Surface Science and Catalysis

Gabor A. Somorjai

Summary. During the last 20 years, surface scientists have developed a variety of techniques that make it possible to study, on the molecular level, the structure, composition, and chemical bonding in the surface monolayer. Both single-crystal model catalysts and real catalyst systems that are active in important chemical processes have been investigated by a combination of ultrahigh-vacuum surface science techniques and high-pressure kinetic techniques in an effort to determine the relation between the structure and composition of the surface and the rates of reaction and selectivities. The structure of the atomic surface, a strongly adsorbed overlayer, and the oxidation states of surface atoms are the important molecular features of an active catalyst. As a consequence of modern surface science, the design and preparation of catalysts has developed from an art into a high technology.

Over the past 20 years techniques have been developed that permit the investigation, on the molecular level, of surfaces in ultrahigh vaccuum and at solid-gas interfaces (Table 1). With these techniques, the structure and composition of surfaces and the oxidation states of surface atoms can be identified. The bonding of atoms and molecules in surface monolayers has been studied by surface crystallography and spectroscopies of different types (*1*, *2*). Molecular-beam and low-pressure studies probe the energy transfer that occurs upon collision of a gaseous atom or molecule with the surface, the interaction potential of that collision, and the elementary steps of surface reactions: adsorption, bond breaking, and desorption (*1*, *2*).

The intellectual challenge to understand the properties of surface monolayers made surface science an important topic of academic research in chemistry and chemical engineering departments. This research has influenced many technologies in which surfaces optimize reactivity, chemical change, or charge transport, including catalysis, electrochemistry, photography, and electronic circuitry. Modern surface science can be used to improve existing systems and serves as the foundation for the development of new devices. By converting many standard technologies to high technology, surface science induces rapid development in both technology and long-range basic research, since these two areas are interrelated.

In this review I shall concentrate on my work in the surface science of catalysis and the influence this work has had on catalyst manufacture. As a result of recent research, catalyst design and fabrication has developed from an art to a science. Since catalysts lie at the heart of most chemical processes, this development affects the future of chemical and petrochemical technologies and the ability to produce, convert, and transport energy.

Catalytic Versus Stoichiometric Reactions

One of the deficiencies of our chemical education system is the lack of emphasis on catalytic processes. A molecule adsorbs on a catalyst surface; it chemically rearranges while visiting several reaction sites by surface diffusion; and then it desorbs, as the product, to the gas phase. During the lifetime of a good catalyst, the reaction turns over a million times (10^6 product molecules per site) or more. If the reactant forms strong chemical bonds upon adsorption on the surface there is no catalysis, and the result is a stoichiometric reaction with a turnover of one (1 product molecule per site). Chemists are usually taught only about stoichiometric reactions during their formal training; yet many important life-sustaining reactions, including photosynthesis, the biological processes of our bodies, and the synthesis of ammonia, are catalytic.

During the catalytic process, therefore, a reactant cannot be strongly bound since that would poison the catalyst. However, if the bonding were too weak there would be no opportunity for chemical bond breaking. Thus, bonding of intermediate strength between the catalyst and the surface is needed, and surface sites are required where both bond breaking and bond formation are possible within the residence time of the intermediates.

Selected Properties of Surfaces

The structure of solid surfaces. The surfaces of single crystals of metals exhibit a variety of structures, depending on the angle of cut. The surface may be flat and close-packed where each atom is surrounded by a large number of nearest neighbors. It may be "rough" with atom-size openings between surface atoms that expose atoms in the second or even in the third layer to the incoming molecules. It may be stepped with terraces several atoms wide separated by steps the height of one atom, and there may be kinks in the steps. Small particles contain sites with many or all of these surface characteristics. Very small particles may have all of their atoms at the surface (dispersion of unity) in close-packed configurations. As a particle grows, the relative concentrations of terraced, stepped, and kinked sites are altered. If the particle grows slowly, it is bound mostly by close-packed surfaces that are thermodynamically stable. However, rapid and kinetically controlled growth processes can stabilize rough, more open surfaces.

Surface crystallography studies by low-energy electron diffraction (LEED) indicate that the distance between the first and second layer of atoms at the surface can be considerably shorter than interlayer distances in the bulk (*3*). The more open or rough the surface is, the greater this contraction. The contraction observed at the surface is called relaxation. It is the consequence of the anisotropic surface environment and is due to the reduction of the number of nearest neighbors around atoms at the surface.

Frequently, atoms at the surface will seek new equilibrium positions to optimize their bonding configuration to such an extent that the surface reconstructs. That is, the periodic arrangement of surface atoms becomes different from what is expected from inspection of the bulk

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unit cell. The surface becomes buckled (Fig. 1a), or there are periodically arranged dimers (Fig. 1b), or there are surface vacancies. The surface structure of clean solids is as fascinating as it is unpredictable at present in the absence of sufficient experimental information.

Surface composition. Frequently, impurities that are present in minute amounts (parts per million) in the bulk of the solid segregate on the surface in such large concentrations that they could completely cover it. This occurs if their chemical bonds to surface atoms are strong and if their presence greatly reduces the positive free energy of the surface as compared to that of the clean surface. Similar thermodynamic characteristics are responsible for the enrichment of one constituent at the surface of binary or multicomponent alloys. There is excess silver at Ag-Au alloy surfaces, copper at Cu-Ni surfaces, and gold at Au-Sn surfaces. Thermodynamic models have been developed to predict the composition of a clean surface for a particular alloy (*1*, *4*), but adsorbed atoms or molecules can alter the surface composition from what is predicted by forming stronger chemical bonds with one of the alloy constituents.

When alloy particles are produced with all or most of the atoms at the surface, their phase diagram is different from that in three dimensions. Often called bimetallic clusters (*5*), these particles form solid solutions and exhibit complete miscibility when phase separation is observed in the bulk phases. This unique behavior in two dimensions has been treated theoretically.

Adsorbed Atoms and Molecules

The surface chemical bond. Surface crystallography studies by LEED have revealed the formation of a large number of ordered atomic and molecular layers of adsorbed species on surfaces of crystals (*1*, *6*). The location of the adsorbates, their bond lengths, and their bond angles have been determined. On flat surfaces with high symmetry, atoms like to occupy sites of high coordination. Some of the structures that are encountered most frequently are shown in Fig. 2. Sites with tetracoordination and tricoordination are frequently occupied first by atoms such as sulfur, iodine, oxygen, or carbon. An interesting bonding situation is encountered with small atoms, such as hydrogen and nitrogen, that can lie under the first atomic layer instead of on top of it.

Table 1. Frequently used techniques of surface science for studies of catalysts.

Electron scattering

Electron spectroscopies (x-ray photoelectron spectroscopy, high resolution electron energy loss spectroscopy, Auger electron spectroscopy)
Low-energy electron diffraction
Electron microscopy

Photon scattering
(high and low intensities)

Spectroscopies (infrared, Fourier-transform infrared, Raman, solid-state nuclear magnetic resonance, electron spin resonance, extended x-ray absorption fine structure, near-edge x-ray absorption fine structure, laser)
Grazing-angle x-ray diffraction

Molecule and ion scattering

Molecular beam–surface interaction
Secondary ion mass spectroscopy
Ion scattering spectroscopy

Other techniques

Radiotracer labeling
Mössbauer spectroscopy
Thermal desorption

Among small molecules, CO has been studied most frequently. The molecule usually adsorbs with its C–O bond axis perpendicular to the surface and binds to metal surfaces through the carbon atom (*7*). It can occupy a top site (Fig. 3a) or a bridge site (Fig. 3b) with only a small difference in its heat of adsorption at these two locations. However, as the coverage of CO is increased above one half of a monolayer, some of the CO molecules occupy sites of lower symmetry (*8*) to stay apart as much as possible because of repulsive interactions among the molecules. The average heat of adsorption then declines rapidly with coverage, as shown in Fig. 3C.

The structure of ethylene adsorbed on metal surfaces has also been studied in great detail (*9*). This molecule loses a hydrogen atom and forms a stable ethylidyne C_2H_3 species on the (111) crystal faces of platinum, rhodium, and palladium at room temperature. The C–C bond is perpendicular to the metal surface and elongated to a single bond. The carbon that bonds to the metal is in a tricoordinated site and forms short strong bonds to the metal, as seen in Fig. 4. The structure is similar to the structures of several organometallic clusters, indicating that the surface chemical bond is localized and cluster-like.

One of the striking properties of the surface chemical bonds of adsorbed organic molecules is their temperature-dependent variation (*10*). Upon heating, a sequential loss of hydrogen occurs and

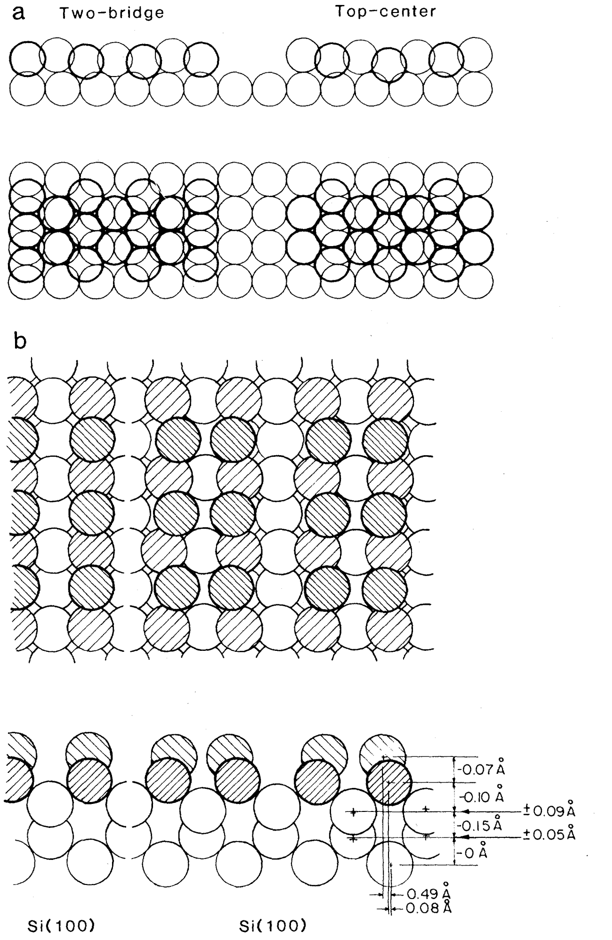


Fig. 1. (a) Structure of the reconstructed Ir(100) crystal face, as determined by surface crystallography. (b) Top and side views of ideal, bulk-like Si(100) at the left and the Si(100) reconstructed real surface at the right. Layer-spacing contractions and intralayer atomic displacement relative to the bulk structure are given; shading differentiates surface layers.

the molecules form organic fragments, CH, CH_2, C_2H, and so on, with well-defined stoichiometry (Fig. 4). Only at higher temperatures ($\geq$800K) will the fragments lose all their hydrogen and form a graphitic or carbidic overlayer, the most stable structure thermodynamically. The fragments are stable in a well-defined temperature range and the surface remains chemically reactive and catalytically active in their presence. The metal surface is deactivated only when the graphitic overlayer is produced.

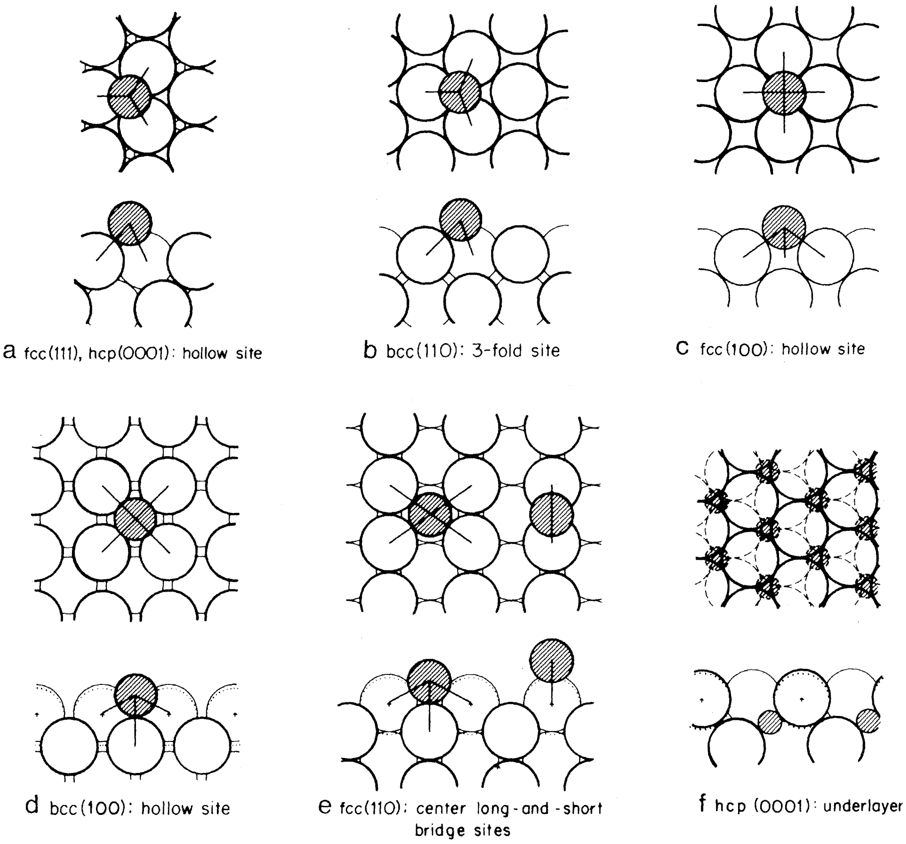

a fcc(111), hcp(0001): hollow site
b bcc(110): 3-fold site
c fcc(100): hollow site
d bcc(100): hollow site
e fcc(110): center long-and-short bridge sites
f hcp (0001): underlayer

Fig. 2. Top and side views (in top and bottom sketches of each panel) of adsorption geometries on various metal surfaces. Adsorbates are drawn shaded. Dotted lines represent clean surface atomic positions; arrows show atomic displacements due to adsorption. Abbreviations: face-centered cubic, fcc; hexagonal close packing, hcp; and body-centered cubic, bcc.

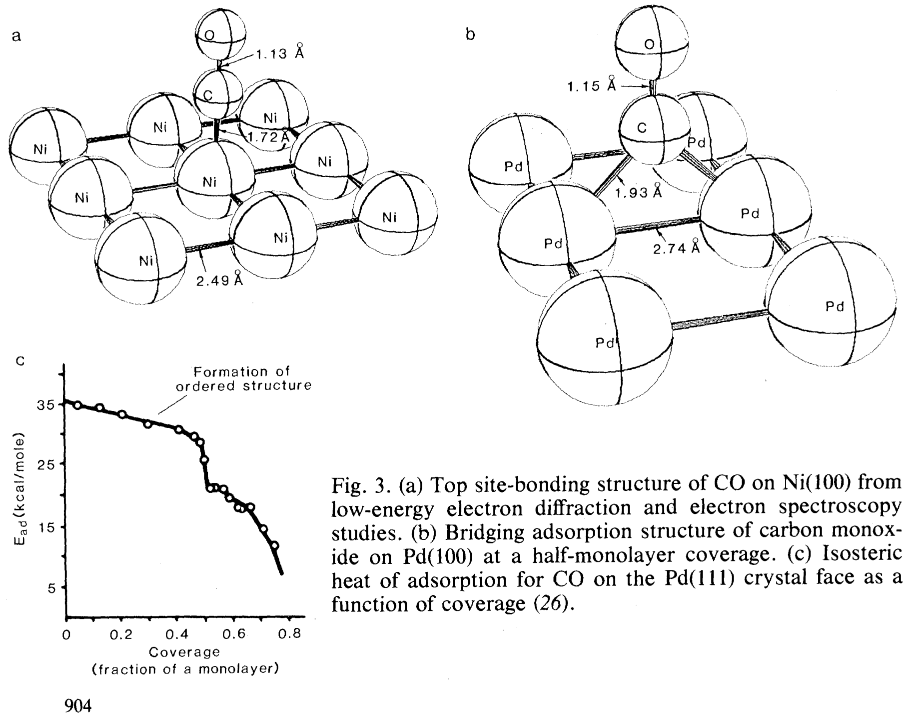


Fig. 3. (a) Top site-bonding structure of CO on Ni(100) from low-energy electron diffraction and electron spectroscopy studies. (b) Bridging adsorption structure of carbon monoxide on Pd(100) at a half-monolayer coverage. (c) Isosteric heat of adsorption for CO on the Pd(111) crystal face as a function of coverage (*26*).

On more heterogeneous surfaces molecules usually form stronger chemical bonds at kinks and steps than on the flat portions of the surfaces. Thermal desorption spectroscopy reveals (Fig. 5) that CO molecules or H atoms adsorbed at kink sites desorb at higher temperatures (*10*) than those adsorbed at steps, and those adsorbed at flat terraces are bound even less strongly. The chemical bond of adsorbates is thus sensitive to surface structure, so it is not surprising that one observes a sequential filling of sites upon exposure of the clean surface to adsorbates, the most strongly binding sites filling up first.

Coadsorption on surfaces. Often, when two different species are adsorbed, they markedly influence each other's bonding. For example, when CO and benzene are adsorbed together on Pt or Rh (111) surfaces, ordered structures form with both CO and benzene in the same unit cell (*11*). There is clearly an attractive interaction between these two molecules in the adsorbed monolayer. When sulfur is adsorbed with other molecules on metal surfaces, it blocks sites thereby reducing the concentration of the other adsorbed species (for example, sulfur blocks the adsorption of two hydrogen atoms per sulfur or one CO per sulfur on molybdenum single-crystal surfaces) (*12*). By filling up those sites first that would adsorb molecules very strongly, sulfur attenuates the strong chemical interaction between the metal and the coadsorbed molecule. For example, a clean molybdenum metal surface would decompose thiophene, C_4H_5S, an important sulfur-containing molecule. When thiophene is coadsorbed on molybdenum that is partially covered with sulfur, it is adsorbed as a molecule because the sites where it would decompose are blocked by sulfur.

Alkali metals exert pronounced electronic effects when coadsorbed with other molecules (such as CO, N_2, and hydrocarbons) on transition metal surfaces. By donating electrons to the transition metal, potassium, for example, becomes ionized. The excess charge donated to the transition metal finds its way to the molecular orbitals of the coadsorbed molecules if those orbitals overlap with the charge density of the metal. This is the case for CO when it is coadsorbed with potassium: the C–O bond is greatly weakened and the metal-carbon bond strengthened by as much as 12 kcal (*13*). Such modification of bonding leads to CO dissociation on rhodium surfaces in the presence of potassium, whereas CO adsorbs only molecularly in the absence of potassium. The presence of alkali metals strongly modifies the reaction path during CO hydrogenation, altering the product distribution (more dissociative CO adsorption and less hydrogenation lead to the formation of alkanes and alkenes of higher molecular weight) (*13*). The N_2 bond is also weakened by alkali metals, and as a result the presence of alkali metals increases the rate of NH_3 synthesis over iron surfaces. On the other hand, coadsorbed alkali metal atoms decrease the reaction rates of hydrocarbons on transition metal surfaces by strengthening the C–H bonds, which therefore break less readily (*14*).

Thus, the coadsorption of two species can markedly influence the chemical bonding of adsorbed molecules. An attractive adsorbate-adsorbate interaction may induce ordering or modify bonding. The blocking of chemically active sites by one of the adsorbates can attenuate the chemical interaction of the other adsorbate with the surface. Charge transfer from one of the coadsorbed species to the other through the metal substrate can strongly influence its chemical bond. Finally, certain adsorbates (such as potassium and sulfur), by adsorbing more strongly on one crystal face than another, can induce restructuring of the whole surface.

The Surface Science of Catalytic Reactions

Strongly chemisorbed molecules rarely participate directly in catalytic reactions. Because of their tenacious bonding, their surface-residence times are too long for the reaction to proceed with rapid turnover, as required by catalytic process. They are surface compounds not unlike the stable compounds that form during stoichiometric reactions in the gas phase, in solutions, or in the solid state. There must be other surface sites that adsorb the reactant molecules only weakly and carry out the catalytic process with high turnover rates. Because of the decreasing heat of chemisorption with increasing coverage (Fig. 3c), catalytic processes are likely to occur at high surface coverages.

There are three molecular components of heterogeneous catalysis that control reaction rates and product selectivity. These are: (i) the atomic surface structure, (ii) an active overlayer that is deposited before or during the reaction on the active catalyst surface, and (iii) the oxidation states of the surface atoms. The studies that verified the important roles of these surface components have mostly been of model catalysts, single-crystal surfaces of well-defined structure and composition. The use of these model systems required mating the ultrahigh-vacuum and high-pressure techniques used for characterizing the surface structure and composition and the chemical reactivity of the surface, respectively. An apparatus that can operate in the pressure range of 10^{-10} to 10^5 torr has been developed in our laboratory for this purpose, and it is widely used by surface scientists (*15*).

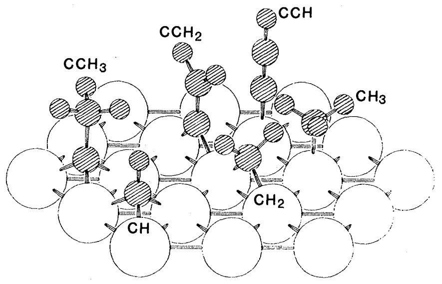


Fig. 4. Schematic representation of the various organic fragments present on metal surfaces at high temperature. The presence of CH, C_2, C_2H, CH_2, and CCH_3 has been detected.

Surface-structure sensitivity. Rough surfaces are much better catalysts than smooth surfaces. For example, the (111) crystal face of iron produces ammonia from N_2 and H_2 at about 500 times the rate of the (110) face under industrial conditions, 20 atm and 450°C (Fig. 6) (*16*). The (11$\bar{2}$1) or (11$\bar{2}$0) crystal faces of Re produce ammonia 2000 times faster than the close-packed (0001) Re surface. These catalytically active metal surfaces contain many atoms with large numbers of nearest neighbors (high coordination). In addition, the top layers have an open structure, so atoms with high coordination in the second layer are also accessible to incoming reactant molecules. Thus, it appears that sites with highly coordinated atoms are key components of catalysts with high turnover rates. Stepped surfaces and surfaces with large concentrations of kinks in the steps are also active in carrying out catalytic reactions of many types at high rates [for example, the hydrogenolysis of isobutane on kinked Pt surfaces (*17*) and the exchange of H_2 and D_2 at stepped Pt surfaces (*18*)]. At these defect sites atoms of both low and high coordination are exposed, the atoms at the bottom of the step having a high coordination and those at the top of the step having low coordination. Thus, such sites provide both high catalytic activity and strong chemical bonding, at the bottom and at the top of the step, respectively.

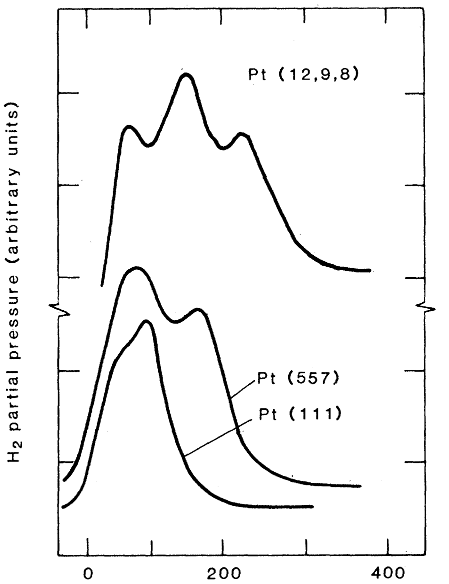


Fig. 5. Thermal desorption spectra for hydrogen chemisorbed on flat Pt(111), stepped Pt(557), and kinked Pt(12,9,8) surfaces.

A recently developed theory (*19*) of metal catalysis proposes correlations between catalytic activity and local electronic fluctuations of low energy in transition metals. Maximum electronic fluctuations take place at metal sites of high coordination. The most active surfaces for carrying out structure-sensitive catalytic reactions are atomically rough surfaces, those that expose large numbers of nonmagnetic or weakly magnetic neighboring atoms to the reactant molecules in the first or second layer and those that are stepped or kinked.

The electronic fluctuations of importance include charge fluctuations, configuration fluctuations, spin fluctuations, and term and multiplet fluctuations. Configuration fluctuations are the largest for those atoms with a large number of metallic neighbors; thus, they should be more catalytically active. In addition, the catalytic activity of the transition metal atoms is directly related to their unfilled *d*-shells.

The role and reactivity of strongly adsorbed overlayers. It is important to point out that not all catalytic reactions are structure-sensitive and that structure-insensitive processes may be mediated by tenaciously held overlayers of strongly adsorbed molecules that insulate the metal from direct contact with some of the reactants. Indeed, the overlayer itself plays an important role in certain catalytic reactions. One of these reactions is the hydrogenation of ethylene, C_2H_4 (*20*). When C_2H_4 is introduced along with H_2 in a steady flow over platinum or rhodium surfaces at 300K and 1 atm, hydrogenation to C_2H_6 occurs with very high rates of turnover. An ethylidyne overlayer forms almost instantaneously, however, and ^{14}C labeling and spectroscopic studies indicate that the hydrogenation occurs by the mediation of this overlayer, which permits H_2 adsorption and atomization on the metal surface but blocks the direct adsorption of C_2H_4 on the metal. A mechanism that explains all of the experimental data is shown in Fig. 7. The hydrogen transfer via formation of an ethylidene intermediate is implicated as the key hydrogenation step, and ethylene does not directly contact the metal surface.

Of course this is not the only mechanism for C_2H_4 hydrogenation. At higher temperatures the strongly adsorbed C_2H_3 groups are rehydrogenated at sufficiently high rates to continuously expose the bare metal sites to the incoming C_2H_4 molecules. At electrode surfaces in aqueous solution, C_2H_4 hydrogenation occurs in the presence of an external potential over a metal surface that is covered with such a large concentration of hydrogen atoms that the hydrogenation of approaching ethylene molecules takes place instantaneously without the formation of ethylidyne groups.

For most hydrocarbon conversion reactions (isomerization, dehydrocyclization, and hydrogenolysis) both the catalyst's surface structure and hydrogen transfer by the strongly held carbonaceous deposit play important catalytic roles (*21*). Thus, the reaction conditions are adjusted to continuously expose some of the bare metal sites to the incoming reactants, which also migrate onto the strongly held deposit to participate in chemical interactions before the final product molecule desorbs. A model of the platinum surface that is active for the conversion of organic molecules in isomerization, dehydrocyclization, and hydrogenolysis reactions indicates the importance of both the metal surface structure and the carbonaceous deposit that performs hydrogen transfer (Fig. 8).

The oxidation state of surface atoms. Several experimental studies in recent years have indicated the importance of oxidation states other than the zero valent metallic state for catalyzed reactions. The hydrogenation of CO over rhodium was reported to yield predominantly C_2 oxygenated products, acetaldehyde and acetic acid, under certain experimental conditions (*22*). In our studies of unsupported polycrystalline rhodium foils, we detected mostly methane, and only small amounts of ethylene and propylene, under similar conditions. This latter product distribution was identical to that obtained by others from supported rhodium catalysts as was the value of the activation energy for methanation that we found: 24 kcal per mole (*22*). It appears that after the dissociation of CO, the organic molecules form by the rehydrogenation of CH_x units in a manner similar to alkane and alkene production from mixtures of CO and H_2 over other transition metal catalysts (iron, ruthenium, and nickel). However, when rhodium oxide (Rh_2O_3) was the catalyst, large concentrations of oxygenated C_2 or C_3 hydrocarbons were produced, including ethanol, acetaldehyde, and propionaldehyde (*22*). Furthermore, the addition of C_2H_4 to the CO and H_2 mixture yielded propionaldehyde, indicating the carbonylation ability of Rh_2O_3. Under similar conditions and over rhodium metal, C_2H_4 was quantitatively hydrogenated to ethane, and carbonylation activity was totally absent. Clearly, rhodium ions of higher oxidation state were necessary to produce the oxygenated molecules. Similar behavior was exhibited by molybdenum. From CO and H_2, molybdenum metal produced methane and alkanes or alkenes that contain two or three carbons, whereas molybdenum compounds that contain molybdenum ions in higher oxidation states produced alcohols.

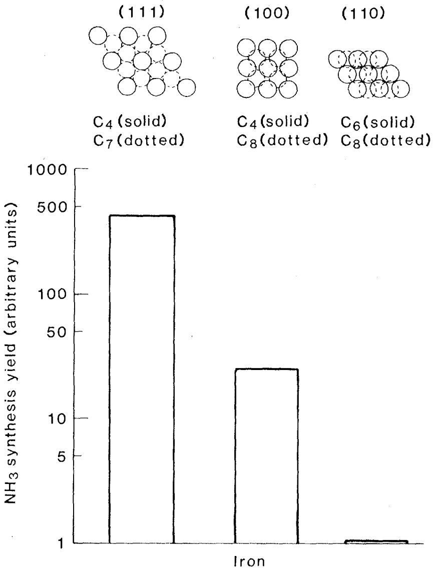
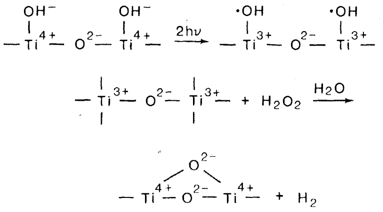


Fig. 6. The sensitivity of the iron-catalyzed ammonia synthesis to the structure of the iron surface.

The marked change of selectivity in reactions of CO and H_2 upon alteration of the oxidation state of the transition metal is due largely to the change in the heats of adsorption of CO and H_2 as the oxidation state of the transition metal ion is varied (*22*). The CO adsorption energy is decreased upon oxidation while the heat of adsorption of H_2 is increased. This in turn changes the relative surface concentrations of CO and H_2. In addition, the metal is primarily active for hydrogenation and CO dissociation, whereas the oxide can perform carbonylation and has reduced hydrogenation activity.

One of the difficulties in preparing selective catalysts for hydrocarbon conversion is the poor thermodynamic stability of the higher oxidation states of transition metal ions in a reducing environment. It appears that the strong interaction between the metal and support that permits the incorporation of the high-oxidation-state transition metal ion into the supporting refractory oxide or sulfide crystal lattice often provides for the kinetic stability of the desired oxidation state, so long as the catalytic reaction temperatures are appreciably below the decomposition temperature of the binary oxide so prepared.

Another example of the importance of the changing oxidation state of transition metal ions at the surface is the catalytic cycle leading to the photocatalyzed dissociation of water on strontium titanate, $SrTiO_3$, surfaces (Eq. 1) (*23*). The oxide surface is completely hydroxylated in the presence of water, and the titanium ions are in the Ti^{4+} oxidation state. When the surface region is irradiated with light of 3.1 eV or more, electron-hole pairs are generated. The electron is utilized to reduce the Ti^{4+} to Ti^{3+}. The electron vacancy induces charge transfer from the hydroxyl group, which produces OH radicals that dimerize to H_2O_2, and splits off oxygen, which evolves. The reduced surface containing Ti^{3+} can now adsorb another water molecule, which acts as an oxidizing agent to produce Ti^{4+} and a hydroxylated surface again, evolving hydrogen in the process (*23*). Clearly, changes of oxidation states of transition metal ions are frequently indispensable reaction steps in catalytic processes (*23*).



$$-\overset{OH^-}{\overset{|}{Ti^{4+}}}-O^{2-}-\overset{OH^-}{\overset{|}{Ti^{4+}}}- \xrightarrow{2h\nu} -\overset{\cdot OH}{\overset{|}{Ti^{3+}}}-O^{2-}-\overset{\cdot OH}{\overset{|}{Ti^{3+}}}- \longrightarrow$$
$$-\overset{|}{\underset{|}{Ti^{3+}}}-O^{2-}-\overset{|}{\underset{|}{Ti^{3+}}}- + H_2O_2 \xrightarrow{H_2O}$$
$$-\overset{\diagup O^{2-} \diagdown}{Ti^{4+}-O^{2-}-Ti^{4+}}- + H_2 \qquad (1)$$

We have thus identified several of the molecular components of heterogeneous catalysis. Models that emphasize the importance of the surface structure of catalysts for selectivity, the presence and involvement of organic fragments in HC conversion reactions, and the need for various oxidation states of surface atoms to obtain desired reaction products are not new to the literature of catalysis. However, the direct relation between these molecular parameters and the catalytic behavior eluded the practitioners of catalysis in the past. Modern surface science provides techniques for determining the atomic structure, composition, and oxidation state of surface atoms and the molecules adsorbed in the monolayer. When these data are combined with studies of the kinetic parameters of catalytic reactions (rates, selectivities, activation energies), the all important relations between the molecular components on the catalyst surface and the high-pressure catalytic reaction behavior can be established.

Direct Study of High-Surface-Area Catalyst Systems

There are many catalyst systems in which the catalyst must be investigated directly rather than by use of models. One of these systems is the zeolites (*24*), alumina silicates with large surface areas and pores of molecular dimensions. These are the catalysts used by the chemical and petroleum industries for alkylation, cracking, hydrocracking, isomerization, cyclization, and dehydrocyclization. Solid-state nuclear magnetic resonance (NMR) spectroscopy, x-ray photoelectron spectroscopy (XPS), and extended x-ray adsorption fine structure (EXAFS) studies with high-intensity synchrotron radiation, along with a variety of chemical probes, were used to determine the structure and composition of these crystalline materials. Metal-oxide catalyst systems that consist of metals dispersed as small particles on oxide supports with large surface areas (alumina, silica, titanium oxide, zirconia, lanthanum oxide, and magnesium oxide) have also been studied extensively, revealing not only the atomic structure and size of the metal particles and the pore structure of the oxides but also the catalysts' nucleation in solution as clusters and their growth, which control their final structure and composition.

Catalysts have a finite lifetime and thus the causes of their deactivation and the development of methods for their regeneration is a continuous concern to practitioners of catalysis science. The new diagnostic techniques developed by surface science have greatly improved our capabilities to extend catalyst life.

New Generations of Catalysts and New Reactions

The tools of surface science were first used to study, in molecular detail, the working of catalysts that are important in technology. These included platinum, which is used in the production of high-octane gasoline because of its ability to convert saturated alkanes to aromatic, cyclic, and branched organic molecules; silver, for the partial oxidation of ethylene to ethylene oxide; iron, for the ammonia synthesis; and molybdenum, for the hydrodesulfurization and hydrodenitrogenation of organic molecules. From this work, the structure and composition of the catalysts became known on the atomic scale along with the oxidation states of surface atoms, and these observations could be correlated with the reaction rates and product distributions.

The role of additives, which are commonly called promoters because they improve catalytic rates and selectivities to produce the desired molecules, has been unraveled in many cases. Alkali metals, halogens, and transition metals that are used as alloying agents were among the first promoters subjected to detailed surface-science studies. The important role of oxide supports with high surface areas in stabilizing the structure and oxidation states of transition metal catalysts and modifying their chemistry was uncovered. By appropriate variation of the catalyst's composition or structure and of the additives, catalytic behavior could be systematically modified, resulting in even more selective and active catalyst systems. One example of this development is the generation of catalytically superior zeolites with high ratios of silicon to aluminum. The research that gave rise to them, in turn, made possible the discovery of zeolites made of aluminum phosphates. It now appears that crystalline solids of various chemical compositions that contain channels of molecular dimensions similar to those in alumina silicates can be attained. New generations of platinum, silver, and molybdenum catalysts of higher selectivity and longer life have also appeared.

The energy crisis accelerated the development of chemical technologies that produce chemicals and fuels from carbon monoxide and hydrogen. Surface science techniques were used extensively in this research (*25*). One discovery from this work was that the strong interaction between the metal and the oxide support can be used to control the oxidation state and the surface structure of catalysts. Another was the discovery of surface compounds with unusual thermodynamic and catalytic properties that are formed from two or more metals (often called bimetallic clusters).

Surface science techniques are increasingly being used to develop catalysts for reactions that have not received much attention. These include the photo-

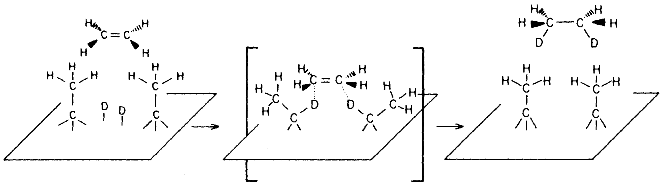


Fig. 7. Proposed mechanism for the rapid, structure-insensitive hydrogenation of ethylene.

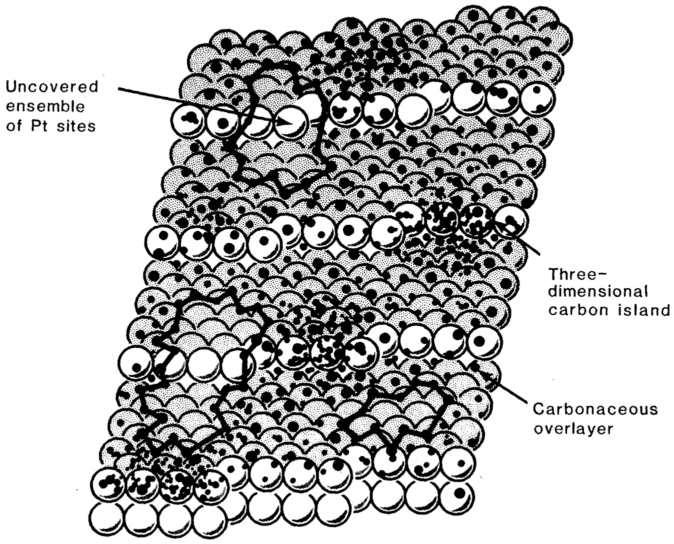


Fig. 8. Model for the working platinum catalyst that was developed from a combination of studies of single-crystal surfaces and studies of the hydrocarbon reaction rates on these same surfaces.

catalyzed dissociation of water, the use of carbon dioxide as a source of carbon reactant, new methods of nitrogen fixation, and the partial oxidation of methane. The surface reactions of molecules in their excited states are also being studied.

While most catalysis studies have focused on reactions that occur at the solid-gas interface, because of the available techniques, research is now being expanded to include catalysis at solid-liquid interfaces. Reactions of electrode surfaces, of colloid surfaces, and in biological systems, all of which occur at these interfaces, will benefit greatly from scrutiny at the molecular level. Laser spectroscopies and solid-state NMR spectroscopy are among the techniques that appear most promising for these studies.

A number of academic institutions now focus on surface science and catalysis research, and there is strong industrial participation in the newly formed research centers intended to educate scientists and engineers in this subdiscipline of chemistry. As catalysis-based technologies are converted to high technologies, the design and development of new catalyst systems will occur with greater frequency and the development of science and technology will continue at an accelerated pace. The future is indeed bright for surface science and for catalysis science.

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Sculpting Horizons in Organic Chemistry

Barry M. Trost

The quality of our lives today has benefited from successes in organic chemistry. Our food, clothing, shelter, and health care have been significantly improved by the creation of new materials based on carbon compounds. Safer and more effective agrichemicals such as pesticides and herbicides enhance the quality and quantity of our food supply. The miraculous polymers have been the basis of new materials that have increased the durability, versatility, and beauty of the clothes we wear and the homes we live in. New drug discoveries contribute significantly to life preservation and extension and an improved quality of living. Can we expect such contributions to continue at the same or perhaps an even greater rate in the future?

In order to address such a question, we must look at the present in order to extrapolate to the future. At a fundamental level, where do the challenges lie and what methods are being developed to meet these challenges? Four general areas may be recognized: structures, reactions, techniques, and concepts. In highlighting some of the specific advances in these areas in a field as broad as organic chemistry in a very brief overview, only a few of the many different exciting developments can be treated. There are undoubtedly developments not included that are as significant as the few illustrations presented here.

Structures

Historically, organic chemistry focused on isolating compounds from nature. Structure determination became the first step in understanding. However, the methods available, which relied on systematic degradation and correlations, required relatively large amounts of material; thus only abundantly occurring natural products were accessible. With

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