered when real catalyst surfaces or surfaces used in selective adsorption are employed. While many of the other techniques that are useful

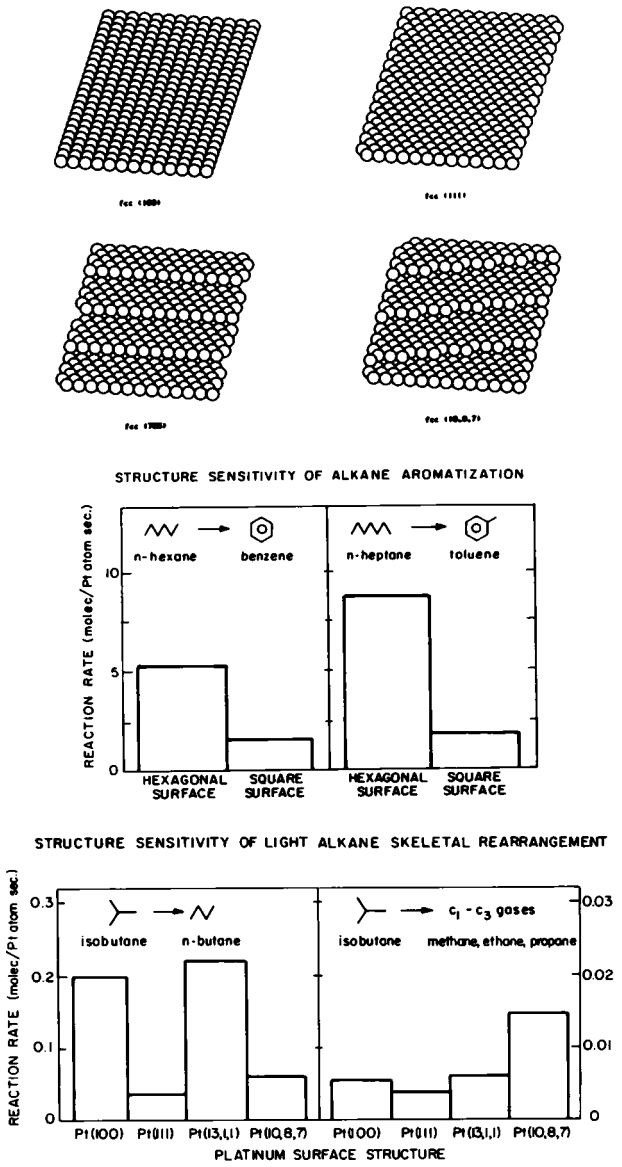


Figure 22. The hydrocarbon conversion as studied on platinum single-crystal surfaces. The structure sensitivity of alkane aromatization and light alkane skeletal rearrangements are detected.

for studies of solid−gas, solid−liquid, and solid−solid interfaces require higher surface areas (UV Raman spectroscopy or NMR, for example), SFG and STM can be readily employed for studies of single crystal and low area flat surfaces.

Polymer Surfaces and Polymerization Catalysis

Polymers always held a fascination for me, and SFG and the atomic force microscope (AFM) provided the means to initiate molecular studies of the properties of their surface monolayers: structure, friction, and hardness.[28] By combining SFG and AFM, we could determine the polymer surface structure and its variation with temperature (through the glass transition, for example) and interface (solid−gas vs solid−liquid) that are responsible for their unique chemical and mechanical properties. We find changes of surface structure underlie variations of surface chemical and surface mechanical properties of polymers. For example, polymer blends place hydrophobic groups preferably at the polymer−air interface and hydrophilic groups at the polymer−water interface. Molecular understanding of important surface properties such as biocompatibility and lubrication are

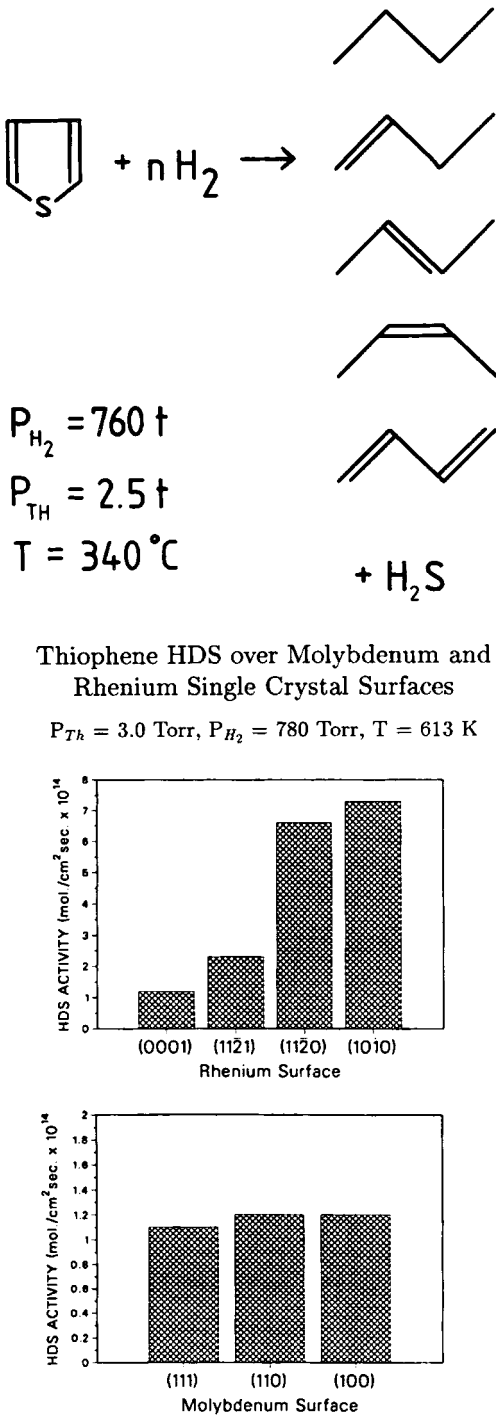


Figure 23. The hydrodesulfurization of tiophene as studied on single-crystal surfaces of molybdenum and rhenium. The reaction is structure sensitive over rhenium and structure insensitive over molybdenum surfaces.

within experimental reach. The surface science of polymerization catalysis has also become an important area of research in Berkeley as polymers are produced catalytically by C−C bond formation, as many as a million bonds per active site.[29] A molecular understanding of this process is one of the directions of research in my laboratory at present.

Metal Nanoparticle Arrays as New Model Catalysts

Over the past 30 years many surface technologies have been developed based on new surface materials science and fabrication methodologies. These include zeolite-based catalysis and

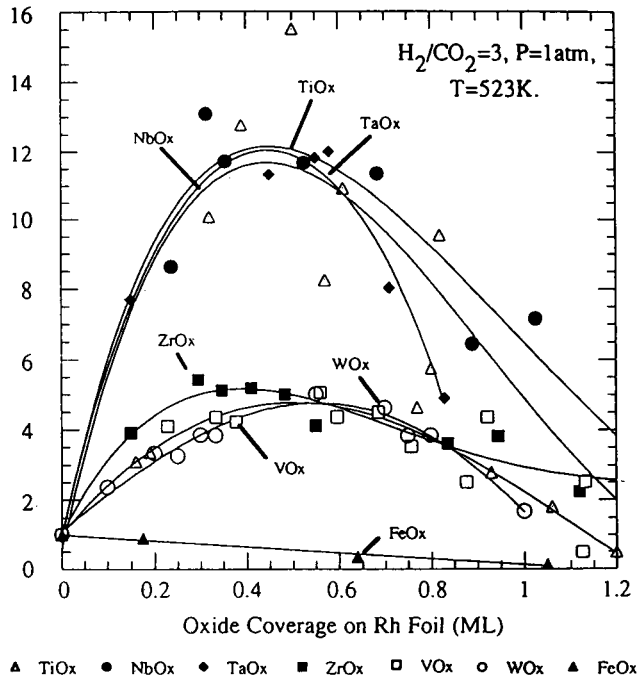


Figure 24. Oxide deposits enhance the rate of methane formation from CO_2 and H_2 over rhodium, implicating the oxide metal interfaces as important catalytic sites.

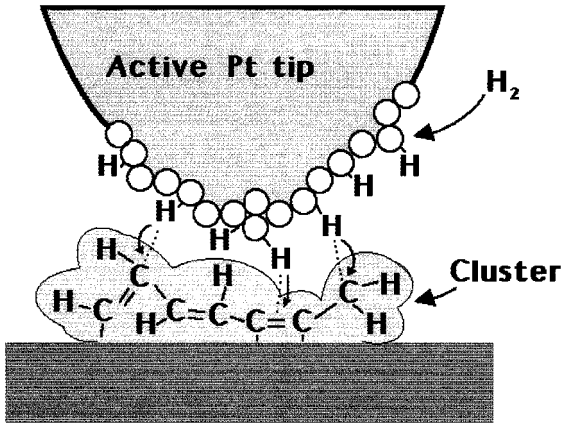


Figure 25. Catalytic hydrogenation by the platinum tip of a scanning tunneling microscope that hydrogenates carbon deposits at 300 K.

gas separation, microelectronics, optical fibers, magnetic information storage, and diamond coatings. These innovations in surface materials fabrication in one technology are making an impact on the surface science of other applications.

Microelectronic circuitry technology uses photolithography and electron beam lithography to produce nanostructures with ever improving spatial resolution. We use electron beam lithography to deposit Pt and Ag nanoparticle arrays in the 10 nm to 1000 nm range[30] to carry out catalytic reactions. By systematic variation of particle size and distances between particles, as well as the oxide−metal interface, we explore the structural ingredients responsible for selectivity and activity in diverse catalytic reactions. It is my hope that by high technology fabrication of metal nanoclusters, all with the same structure and spatial arrangement, we will discover the structural ingredients responsible for attaining 100 percent selectivity and much diminished rates for catalyst deactivation. These nanoparticle arrays are the new model catalysts that will replace the single-crystal surfaces that served us so well over the past 35 years.

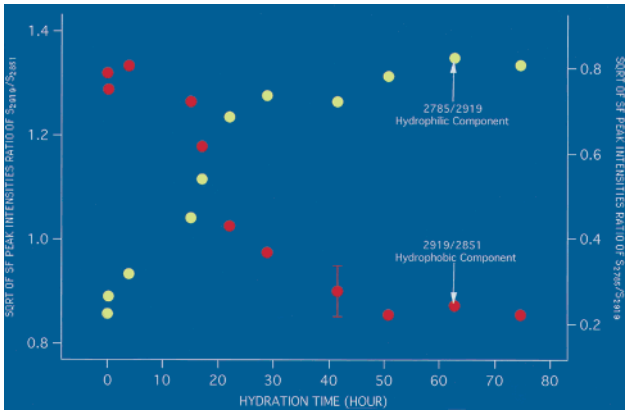


Figure 26. Sum frequency generation surface vibrational spectroscopy of the hydration of polymer blends. The hydrophilic component of the polymer segregates to the water interface. The hydrophobic component segregates to the polymer−air interface.

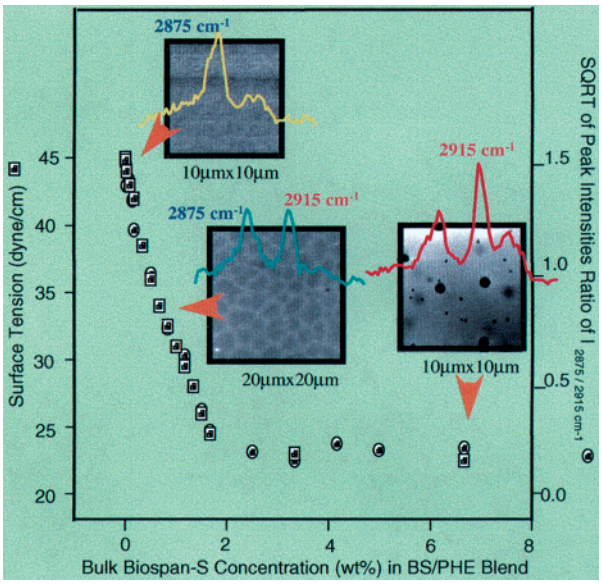


Figure 27. Correlation of SFG and AFM and contact angle data for the surface of a two component polymer blend.

Highlights of Research Results

It is not possible to mention the many accomplishments of more than 110 brilliant graduate students and more than 130 postdoctoral fellows and visiting scientists who worked in my laboratory between 1964 and 2000. There were results of research that were reported from my laboratory for the first time; there were careful and detailed studies of surface structures and of the kinetics and mechanisms of important surface processes. There were reviews and books to focus on concepts of molecular surface science and compile data. There were reports on prototype instruments and model systems developed for our surface studies. Throughout this article are figures selected to convey some of the results of the many research projects and to highlight some of the significant accomplishments.

We have accomplished a great deal in Berkeley during these 35 years to develop molecular surface chemistry and heterogeneous catalysis, thanks to my students and postdoctoral fellows. I had the good fortune to work with the best and the brightest. I had close working relationships and long-term associations with Dr. Miquel Salmeron, Dr. Michel Van Hove, and Professor Ron Shen that I would like to acknowledge with gratitude. The construction of prototype instruments in my laboratory for many years was in the hands of Emery Kozak,

Bob McAlistair, and others; their work was invaluable to my research. I have been a beneficiary of the intense and exciting environment of the Department of Chemistry and LBNL that provided constant stimulation to my students and to me. There is much more to be done as molecular surface science and catalysis move to molecular level studies of surfaces at the solid−gas, solid−liquid, and solid−solid interfaces under real conditions, where most of the important surface phenomena occur.

The future for surface science has never been brighter.

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under contract DE-AC03-76SF00098.

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