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Modern Surface Science and Surface Technologies: An Introduction

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Contents

Gabor A. Somorjai was born in Budapest, Hungary, on May 4, 1935. He was a fourth year student of Chemical Engineering at the Technical University in Budapest in 1956 at the outbreak of the Hungarian Revolution. He left Hungary and immigrated to the United States where he received his Ph.D. degree in Chemistry from the University of California at Berkeley in 1960. He became an American citizen in 1962. After graduation, he joined the IBM research staff in Yorktown Heights, NY, where he remained until 1964. At that time he was appointed an Assistant Professor of Chemistry at the University of California at the Berkeley Campus where he is a Professor of Chemistry. Concurrent with his faculty appointment, he is also a Faculty Senior Scientist in the Materials Sciences Division, and Group Leader of the Surface Science and Catalysis Program at the Center for Advanced Materials, E.O. Lawrence Berkeley National Laboratory. Professor Somorjai has educated more than 85 Ph.D. students and had over 100 postdoctoral co-workers. He is the author of over 700 scientific papers in the fields of surface chemistry, heterogeneous catalysis, and solid-state chemistry. He has written three textbooks, *Principles of Surface Chemistry*, Prentice Hall, 1972; *Chemistry in Two Dimensions: Surfaces*, Cornell University Press, 1981; *Introduction to Surface Chemistry and Catalysis*, Wiley-Interscience, 1994; and a monograph, *Adsorbed Monolayers on Solid Surfaces*, Springer-Verlag, 1979.

I. Introduction

The study of surfaces and surface phenomena on the atomic or molecular level defines modern surface science. There are three events that have had major impact on the genesis and rapid development of the field. First, in the 1950s, the rise of space science and technology made the attainment of ultrahigh vacuum ($\leq 10^{-9}$ Torr) relatively easy and economical.[1] This permitted the production of clean surfaces that remain free of adsorbed gases long enough to carry out most surface studies (hours). Second was the discovery of the transistor in the 1950s and the subsequent rapid development of the semiconductor industry in the next two decades. Since increasing the speed of electrical signal processing could be achieved by decreasing the size of solid-state devices, the fabrication and control of surfaces became the driving force of technological development. Finally, the energy crisis in the 1970s, which necessitated the rapid development of new catalyst-based processes in the oil and chemical industries, propelled the development of surface science. Increased energy consumption in developed countries spawned the need for catalyst-based environmental technologies to clean air, water, and soil, and sensors to detect and control pollution.

The development of both new catalysts, sensors, and ever smaller semiconductor-based devices, required understanding and characterization of surfaces on the molecular level; in turn leading to the birth of new surface science-based technologies.

Early on, studies of clean surfaces often used single crystals; which also found application in semiconductor technologies. The use of crystal surfaces provided control over surface structure, which turned out to be one of the atomic ingredients for controlling surface properties. For other applications, however, high surface area microporous materials had to be employed (catalysis or selective gas adsorption, for example). Many microporous crystalline materials were discovered, including so-called molecular sieves or synthetic zeolites. These materials possessed well-defined pore structures that could be related to their surface chemistry.[1]

Because of the need for atomic level scrutiny of surface properties, a large number of techniques have been invented and developed since the 1950s. These techniques employ photons, electrons, and ions to determine surface structure, surface composition, oxidation states of surface atoms, and bonding of adsorbates; done with ever increasing spatial resolution, time resolution, and energy resolution. Over 50 techniques are available for molecular surface studies, but their discussion is outside the scope of this

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review.[1] Some of these techniques are most useful for studies of external surfaces, while others can be used for microporous materials with large internal surface area.

As a result of the application of these diverse techniques to investigate molecular properties of surfaces, adsorbed monolayers, and surface phenomena (chemical, mechanical, optical, electrical, and magnetic), many new concepts of surface science were uncovered. These concepts helped the development of new surface technologies. The demands of these technologies then provided incentive for the development of new surface characterization techniques and for the investigation of new surface phenomena that led to the uncovering of new concepts. The science push and technology pull in surface science and surface technology have served both very well.

In this paper we shall first focus on several of the new surface science concepts that were developed as a result of studies during the past 30 years. Then, we shall review their impact on the development of several surface technologies: catalysis (including environmental catalysis), microelectronics, disk drive storage, and sensors.

II. Selected Concepts of Modern Surface Science

A. New Surface Instrumentation Concepts

1. Model Catalyst Systems

The heterogeneous catalysts employed in technology are complex, high surface area materials that are optimized to work for millions of turnovers (without deactivation), at high reaction rates, and high selectivity. In addition to the active catalyst components (often small particles of transition metals or oxide surfaces in a given defect state and stoichiometry), the high surface area support provides the proper binding and interface for stabilizing the catalyst. Additives are introduced to "promote" stability, high activity, and high selectivity. All these catalyst components may be altered as new generations of catalysts with more selectivity, higher activity, better deactivation resistance, and the capability to more easily be regenerated after poisoning are formulated.

The principles of catalyst development were laid down by Mittasch[2,3] in the 1920s, and it involves an empirical screening process of many catalytic materials and additives until the most promising combination is found. This research approach for finding a new catalyst system is still followed in many laboratories.

A great deal of knowledge has been accumulated in catalysis science over the past few decades. High surface area crystalline oxides and zeolites with variable pore structure and acidity have been synthesized. Surface science characterization techniques permit the determination of surface structure and surface composition (including oxidation states) on an ever smaller spatial scale. Since many of the surface characterization techniques were only useful for external surfaces (and cannot interrogate the micropores of high surface area catalysts), small area foils, thin films, and single crystals were increasingly studied as "model" catalysts. We developed a concept in my laboratory during the early 1970s to use *small area (~1 cm^2) well-characterized surfaces of transition metals (mostly in single-crystal form)*, and attempted to carry out catalytic reactions over these surfaces under conditions commonly utilized for industrial technology (high pressures and temperatures). If the surface was unreactive, its structure was changed and/or additives were deposited in known concentration, one by one, and the effects of these surface alterations on catalytic activity and selectivity were monitored. We developed a small volume reactor (~100 mL) that could be used in combination with an ultrahigh vacuum (UHV) system.[4] The crystal surface was cleaned in UHV and then inserted in the high-pressure reactor where the reaction was carried out and its kinetics monitored by gas chromatography. The reaction was then interrupted and the model catalyst was again moved to UHV for determination of surface composition, changes in surface structure, and introduction of additives. This approach builds our understanding of the complex catalyst system through component-by-component construction of the catalyst.

One example of a catalyst system which was studied in this manner is ammonia synthesis.

$$N_2 + 3H_2 = 2NH_3 \qquad (1)$$

Figure 1 shows surface structure arrangements of an Fe single-crystal surface.[5] The surface structures that are more open and contain sites that are surrounded by seven iron neighbor atoms (C7 sites) are the most active. These are the (111) and (211) crystal faces. The structure of the (110) crystal face does not allow the adsorbed nitrogen species to bind with second and third layer atoms, and probably for this reason the rate for the synthesis of ammonia is some 500 times lower than on the (111) surface structure.

Additional evidence on the nature of active sites comes from the comparison of turnover rates on industrial, supported, and single-crystal catalysts (Figure 2). In measuring the turnover rates, for practical reasons all atoms on the surface are assumed to be active. Thus, the calculated or nominal turnover rate will be a lower limit to the turnover rate. When the number of iron atoms on the surface are measured by H_2 or CO chemisorption on the supported catalyst, the turnover rate is much lower than the one calculated with N_2 chemisorption (Figure 2). While H_2 and CO adsorb on all the iron sites, N_2 dissociatively chemisorbs only on the (111) crystal face (which is most active for ammonia synthesis). It can be seen that the turnover rates obtained using nitrogen chemisorption for commercial ammonia synthesis catalysts and that obtained for the (111) iron crystal face are the same. This indicates that the iron (111) crystal face exhibits optimum catalytic activity, and that the best industrial catalysts are composed mostly of (111) crystal faces of iron.

Catalytic reactions can be divided into two classes: structure-sensitive and structure-insensitive processes. For structure-sensitive processes—such as ammonia synthesis—single crystals continue to be indispensable tools for understanding reaction mechanisms. For structure-insensitive reactions, small

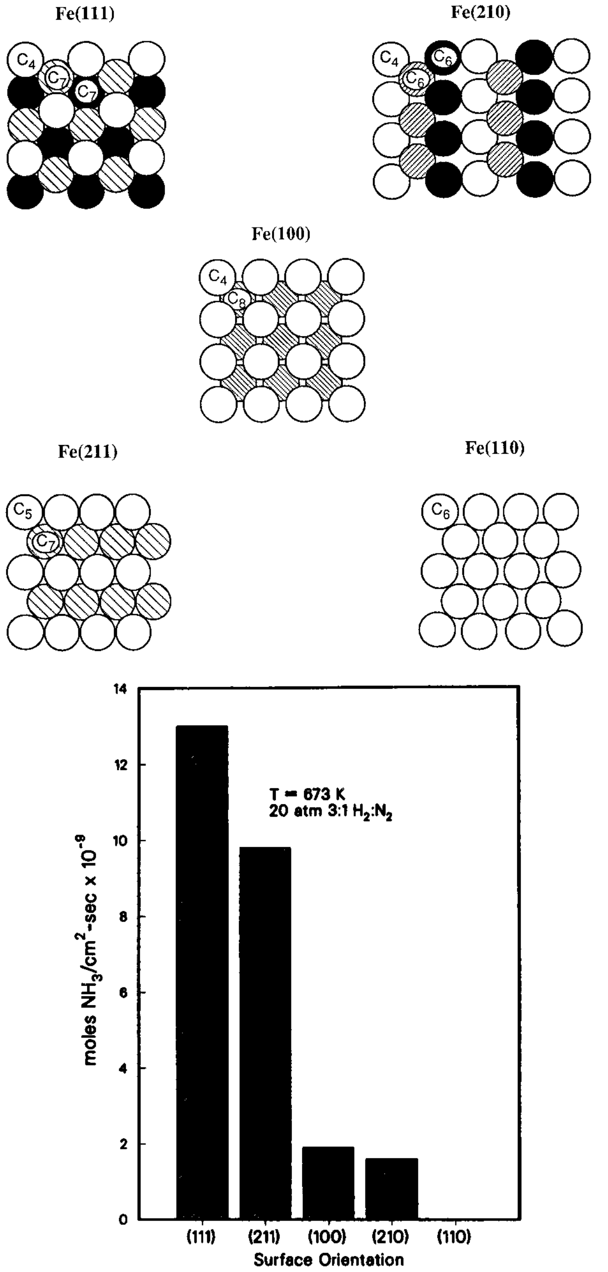


Figure 1. Rates of ammonia synthesis over five iron large single-crystal surfaces with different orientations.[5,47–49]

area polycrystalline foils or thin films of the catalyst, deposited on chemically inert supports, are also excellent model catalyst systems.

2. Surface Characterization with High Spatial Resolution (Nanometer)

Catalysts are usually small metal particles (2–20 nanometers) that are dispersed on a high surface area microporous oxide. Microelectronic devices are presently fabricated using techniques operating at ~100 nm spatial resolution, but devices that must be fabricated and controlled on the 10 nm scale are desired. We increasingly are focusing on nanoclusters in surface chemistry to investigate their physical and chemical properties and to attempt to develop new techniques of surface characterization that operate in this spatial domain.

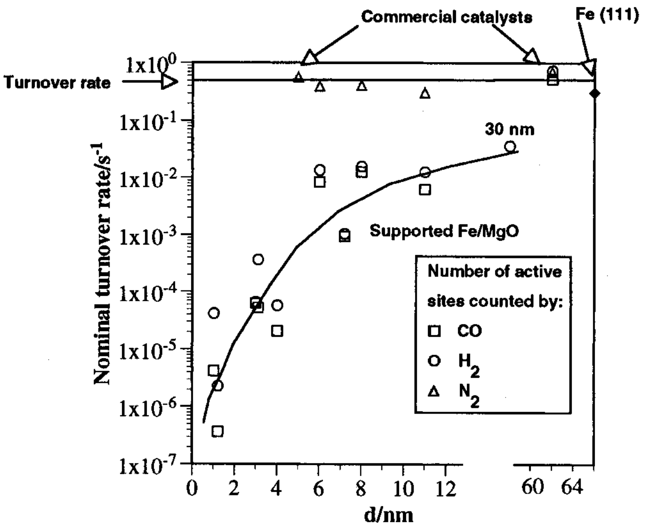


Figure 2. Turnover rates reported for industrial iron ammonia synthesis catalysts, and for the (111) crystal face of iron under identical experimental conditions.

In the future, ordered cluster arrays with uniform nanometer size clusters (3–100 nm) could be used as model catalysts.[6] These clusters could be deposited using electron beam lithography on silica or alumina. Not only their size would be uniform, but the distance between the clusters would be variable and uniform. A surface area ≥ 1 cm^2 could be covered with these cluster arrays (Figure 3). Their structure could be monitored by electron microscopy and the atomic force microscope (AFM), and their composition monitored by scanning Auger spectroscopy (AES). By systematic variation of cluster size and the distance between clusters, the reaction rate, selectivity, and deactivation rate of catalytic reactions could be altered. Since catalyst particles are often clusters in this size range, the results of model cluster catalyst studies could be directly correlated with the behavior of catalyst systems. Increased control of catalyst geometry will permit modernization of catalyst preparation, leading to 100% selectivity and very slow deactivation rates for extended catalyst life.

The electron microscope, the scanning tunneling microscope (STM), and the AFM are capable of providing surface structure analysis with atomic spatial resolution (0.1 nm) for surface studies on the nanometer spatial range. Semiconductor surfaces image much better than metal surfaces (using STM) because their charge density is less uniform. Defects at surfaces (steps, kinks) can be imaged well. The lack of a quantitative theory, at present, makes it difficult to extract accurate bond angles and bond distances from the STM data. These techniques only rarely yield information about the composition of the imaged surface. Since many atoms and most small molecules are mobile on solid surfaces at 300 K, their imaging requires low temperature (<150 K). However, their surface diffusion can be monitored by rapid scanning STM under favorable circumstances.

Scanning Auger microscopy provides surface composition on the nanometer scale. Advances in electron optics makes composition analysis with 10 nm spatial resolution practical. One can obtain an incident electron beam >1 namp in intensity, with a 10 nm spot size. Secondary ion mass spectroscopy

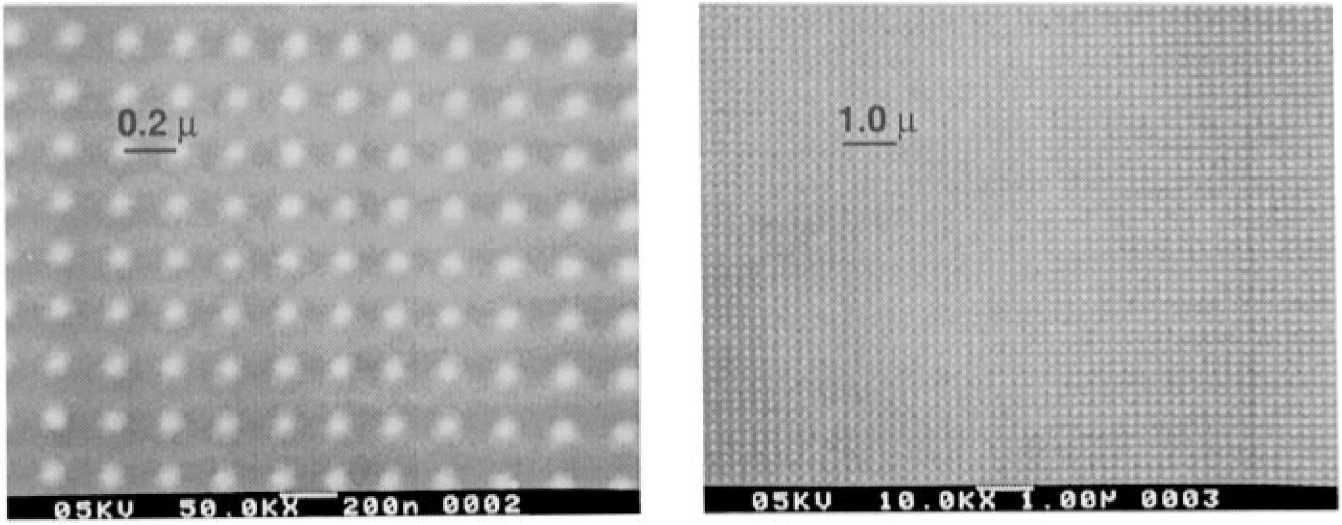


Figure 3. Scanning electron microscope picture of an array of platinum clusters deposited over 1 cm^2 area by electron beam lithography. Particle size is 50 nm; distance between clusters is 100 nm.

(SIMS) can also be used to determine surface composition with 50 nm spatial resolution. Using a liquid metal ion field ionization source, a >50 pamp ion beam can be obtained with a diameter of 50 nm.

Near field optical microscopy is being developed to provide a photon flux of ~10^4 photons/s on the nanometer scale. It is hoped that this technique will contribute to surface analysis on the same scale.

3. In Situ Molecular Level Characterization of Surfaces

The possibility of studying molecular level changes that take place on surfaces during chemical reactions has eluded surface scientists until recently. There are many techniques for studying external surfaces on the molecular level in UHV, or at low pressures in the range of $10^{-9}-10^{-5}$ Torr. Those that are most widely used utilize electron or ion scattering to determine surface structure (LEED, RHEED), surface composition (AES, ISS, SIMS), and the oxidation state of surface atoms (XPS). For those who desire to study the behavior of surfaces at higher pressures without losing the opportunity of atomic level scrutiny, more complex systems had to be designed. A reaction cell was needed that could be operated at high pressures (atmospheres) and high temperatures (1000 K); enclose the small area sample (~1 cm^2) before, during, and after exposure to the reactive ambient gas or liquid; and allow the sample to be transferred into the low pressure of a UHV environment where surface analysis commenced using a combination of surface science techniques.

Several generations of low-pressure/high-pressure instruments have been designed and built in our laboratory and elsewhere that permitted surface analysis *before or after the reaction*,[7] but were incapable of monitoring the surface while a reaction was occurring. These techniques were mainly responsible for uncovering many of the molecular ingredients of surface reactions, whether stoichiometric (chemisorption) or catalytic (many turnovers). These included the *role of substrate surface structure* (including steps and kinks) in forming the adsorbate chemical bond, *adsorbate-induced restructuring*, the *coadsorption bond*, and the *role of surface diffusion in controlling reactivity*.

Infrared spectroscopy, especially in its Fourier transform mode (FTIR), was perhaps the first technique that was utilized for molecular surface studies at high-pressure reaction conditions. By using high surface area microporous systems, the vibrational spectra of adsorbates could be monitored during the catalytic reactions. Improvement in detector technology should permit FTIR studies using low surface area model catalyst systems in the near future. Electron microscopy studies could also be performed under reaction conditions by using an environmental cell, as long as the pressure remained low enough to not interfere with the electron mean free path in and out of the reaction chamber.

Two independent, but complementary, techniques were reported for molecular level studies of surfaces, under dynamic high-pressure reaction conditions: surface specific vibrational spectroscopy by sum frequency generation (SFG), and high-pressure/high-temperature scanning tunneling microscopy (STM). The first technique more readily yields the molecular structure of adsorbates and reaction intermediates,[8] while the second is more sensitive for monitoring changes of substrate surface structure during chemical reactions.[9]

The sum frequency experiment has been described in detail elsewhere.[8,10,11] Briefly, signal is obtained only where inversion symmetry is broken. This occurs only at the interface between the bulk metal crystal and the gas phase. Hence, a vibrational spectrum comes mainly from the interface in this experiment, unlike the circumstance encountered in infrared spectroscopy where the signals generated from the bulk and gas phase must be subtracted.

The vibrational spectrum obtained from the platinum (111) crystal face during propylene hydrogenation under conditions of 715 Torr hydrogen and 55 Torr propylene is shown in Figure 4. Under these conditions the spectrum shows the presence of two distinct features. Below 2850 cm^{-1} are two peaks which can be assigned to the half-hydrogenated secondary propyl group bonded to the surface through the middle carbon [$Pt-CH(CH_3)_2$], and a broad feature above 3000 cm^{-1} which corresponds to π-bonded propylene.[12] These two species provide convincing

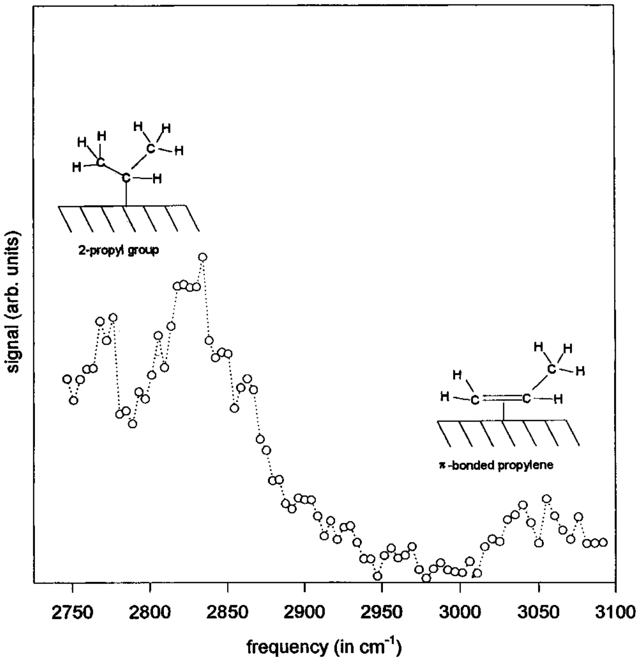


Figure 4. SFG spectrum of propylene hydrogenation on Pt(111) at 295 K with 715 Torr H_2 and 55 Torr C_3H_6.

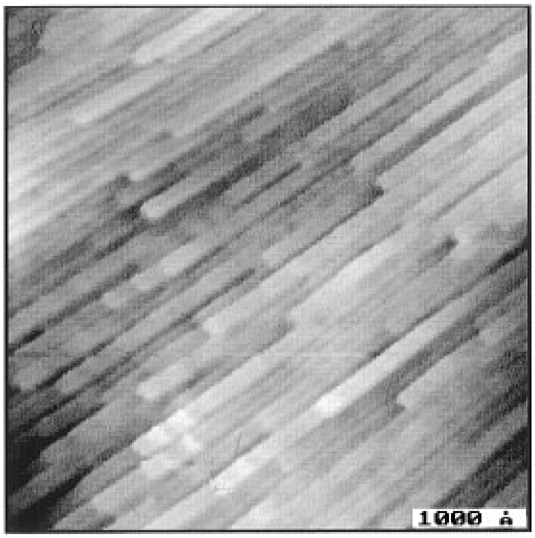


Figure 5. STM image of Pt(111) crystal surface in the presence of a 10:1 mixture of hydrogen to propylene above a Pt(111) crystal at room temperature. (Reprinted from ref 12. Copyright 1995 Baltzer Science Publishers.)

evidence for a stepwise hydrogenation mechanism. Propylene is physisorbed on the surface through its π molecular orbital. It hydrogenates first at the outer carbon of the carbon−carbon double bond to form a secondary propyl group. This species is hydrogenated to propane which desorbs from the surface.

When a H_2/C_3H_6 (10:1) mixture is left in equilibrium with the surface at 1 atm and room temperature, STM images reveal featureless terraces separated by straight monatomic height steps. It should be noted that under these conditions the surface is catalytically active and propylene is hydrogenated to propane during STM imaging. The high mobility of the surface species prevented their detection by the STM. Figure 5 shows the step structure of this catalytically active surface.

The most significant result of the *in situ* STM images is that the underlying platinum atoms were not significantly reconstructed by the adsorbed species. Lack of reconstruction is consistent with the structure insensitive nature of the olefin hydrogenation reaction. Control experiments performed by annealing the sample to temperatures >770 K in propylene to form carbon clusters gave rise to substantial surface reconstruction. The steps were no longer straight, with many kinks or protrusions in the steps that are pinned on top of some clusters. This clearly demonstrated that had surface reconstruction occurred during reaction, the STM was sensitive enough to observe it.

Both SFG vibrational spectroscopy and STM can provide molecular level information about chemical and structural changes that occur on surfaces *during catalytic reactions at high pressure and complementary elevated temperatures*. SFG, because of its superior signal to noise qualities, can detect adsorbed species in concentrations less than 1% of a monolayer. As the spectra in Figure 4 demonstrates, SFG can detect the presence of catalytic reaction intermediates *in situ* on solid surfaces.

The major limitation of SFG has been its limited frequency range (2650−4000 cm^{-1}), which only allowed the observation of stretching modes. However, the availability of new non-linear optical crystals such as $AgGaS_2$ will permit us to extend this range to 1100−4000 cm^{-1} in the near future.

STM is sensitive to the atomic surface structure and is especially suitable for imaging defects (steps and kinks) at high pressures and elevated temperatures. It cannot, at present, image mobile surface species; which includes most small chemisorbed organic molecules at 300 K or above. However, STM detects stationary species like those that form upon propylene decomposition, as well as readily detecting adsorbate-induced surface restructuring if it occurs during chemisorption or a catalytic reaction.

While surface restructuring could not be detected in the presence of 1 atm of hydrogen and propylene gas mixtures, it was instantly detectable under 1 atm of CO. Thus, these two techniques (SFG and STM) provide complimentary molecular information during catalytic reactions when applied at high pressures and elevated temperatures. At present, the rapid depolarization of the piezoelectric $ZrBa(TiO_3)_2$ ceramics (which permit movement of the STM tip), as temperature rises near or above their Curie temperature (~450 K), limits the accessible temperature range in these studies. It is hoped that more suitable piezoelectric materials will be found to permit higher temperature STM operation, which will make many more catalytic reactions available for investigation.

The application of these techniques allows *in situ* analysis of reactive surfaces during catalytic reactions. This includes detection of short-lived reactive intermediates in small surface concentrations, and reaction-induced restructuring of metal surfaces. The investigations reported here already provided definitive evidence for a physisorbed intermediate and an unreconstructed surface during catalysis. In light of this, it is likely that new molecular surface phenom-

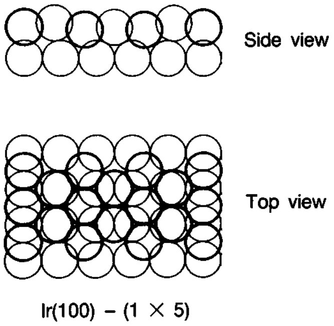


Figure 6. The structure of the reconstructed iridium (100) crystal face obtained from LEED surface crystallography. Hexagonal packing in the surface layer induces buckling. The second layer retains its square unit cell.[16,17]

ena which have eluded detection until now will become observable.

B. New Concepts of Surface Structure and Bonding

1. Reconstruction

The anizotropic surface environment leads not only to changes in the equilibrium position and bonding of surface atoms, but can also give rise to more drastic reconstruction of the outermost layers; that is, the surface can assume an atomic structure that differs fundamentally from the structure one would expect if the bulk structure terminated abruptly at the surface. For semiconductor surfaces (Si, Ge, GaAs, InSb, etc.), which are covalently bonded, the surface atoms find it difficult to compensate for the loss of nearest neighbors. The dangling bonds created at the surface cannot easily be satisfied except through more drastic rearrangements of these atoms. Therefore, most semiconductor surfaces reconstruct, and major rebonding between surface atoms occurs in this process. The associated perturbation propagates several layers into the surface until the bulk lattice is recovered.

Many metal surfaces also reconstruct. For example, at the (100) surface of Ir,[13−17] Pt,[16−19] and Au,[16,17,20−22] the interatomic distance in the topmost layer shrinks by a few percent, parallel to the surface. It then becomes more favorable for this square unit cell to collapse into a hexagonally close-packed layer rather than maintain the square lattice of the underlying layers (Figure 6). The (110) crystal face of face-centered-cubic (fcc) metals often exhibits the so-called "missing row" reconstruction. In this circumstance, a whole row of metal atoms is periodically missing, giving rise to a (1×2) surface structure.

2. Adsorbate-Induced Restructuring: The Flexible Surface

The chemisorption of an atom or a molecule often induces rearrangement of the substrate atoms around the adsorption site. For example, the chemisorption of carbon atoms on the nickel (100) surface (an exothermic process) occurs at the 4-fold site. The nearest-neighbor nickel atoms are displaced away from the carbon, permitting it to move more into the metal surface and bond to the metal atom in the second layer.[23,24] A small in-plane rotation of the surface nickel atoms around the carbon (Figure 7) relieves the stress that would have been caused by the shortened distance between the nearest-neighbor and next nearest-neighbor metal atoms. This massive local restructuring around the chemisorption site weakens the metal−metal bonds at the surface (an endothermic process) and provides the energy needed for the restructuring of the substrate.

Another example of adsorbate-induced restructuring is sulfur chemisorption on the Fe(110) crystal face. In this case, the nearest-neighbor iron atoms move closer to the sulfur chemisorption site, forming an Fe_4S-like cluster.[25] Again, the weakening of the metal−metal bonds nearest to the next-nearest-neighbor bonds is more than offset by the formation

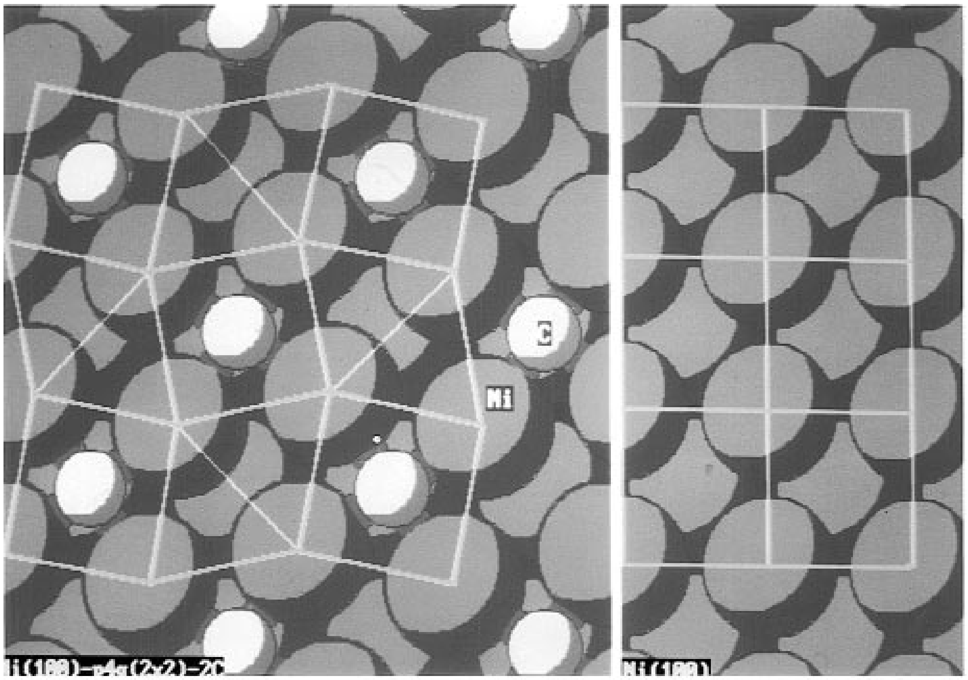


Figure 7. Carbon−chemisorption-induced restructuring of the Ni(100) surface.[23,24]

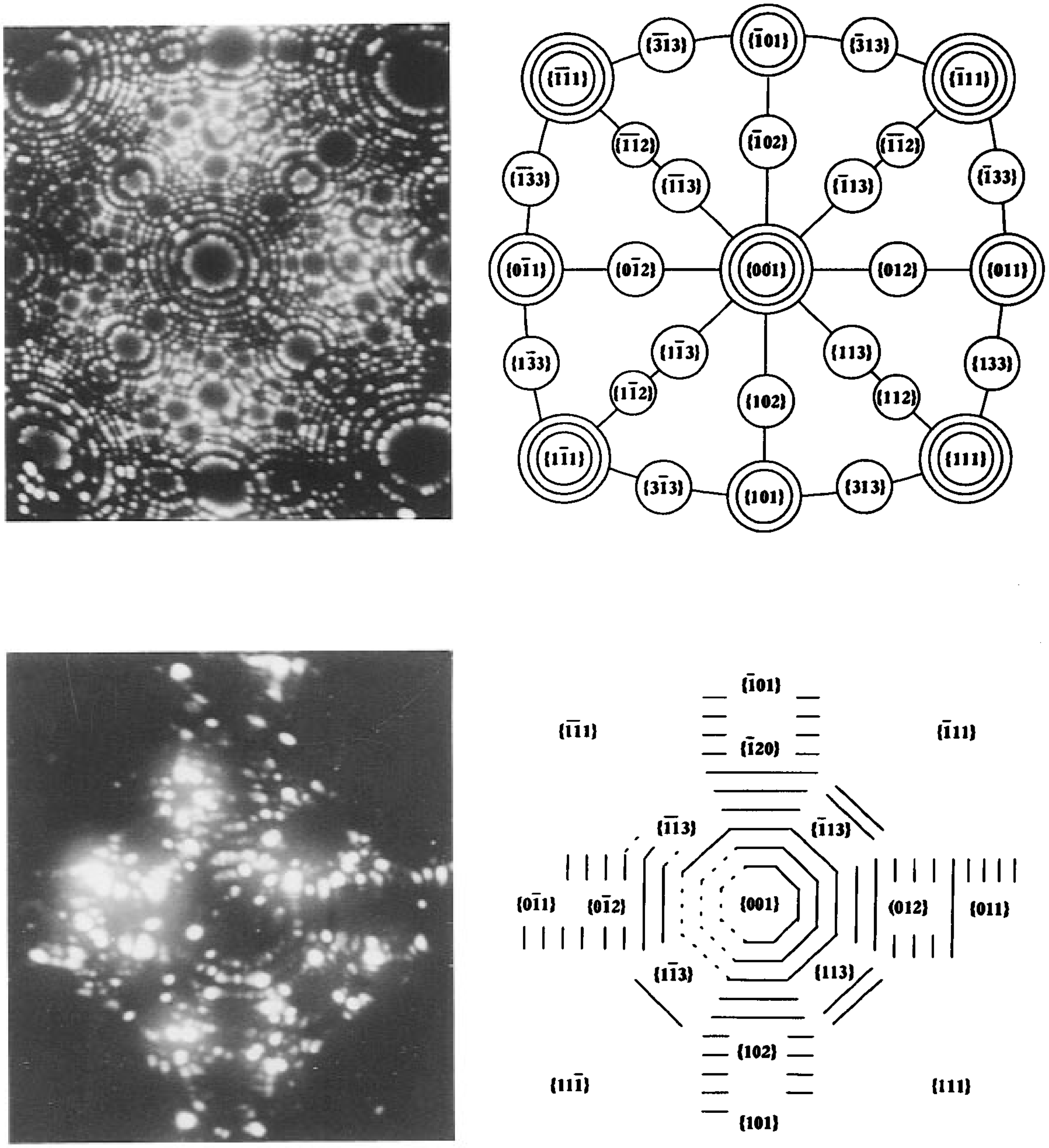


Figure 8. Field ion micrographs (image gas: Ne; $T = 85$ K) of a (001)-oriented Rh tip before (top left) and after reaction with 10^{-4} Pa CO during 30 min at 420 K (bottom left); stereographic projections at the right demonstrate the change in the morphology from nearly hemispherical to polygonal (scheme at the bottom right indicates the coarsening of the crystal and the dissolution of a number of crystallographic planes due to the reaction with CO).[26]

of the four strong Fe–S bonds. The restructuring of the Cu(110) surface was induced by chemisorbed oxygen.

Chemisorption-induced restructuring can be seen very well using a small metal tip and field ion microscopy (FIM). In Figure 8, an FIM picture of a rhodium tip is shown; both before and after exposure to carbon monoxide at 420 K and low pressure ($\sim 10^{-4}$ Pa).[26] The metal tip has been completely reshaped as a result of CO chemisorption. The tip becomes faceted and rougher, the step density is reduced, and extended low-Miller index terraces are formed.

Rough surfaces that are also chemically active appear to be flexible.[27] The uncovered surface atoms move toward the bulk and to new equilibrium positions. The more open the surface, the larger the movement and the more flexible the surface atoms. Upon chemisorption, these surfaces restructure more readily. It is perhaps instructive to divide surfaces according to their flexibility. Close-packed surfaces (like fcc (111) crystal faces) are fairly rigid as a result of a large number of nearest neighbors (high coordination); the atoms stay close to their bulklike equilibrium positions in spite of the anisotropy of the surface environment. Upon chemisorption, these surfaces may restructure; however, the thermodynamic driving force for such restructuring is not large. Clusters of atoms are perhaps the most flexible. The atoms are ready to relocate because of the low coordination of atoms at each surface site. Upon chemisorption, massive restructuring of these clusters may occur because the thermodynamic stability of the chemisorption bonds readily offsets the weakening of the few metal–metal bonds.

Substrate restructuring occurs during the chemisorption of molecules as well. The metal surface

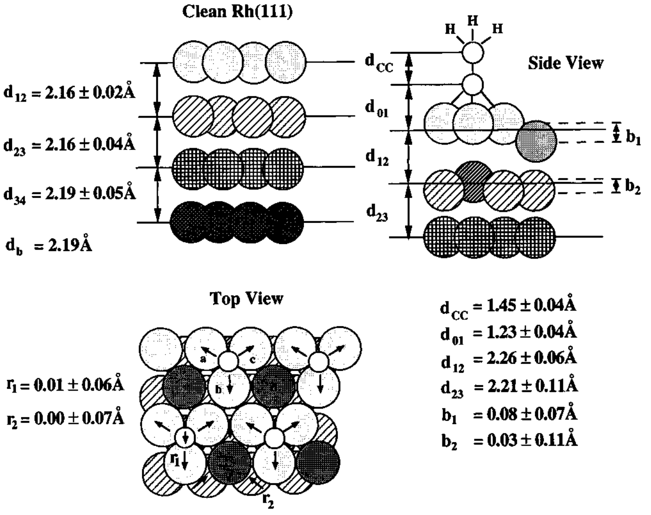


Figure 9. Ethylene chemisorption restructures the Rh(111) surface. The Rh atoms move away from the bonding site, the next-nearest-neighbor metal atom moves downward, and the Rh atom in the second layer moves upward.[28]

atoms that are "relaxed" by moving inward when the surface is clean move outward during the formation of the chemisorption bond. When ethylidyne forms on the rhodium (111) surface,[28,29] in addition to outward movement of the surface atoms, the nearest-neighbor metal atoms move away from the adsorption site, and the next-nearest-neighbor Rh atom moves inward (causing a slight corrugation of the surface), while the Rh atom underneath the adsorption site moves up toward the carbon atom (Figure 9).

Adsorption-induced restructuring can occur on the chemisorption time scale ($\sim 10^{-15}$ s for charge transfer, or $\sim 10^{-12}$ s for vibrational times). There is evidence, however, that adsorbate-induced restructuring can occur on the time scale of catalytic reactions (seconds).[30] CO oxidation to CO_2, or ammonia reacting with NO to produce N_2 and H_2O, show oscillatory behavior under certain circumstances of temperature and reactant partial pressures. The reaction rate alternates periodically between two values. One reason for the oscillation is the periodic restructuring of the surface. In this circumstance, the sticking probability of one of the reactants is greater on one type of surface structure, while the sticking probability of the other reactant is greater on the surface structure of the other type. Thus, the reaction rate alternates between the two branches of the reaction, one taking place on the CO- or NO-covered metal surface.

Adsorbate-induced restructuring can occur on even longer time scales (hours), involving massive restructuring of the surface by atom transport. For example, sulfur restructures the (111) crystal face of nickel until the metal surface assumes the (100) orientation. Alumina restructures iron through the formation of an iron–aluminate phase to produce (111) crystal faces during ammonia synthesis, regardless of the original crystallite orientation. In this circumstance, the chemisorption-induced restructuring can be viewed as the initial phase of a solid-state reaction whose kinetics are controlled by atom transport (by diffusion).

Restructuring occurs in order to maximize the bonding and stability of the adsorbate–substrate complex. Thus it is driven by thermodynamic forces and is most likely to occur when the stronger adsorbate–substrate bonds that form compensate for the weakening of bonds between the substrate atoms, an inevitable accompaniment to the chemisorption-induced restructuring process.

3. Structure Sensitivity of Bonding and Reactivity: Rough Surfaces Do Chemistry

Tensor LEED surface crystallography, vibrational spectroscopy, and thermal desorption studies have been very effective in revealing the structure sensitivity of adsorption and the bonding of monolayers of atoms and molecules. The investigations that were carried out mostly on low Miller Index metal surfaces revealed preference for defect sites (steps and kinks), and for high coordination sites—especially at lower coverage. It appears that adsorbed atoms or molecules choose sites of the highest bond energy possible and move to occupy other sites only when all these sites are filled. Usually, defect sites (steps and kinks) have the highest binding energy, followed by 4-fold or 3-fold sites. There are exceptions to this rule; for example, carbon monoxide—after filling all available defect sites—occupies bridge and top sites on a large number of transition metal surfaces.

Surface reactivity, bond dissociation, or catalytic turnovers also frequently occur at sites of high heat of adsorption. The activation energy barrier for chemical rearrangement appears to be lower at these sites than at other surface sites. H_2–D_2 exchange at stepped surfaces of platinum has been observed when no exchange was occurring on atomic terraces under the same experimental conditions.[1] CO dissociation at platinum kink sites was detected, even though platinum is not active for CO dissociation at any other surface site. Ethylene dehydrogenation to acetylene occurs at much lower temperatures (<150 K) at stepped nickel surface then on any other nickel surface site (~230 K).[1]

Open, low-density crystal faces of transition metals are much more active during catalysis than close packed surfaces. For example, the active sites for N_2 bond dissociation that controls ammonia synthesis are the seven coordinated sites found in the open (111) and (211) surfaces of iron.[31] As a result, these surfaces have 2 orders of magnitude higher rates for ammonia synthesis than the close-packed (110) crystal face. Similar structure sensitivity is found for rhenium with the $(11\bar{2}0)$ open crystal face being much more active than the close-packed (0001) crystal surface. There is much less information available from surface science studies on the bonding of adsorbed molecules on atomically rough surfaces, mostly because the higher reactivity of rough surfaces makes these studies more difficult as compared to adsorption studies on close-packed metal surfaces. The general statement, "rough surfaces do chemistry", applies to most transition metal surfaces studied, where atomic roughness implies defects (steps and kinks) as well as more open, lower packing density crystal faces.

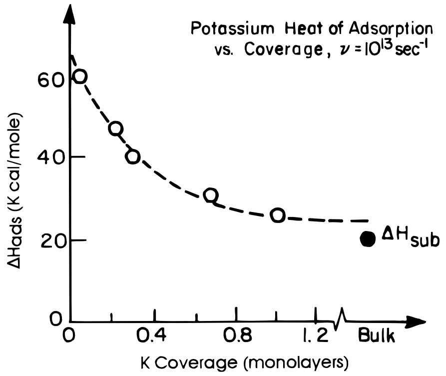


Figure 10. The heat of adsorption (ΔH_{ads}) of potassium as a function of coverage on the rhodium (111) crystal face.

4. Coadsorption-Induced Modification of Bonding and Reactivity: Promoters and Poisons

When the coverage of a chemisorbed atom or molecule is increased, its heat of adsorption per molecule decreases rather markedly. This has been shown for an adsorbed layer of potassium on the Rh(111) crystal face (Figure 10) or for carbon monoxide on several transition metal surfaces.[1] At high coverage (~80–90%), the average heat of adsorption can be 30% of the low coverage heat of adsorption. The declining binding energy is due to an adsorbate–adsorbate interaction that is repulsive, which leads to a weakening of adsorbate–substrate bonds as coverage is increased. The location of the molecule (the adsorption site) can also change with coverage.

The restructuring of the substrate induced by chemisorption can sometimes turn the repulsive adsorbate–adsorbate interaction attractive. This appears to be the case for sulfur adsorbed on the (0001) crystal face of rhenium.[32] At low coverage, sulfur occupies 3-fold sites on the metal surface. At high coverage of 0.5 monolayer, sulfur adsorbs close to 3-fold hcp hollow sites and forms a distorted hexamer structure in a $(2 \times \sqrt{3}) \times (2 \times \sqrt{3})R30°$ pattern. The sulfur hexamers show rather pronounced lateral distortions, with long and short sulfur–sulfur distances of 3.32 and 2.95 Å, respectively. What is most significant is the upward and outward relaxation of the rhenium atoms in the center of the ring of sulfur atoms.[32] It appears that the displacement of the rhenium atoms destroys the repulsive interaction between sulfur atoms which would dominate at high coverage. As a result, the aggregation of sulfur atoms is permitted at high coverage. STM studies show the presence of trimers, tetramers, and hexamers of sulfur clusters on the (0001) face of rhenium, which form with increasing sulfur coverage.[32]

Low coverage of sulfur chemisorbed on the Re(0001) and Pt(111) surfaces were studied by STM and LEED.[33] On both of these surfaces of triangular symmetry, the lowest coverage (0.25 monolayer) ordered structure is (2×2). Exposure of the ordered sulfur overlayer to low pressures of carbon monoxide (10^{-9} Torr) on either surface induces compression of the sulfur layer to a structure associated with higher local coverage.[33] Carbon monoxide chemisorbs in the holes created in the sulfur layer. This is shown for one of the systems in Figure 11. The reordering by compression was observed by both a change in the LEED pattern and by real-space STM imaging of the surface (Figure 11). On both surfaces, the overlayers can be returned to the original (2×2) surface structure by annealing for several seconds at 600 °C, during which carbon monoxide desorbs and sulfur atoms reoccupy the vacant metal sites. This phenomenon of the compression of atoms in a strongly chemisorbed layer upon coadsorption of another molecule provides a mechanism for carrying out catalytic reactions on metal surfaces covered with strongly chemisorbed layers that do not participate in the reaction. Because one of the two coadsorbed species (sulfur) forms ordered arrays in these examples, it was possible to monitor the compression by the coadsorption of another molecule by both STM and LEED. The reverse process, the healing of the original overlayer by sulfur back diffusion upon CO desorption, can also be monitored.

As early as 1976, two different adsorbates had been found that could mix and form two-dimensional structures where both atoms are part of the surface unit cell. This was observed with sodium and sulfur

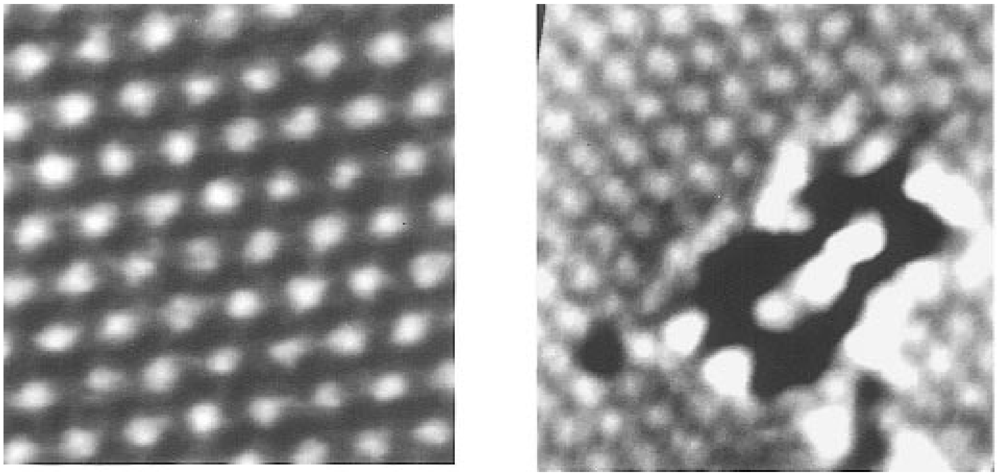


Figure 11. Compression of the low coverage sulfur overlayer on the rhenium(0001) crystal face upon carbon monoxide coadsorption. Carbon monoxide occupies the island formed by the compression of sulfur to a higher coverage structure at the periphery of the island. Upon desorption of CO, the sulfur atoms diffuse back to their equilibrium positions to fill up the island: (left) before CO exposure, 40 × 40 Å; (right) after CO exposure, 55 × 55 Å.

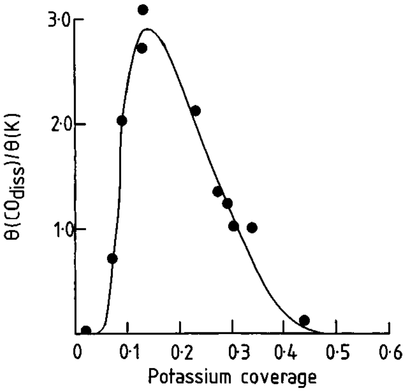


Figure 12. Number of CO molecules that dissociate per potassium atom on Rh(111) as a function of potassium coverage.[50]

coadsorbed on Ni(100),[34] and the structure was solved with LEED in three different conditions of sodium and sulfur coverage. The arrangement is such that one of the adsorbates is surrounded by the adsorbates of the other type, and vice versa. It was discovered in our laboratory that carbon monoxide induces order in many adsorbed organic monolayer systems on Rh(111) and Pt(111) surfaces.[35,36] Carbon monoxide-induced ordering was observed for acetylene, ethylidyne, propylidyne, benzene, fluorobenzene, sodium, potassium, and hydrogen on several metal surfaces.[37,38] Coadsorption-induced ordering occurs if one of the adsorbates is an electron acceptor (such as carbon monoxide usually is), and the other adsorbate is an electron donor (as are most organic molecules) to the transition metal surface.[39] The electron-accepting and electron-donating properties can be measured by monitoring the work function change upon adsorption and coadsorption. The CO-induced ordering occurs when CO is coadsorbed with an adsorbate (e.g. sodium) or an organic molecule that has a surface dipole oriented opposite to that of adsorbed CO. Conversely, disorder or segregation occurs when CO is coadsorbed with an adsorbate that has a similarly oriented dipole.[40]

Strong attractive interaction among coadsorbates can lead to dissociation of the molecular species. This is observed during the coadsorption of potassium (donor) and CO (acceptor) on several transition metal surfaces. Thermal desorption data indicate CO desorbing at much higher temperatures than normal in the presence of the adsorbed alkali metal, often showing a 17 kcal/mol (71 kJ/mol) increase in its heat of adsorption. The CO stretching frequency decreases with an increasing dipole moment of coadsorbed donors. Isotope-labeling studies (using $^{12}C^{18}O$ and $^{13}C^{16}O$) indicate scrambling of the two isotopic species in the presence of potassium, signaling molecular dissociation; while no dissociation is apparent in the absence of potassium on rhodium. Up to three CO molecules dissociate per potassium atom at an alkali metal coverage of 20% of a monolayer, as shown in Figure 12.

Repulsive interaction is also observed with the coadsorption of potassium and ammonia. Both species are electron donors to transition metals. On iron, a 4 kcal/mol (17 kJ/mol) decrease in the heat of chemisorption of NH_3 is observed due to coadsorbed potassium.[31]

Alkali metals are often used as additives during catalytic reactions. They are "bonding modifiers"; that is, they influence the bonding (and thus the reactivity) of the coadsorbed molecules. Potassium is a promoter in CO hydrogenation reactions where CO dissociation is desired and is one of the elementary reaction steps. The alkali metal also reduces the hydrogen chemisorption capacity of the transition metal. Potassium is a promoter in ammonia synthesis for the opposite reason. It weakens the NH_3 product molecule bonding to the metal, thereby reducing its surface concentration, and blocking important reaction sites. It also aids in the dissociation of dinitrogen.

Halogen species can also be important bonding modifiers, because they are powerful electron acceptors. Indeed, they are used as promoters in several catalytic processes (for example, ethylene oxidation to ethylene oxide over silver, or during partial oxidation of methane). Nevertheless, their molecular and atomic chemisorption behavior has been studied less and, therefore, is not as well understood as the role of coadsorbed alkali metal ions.

III. Technological Impact of Modern Surface Science: Selected Examples

A. Catalysis

Since the early 1970s, surface science has made significant contributions to our understanding of catalyst-based chemical and petroleum technologies. These contributions led to the development of the next generation of chemical processes. The *hydrogenation of carbon monoxide* yields methane or methanol exclusively, oxygenated molecules containing several carbon atoms or liquid, and high molecular weight hydrocarbon products (depending on the type of catalyst employed).[1] The dissociation of CO was found to be the dominant reaction step in producing methane, followed by stepwise hydrogenation of the surface carbon over several transition metal surfaces. Potassium was found to be an outstanding "promoter" of CO dissociation through weakening of the C−O bond by charge transfer. Potassium also decreased the hydrogen surface concentration, thereby producing more unsaturated reaction intermediates and products. It also retarded the graphitization of the active surface carbon that hydrogenated readily. Methanol production was found to occur through the hydrogenation of undissociated CO_2 or CO, with either of these reactions dominating, depending on catalyst formulation. Higher molecular weight hydrocarbons are produced by secondary polymerization reactions. These secondary reactions commence when ethylene or propylene initiate and propagate chain growth. The oxidation state of the transition metal catalyst was shown to be very important in controlling product distribution.

The *reforming of naphtha* over platinum was found to be a structure-sensitive reaction.[1,41] By altering the surface structure of platinum particles [(111) or (100) orientation] the product distribution could be altered. Bimetallic platinum-based catalysts (Pt−Re, Pt−Ir, and Pt−Sn) have also been investigated by surface science studies. These studies have contributed greatly to their optimization in this important high octane fuel-producing technology.

Surface science studies of the Co−Mo−S *hydrodesulfurization* catalyst identified the surface compounds responsible for the high rate of this reaction as compared to only using Mo−S. Thus the activity of the commercial catalyst could greatly be improved.[42]

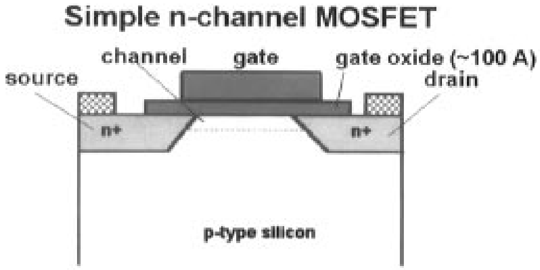
The same is true for the iron-based catalyst that produces *ammonia from* N_2 *and* H_2. The structure sensitivity of this reaction was uncovered, implicating the (111) and (211) crystal faces of iron as the most active. The role of potassium promoters as bonding modifiers in aiding the dissociation of N_2, as well as weakening the bonding of ammonia to the iron surface to inhibit product poisoning, has been uncovered. The role of alumina as a structure modifier, aiding the restructuring of iron particles to possess crystal faces most active for ammonia synthesis [(111) and (211)] has been proven by surface science studies. As a result, a new generation of catalysts could be prepared with superior activity for this important industrial process.[42]

The *partial oxidation of ethylene to ethylene oxide* over silver has been investigated in detail by surface science studies. The interaction of the alkali promoters with the impurities of the alumina support has been verified and has necessitated the use of ultrapure alumina.[43] A reaction mechanism that utilized atomic instead of molecular oxygen has been uncovered, giving rise to much higher selectivity over a newly formulated silver catalyst. This represented a revolutionary change in this important chemical process.

Environmentally important catalytic processes have become the focus of rapid development in recent years. None of them is more important than the three-way *catalytic converter utilized to clean automobile exhaust*. Surface science has contributed in major ways to the understanding and development of new generations of improved catalysts that use Pt, Pd, Rh, and cerium oxide as an important promoter.[44] The challenge is to fully oxidize unburned hydrocarbons and CO while reducing NO_x to N_2 under all conditions of engine use: cold start, steady-state operation, and in a broad range of air and fuel mixtures. This technology works well on the present day automobile. Lean burning, more fuel-efficient cars present new challenges to surface science and the development of the technology used to clean automobile exhaust. A reduction in noble metal concentration is also a major goal of ongoing studies. The development of these important and successful catalyst systems (which have improved air quality when used in urban areas) could not have happened without major contributions from modern surface science.

B. Selected Surface Science Problems of Semiconductor Technology

Semiconductor-based technologies are at the heart of computer manufacturing. The fabrication of microelectronic circuits often involves layer-by-layer deposition of semiconductor (Si, GaAs, etc.), metal (Al, Cu, etc.), and insulator (SiO_2, polymer) thin films, in various configurations. The film thickness of each of these materials is presently in the 10^3-10^4 Å range, and these layers alternate in both two and three dimensions. The fabrication of these layers are carried out by surface processes using chemical vapor deposition, sublimation, or sputter deposition from a radiofrequency plasma. The nucleation and growth mechanisms are monitored by surface science techniques such as reflection high-energy electron diffraction (RHEED) and electron microscopy. Making ohmic contacts to semiconductor devices often involves the formation of surface compounds; that is, materials with a two-dimensional phase diagram that is very different from their bulk phase diagram. Transition metal silicides are often used to obtain desirable electrical properties at metal−semiconductor contacts. We shall look at two problems of semiconductor device technology that are currently the focus of intense surface science studies.



Semiconductor Industry Association (SIA) roadmap (1994 edn.)

	1995	1998	2001	2004	2010
Bits/Chip (DRAM)	64 M	256 M	1 G	4 G	64 G
Minimum Feature, µm	0.35	0.25	0.18	0.13	0.07
Gate Oxide Thickness, nm: Desktop	8.3	7.3	5.0	4.5	?
Portable	6.3	4.5	4.5	3.4	?

Figure 13. Metal oxide surface field effect transistor (MOSFET) showing a gate oxide configuration and the expected future decrease in film thickness.

Insulating gate oxides are produced by oxidizing silicon to SiO_x. Both the oxygen to silicon ratio and the thickness of the oxide are important process variables, as they control device performance. In Figure 13 the likely change in device dimensions are shown, as projected by the National Technology Roadmap for semiconductors.[45] The gate oxides must become thinner, their surfaces or interfaces must be atomically smooth, and their impurity concentrations must be minimized in order to increase the speed of electron transport and device reliability. These criteria are major challenges to surface science.

The chemical and mechanical integrity of the metal−insulator interfaces can be compromised by water vapor or by the chemical attack of impurities segregating at the interface (alkali atoms, carbon, oxygen, etc.). When this happens, the adhesion of the insulator (oxide or polymer) to the metal is altered and delamination occurs. All these changes of chemical and mechanical properties at the inter-

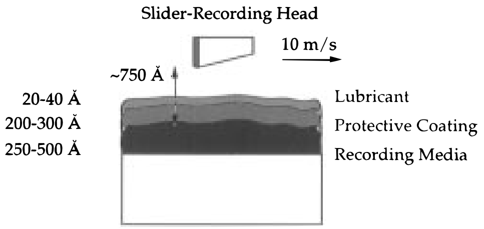


Figure 14. Hard disk–recording head interface.

face can have very deleterious effects on the electrical properties. It is essential that we learn how to fabricate chemically stable insulator–metal interfaces that maintain adhesion under changing ambient conditions (temperature, humidity, etc.). As the insulating oxide is replaced by a polymer with a smaller dielectric constant, the studies of metal–polymer interfaces becomes a frontier area of the science of semiconductor surface technology.

C. Disk Drive Magnetic Storage

Information in a computer is usually stored on a hard disk (ceramic or glass) that is coated with a thin magnetic film ($\leq$1000 Å) made from a mix of transition metal oxides. The film is then coated by a sputtered carbon film ($\sim$200 Å thick) that contains various amounts of hydrogen, which is then lubricated by a monolayer of high molecular weight polyfluoro ether. The drive moves the tip of a magnetic material over the disk at a high speed to transmit a magnetic signal, thereby storing or retrieving information on the disk (Figure 14).

The closer the tip tracks the disk, the higher the density of information that can be stored. At present, the gap between the tip and disk approaches 200 Å and the tip velocity is increasing to meters per second. Such a surface and interface device poses unique challenges to surface scientists. The carbon coating must be smooth on the atomic scale, and hard enough to withstand the pressure of the crashing tip. The lubricant has to provide a very low friction surface under all environmental conditions, including high humidity and low temperatures. The field of molecular tribology has been created as a result of these technical challenges; the STM and AFM were discovered by research conducted while working on technical problems related to disk drive technology. Forces in the 10^{-9} Newton range can now be measured; hardness and friction coefficients, and the work of adhesion can readily be determined on the molecular scale. Carbon films with diamondlike hardness can be fabricated, with the hydrogen content of these films appearing to control many of its mechanical properties. Lubrication science is developing rapidly, and the nature of lubricant bonding and modes of altering surface mechanical properties are being identified.

Disk drive technology improves by tracking the magnetic film; using ever smaller gaps between the reader tip and surface, and thinner hard coatings without compromising its mechanical properties. As a result surface mechanical properties and their atomic level control will be the focus of frontier research studies for many years to come.

D. Chemical Sensors[46]

The detection of chemical species that are present in air, water, soil, or the human body—in ever decreasing concentrations—has been the aim of technology since the methane detector was developed for coal mines in the early 19th century. With the rise of environmentally friendly technologies, the monitoring of various chemicals becomes an integral part of the process. One of the most successful sensing devices is the oxygen detector on automobiles which helps adjust the air to fuel mixture entering the internal combustion engine, and optimize the efficiency of the three-way catalytic converter. The converter oxidizes unburned hydrocarbons, CO to CO_2 and H_2O, and reduces NO_2 to N_2. The oxygen sensor is ytterbium-doped ZrO_2 that is a selective oxygen ion conductor above 400 °C. A potentiometer device for measuring O_2 partial pressures can be designed as a concentration cell based on the equilibrium between gas phase O_2 and O^{2-} in the zirconium oxide crystal lattice.

$$O_{2(g)} + 4e^- \leftrightarrow 2O^{2-} \tag{2}$$

If there is a higher oxygen concentration on one side of a ZrO_2 film or membrane, a potential difference (ΔV) develops that is proportional to the logarithm of the ratio of oxygen pressures at the two sides of the oxide film,

$$\Delta V = \frac{RT}{4F} \ln \frac{P_{O_2}{}^{(1)}}{P_{O_2}{}^{(2)}}$$

where F is Faraday's constant and R is the gas constant. This is called the λ-probe and can measure a large range in oxygen concentration at a constant temperature with about 2% relative precision ($\sim$0.1 mV). By applying an external voltage, the ZrO_2 film can be used as an "oxygen pump" that transports oxygen from one side of the film to the other. The oxygen ion current is directly proportional to the oxygen partial pressure to be measured. In this configuration, the detector can be used at temperatures below 400 °C.

Another type of gas detector is the semiconductor sensor that usually employs SnO_2 or ZnO_2 to detect the concentration of weakly adsorbed molecules by change in their conductivity. Adsorption induces charge transfer through the surface space charge, which can then be measured with great sensitivity even though no more than one electron is transferred for every 100 molecules adsorbed. Such a detector is reversible although not very selective. The sensor can be made selective by employing a catalyst near the semiconductor detector to selectively oxidize or reduce certain gas molecules.

There are many other types of sensors that are employed with success. Fiber optic sensors detect adsorption of molecules from the vapor phase by changes of refractive index, light scattering, or fluorescence. Mass-sensitive sensors measure adsorption by changes in oscillation frequency of quartz oscillators: changes in mass as little as 10^{-9} g can be detected this way. Chemosensors detect molecules by selective chemical reactions (NO, SO_2, NH_3, CO, and CO_2 are detected this way). There are ion-selective electrodes that detect H^+, Na^+, K^+, F^-, and NO_3^-. Biosensors are being developed in increasing numbers, with the selectivity of a biological recognition mechanism. Enzymes are anchored to surfaces that react with complex organic molecules such as alcohols, formaldehyde, glycerol, lactate, phenol, glucose, choline, etc., and the product of the reaction (H_2O_2, quinone, NaDH) is detected. Biochips are being developed that can detect several organic adsorbates simultaneously such as glucose, urea, and triglycerides. Major applications of biosensors are in controlling fermentation processes, food technology (fruit drinks, milk processing, fish freshness) and food testing, and controlling water quality (presence of nitrates, microorganisms, and phosphates). Finally, medical technology provides major applications for sensors to control insulin pumps and to detect glucose and lactose. In *in vivo* applications of biochemical sensors, it is of utmost importance that they are biocompatible and physiologically harmless.

IV. Acknowledgments

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