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Author
Somorjai, G.A.

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G.A. Somorjai

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SURFACE SCIENCE AND CATALYSIS

By Gabor A. Somorjai

Materials and Molecular Research Division,
Lawrence Berkeley Laboratory and
Department of Chemistry
University of California
Berkeley, California 94720, USA
ABSTRACT

The large number of techniques developed by surface scientists during the last twenty years permits the study, on the molecular level, of the structure, the composition and the chemical bonding in the surface monolayer. Both, model single crystal and high surface area real catalyst systems that are active in important chemical processes have been investigated by a combination of ultra high vacuum surface science and high pressure techniques to correlate the surface structure and composition with the reaction rates and selectivities. The atomic-surface structure, a strongly adsorbed overlayer and the oxidation states of surface atoms are the important molecular ingredients of an active catalyst. As a consequence of these surface science investigations the design and preparation of catalysts to carry out chemical processes became high technology.
Surface science investigations, on the molecular level converted the design and preparation of catalysts to carry out chemical processes to high technology.
SURFACE SCIENCE AND CATALYSIS

Over the past 20 years a multitude of techniques were developed that permitted the investigation, on the molecular level, of surfaces in ultra-high vacuum and at solid-gas interfaces. Many of these techniques are listed in Table 1. The atomic structure, the composition and the oxidation states of surface atoms could be identified. The bonding of atoms and molecules in the surface monolayer have been studied by surface crystallography and spectroscopies of different types. Molecular beam and low pressure studies probe the energy transfer that occurs upon collision of a gas atom or molecule with the surface, the interaction potential and the elementary steps of surface reactions, adsorption, bond breaking and desorption.

The excitement and the intellectual challenge to understand the properties of surface monolayers propelled modern surface science into the mainstream of academic research in departments of chemistry and chemical engineering. The impact of this research is much broader and has reached many important technologies. Surfaces are used as active agents in catalysis, electrochemistry, photography, and electronic circuitry to optimize reactivity and chemical change or charge transport. Modern surface science provides a science base and a molecular level understanding that can be used to improve existing systems and serves as the foundation for the development of new generations of devices. By providing the science base it converts many technologies to high technology which induces an even more rapid development in both technology and long range basic research since these two areas feed on each other.
In this review I shall concentrate on the surface science of catalysis and its striking impact on catalyst manufacture that developed it into science from art. As a result catalyst design and fabrication became a high technology industry. Since catalysts lie at the heart of most chemical processes this development deeply affects the future of chemical and petrochemical technologies and our ability to produce, convert and transport energy.

Catalytic vs. Stoichiometric Reactions

One of the deficiencies of our chemical education is the lack of emphasis of catalytic processes. The molecule adsorbs on a catalyst surface, it chemically rearranges while visiting several reaction sites within its residence time via surface diffusion, then it desorbs as the product molecule to the gas phase which also permits the adsorption of the next reactant molecule. During the lifetime of a good catalyst, the reaction turns over a million times ($10^6$ product molecules produced per site) or more. If the reactant forms strong chemical bonds upon adsorption on the surface there is no catalysis and we have a stoichiometric reaction with a turnover of one (1 molecule/site). Generations of chemists are being trained through their exposure to only stoichiometric reactions. It should be remembered that most of the important life sustaining reactions that include photosynthesis, the biological processes of our body, and the synthesis of ammonia are all catalytic reactions.
During the catalytic process therefore the reactant cannot be strongly bound since that would "poison" the catalyst. If the bonding is too weak there are no opportunities for chemical bond breaking. Thus, bonding of intermediate strength is needed and surface sites where both bond breaking and its formation are possible within the residence time of the intermediates are required.

**Selected Properties of Surfaces That Were Uncovered by Modern Surface Science**

First we shall review some of the important findings of modern surface science that are utilized to build a physical-chemical picture of surfaces on the molecular level. Then we shall focus on the molecular ingredients of surfaces that are uniquely important in heterogeneous catalysis.

**The Structure of Solid Surfaces**

The surfaces of single crystals of metals exhibit a variety of structures depending on the angle of cut. These are shown in Figure 1. The surface may be flat and close packed where each atom is surrounded by a large number of nearest neighbors (Fig. 1a and 1b). It may be "rough" with atomic size openings between surface atoms that expose atoms in the second or even in the third layer to the incoming molecules (Fig 1c, 1d and 1e). It may be stepped with terraces of several atoms wide separated by monatomic height steps (Figure 1f). There could be kinks in the steps in large concentrations (Figure 1g). Small particles contain many or all of these sites depending on their size and shape. 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 terrace, step and kink sites are altered. If the particle grows slowly it is bound mostly by close packed surfaces that are thermodynamically more stable. However, rapid, kinetically controlled growth processes can stabilize rough, more open surfaces.

Surface crystallography studies by low energy electron diffraction (LEED) indicate that the interlayer distance between the first and second layer of atoms at the surface can be considerably shorter than interlayer distances in the bulk. The more open or rough the surface is, the larger this contraction. The contraction observed at the surface is called "relaxation", and is the consequence of the anisotropic surface environment and is due to the reduction of the number of nearest neighbors around atoms in the surface (Figure 2a).

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 the inspection of the bulk unit cell. The surface becomes buckled (Figure 2b) or there are periodically arranged dimers (Figure 2c) or surface vacancies. The surface structure of clean solids is as fascinating as it is unpredictable at present in the absence of a sufficiently large body of experimental information.
The Surface Composition

It is frequently observed that impurities that are present in minute amounts (ppm) in the bulk of the solid segregate to the surface in such large concentrations that they could completely cover it. This occurs if their chemical bonds to surface atoms is strong and their presence greatly reduces the positive surface free energy as compared to that for the clean surface. Similar surface thermodynamic reasons are responsible for the enrichment of one alloy constituent at the surface of binary or multicomponent alloy systems. There is excess silver at Ag-Au, Cu at Cu-Ni, Au at Au-Sn alloy surfaces, just to mention a few systems that were investigated. Thermodynamic models have been developed to predict the surface composition that is expected for a given bulk composition. (1a, 3) Adsorbed atoms or molecules on the surface can often modify the surface composition that is predicted for the clean alloy surface by forming stronger chemical bonds with one of the alloy constituents.

When small alloy particles are produced where all or most of the atoms are at the surface, their phase diagram is very different from that in three dimensions. Often called bimetallic clusters (4) 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.
The Structures of Monolayers of Adsorbed Atoms and Molecules.
The Surface Chemical Bond.

Surface crystallography studies by LEED have revealed the formation of a very large number of ordered atomic and molecular layers of adsorbed species on surfaces of crystals.\(^{(1a, 5)}\) The location of the adsorbates, their bond lengths and bond angles have been determined. Below we give a few examples of the structural behavior that has been found. On flat, high symmetry surfaces, atoms like to occupy sites of high coordination where they are surrounded by large numbers of nearest neighbors. Some of the structures that are encountered most frequently are shown in Figure 3. 4-fold and 3-fold coordinated sites are frequently occupied first by atoms like sulfur, iodine, oxygen and carbon. An interesting bonding situation is encountered with small atoms such as hydrogen and nitrogen that can locate under the first atomic layer instead of on top of it.

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.\(^{(6)}\) It occupies a bridge site and a top site with only a small difference in its heat of adsorption at these two locations (Figures 4a and 4b). As the coverage of CO is increased however above one half of a monolayer some of the CO molecules occupy different low symmetry sites\(^{(7)}\) to stay apart as much as possible because of repulsive interactions among the molecules (Figure 4c). The average heat of adsorption of the molecule then declines rapidly with coverage and this is shown in Figure 5. Among small organic molecules the structure of ethylene adsorbed on metal surfaces was studied in the greatest detail.\(^{(8)}\) This molecule loses
a hydrogen atom and forms a very stable ethylidyne \( \text{C}_2\text{H}_3 \) specie on the (111) crystal faces of Pt, Rh and Pd at room temperature. This structure is shown in Fig. 6. The C-C bond is perpendicular to the metal surface and is elongated to a single bond. The carbon that bonds to the metal is in a 3-fold site and forms short, strong bonds to the metal. The structure is similar to several organo-metallic cluster structures indicating that the surface chemical bond is localized and cluster like.

One of the striking properties of the surface chemical bond of adsorbed organic molecules is its temperature-dependent variation. Upon heating, a sequential loss of hydrogen occurs and the molecules form organic fragments, CH, CH\(_2\), C\(_2\)H etc. with well defined stoichiometry (Figure 7). Only at higher temperatures (>800K) will the fragments lose all their hydrogen and form a graphitic or carbidic overlayer, the thermodynamically most stable structure. 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.

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 studies clearly reveal (Figure 8) that CO molecules or H atoms adsorbed at kink sites desorb at higher temperatures (9) than these species when adsorbed at steps, and those that adsorb at flat terraces are bound even less strongly. There is a surface structure sensitivity of the chemical bond of adsorbates and therefore it is not surprising that one
observes a sequential filling of sites upon the exposure of the clean surface to adsorbates, the most strongly binding sites filling up first.

**Co-adsorption 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, beautiful ordered structures form with both CO and benzene in the same unit cell. 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). 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, $\text{C}_4\text{H}_5\text{S}$, an important sulfur containing molecule. When thiophene is coadsorbed on molybdenum that is partially covered with sulfur, its chemisorption is molecular as the sites where it would decompose are blocked by sulfur.

Alkali metals exert profound electronic effects when coadsorbed with other molecules (such as CO, $\text{N}_2$ 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 at the Fermi edge. This is the case for
CO where the C-O bond is greatly weakened and the metal carbon bond
strengthened by as much as 12 kcal when it is coadsorbed with potassium.\(^{(12)}\)
This modification of bonding leads to CO dissociation on rhodium surfaces in
the presence of potassium while CO adsorbs only molecularly in the absence of
coadsorbed potassium. The \(N_2\) bond is weakened by alkali metals that enhance
its dissociation. As a result the presence of alkali metals increases the
rate of \(NH_3\) synthesis over Fe surfaces and strongly modifies the reaction
path during CO hydrogenation that alters the product distribution (more
dissociative CO adsorption, reduced hydrogenation ability which leads to the
formation of higher molecular weight alkanes and alkenes).\(^{(12)}\) 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.\(^{(13)}\)

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 K and S), by adsorbing
more strongly on one crystal face than on 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 to turn over rapidly (adsorb, react and desorb), as required by the 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 (see Figure 5), catalytic processes are likely to occur at high surface coverages.

There are three molecular ingredients of heterogeneous catalysis which have been identified by surface science that control reaction rates and product selectivity. These are: a) the atomic surface structure, b) an active overlayer that is deposited before or during the reaction on the active catalyst surface and the c) oxidation states of surface atoms. Studies that verified the important roles of these surface ingredients have mostly utilized model, single crystal catalyst surfaces of well defined structure and composition. The use of these model systems required the mating of ultra-high vacuum and high-pressure techniques that are required for characterizing the surface structure and composition, and the chemical reactivity of the surface, respectively. An apparatus that can operate in the extreme pressure range of $10^{-10} - 10^5$ Torr has been developed in our laboratory for this purpose and it is widely used by surface scientists.(14)
a) **Surface-Structure Sensitivity**

It has been found that atomically rough surfaces are much better catalysts than smooth surfaces. For example, the (111) crystal face of iron produces ammonia from N\textsubscript{2} and H\textsubscript{2} at about 500 times the rate as the (110) face under industrial conditions (20 atm, 450\textdegree C)(15) (Figure 9). The (11\overline{2}1) or (11\overline{2}0) crystal faces of Re produce ammonia 2000 times faster than the close packed (0001) Re surface. These catalytically very active rough metal surfaces are displayed in Figures 1c, 1d and 1e. They contain many sites with large numbers of nearest neighbors (high coordination). Because the top layer has an open structure, high-coordination atoms that are in the second layer are also accessible to the incoming reactant molecules. Thus it appears that sites which contain high-coordination atoms are very active for high turnover rate catalysis. 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 (e.g. hydrogenolysis of isobutane on kinked Pt surfaces(16) and H\textsubscript{2}/D\textsubscript{2} exchange at stepped Pt surfaces).(17) At these defect sites both low and high coordination atoms are exposed, the atoms at the bottom of the step having a large number of nearest neighbors while those at the top of the step have low coordination. Thus, such sites provide for high catalytic activity and also for strong chemical bonding at the bottom and at the top of the step, respectively.

A recently developed theory(18) of metal catalysis proposes correlations between catalytic activity and low energy local electronic fluctuations in transition metals. Maximum electronic fluctuations take place at high coordination metal sites. Either atomically rough surfaces that expose large
numbers of nonmagnetic or weakly magnetic neighbors to the reactant molecules in the first or second layer or stepped and kinked surfaces are the most active in carrying out structure-sensitive catalytic reactions.

Electronic fluctuations that are of importance include charge fluctuations, configuration fluctuations, spin fluctuations and term and multiplet fluctuations. Configuration fluctuations are larger for those atoms which have a large number of metallic neighbors and these should thus be more catalytically active. Also, the catalytic activity of the transition metal atoms is directly related to their unfilled d-shells. 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 which insulate the metal from direct contact with some of the reactants.

(b) The Role and Reactivity of Strongly Adsorbed Overlayers

The overlayer of strongly adsorbed molecules also plays important roles in certain catalytic reactions. One of these reactions is the hydrogenation of ethylene, $\text{C}_2\text{H}_4$. (19) When $\text{C}_2\text{H}_4$ is introduced along with $\text{H}_2$ in a steady flow over Pt or Rh surfaces at 300K and 1 atm., hydrogenation to $\text{C}_2\text{H}_6$ occurs with very high turnover rates. An ethylidyne overlayer forms almost instantaneously, however, and $^{14}\text{C}$ labeling and spectroscopic studies indicate that the hydrogenation occurs by the mediation of this overlayer that permits $\text{H}_2$ adsorption and atomization on the metal surface but blocks the direct adsorption of $\text{C}_2\text{H}_4$ on the metal. A mechanism that explains all of the experimental data is shown in Figure 10. The hydrogen transfer via
formation of an ethylidene intermediate is implicated as the key hydrogenation step, while ethylene does not contact directly the metal surface.

Of course this is not the only mechanism for \( \text{C}_2\text{H}_4 \) hydrogenation. At higher temperatures the strongly adsorbed \( \text{C}_2\text{H}_3 \) groups are rehydrogenated at sufficiently high rates to expose the bare metal sites to the incoming \( \text{C}_2\text{H}_4 \) molecules continuously. At electrode surfaces in aqueous solution, \( \text{C}_2\text{H}_4 \) hydrogenation occurs in the presence of an external potential over a metal surface which is covered with a large concentration of hydrogen atoms that makes the hydrogenation of approaching ethylene molecules instantaneous without the formation of the ethylidyne groups.

For most hydrocarbon conversion reactions (isomerization, dehydrocyclization and hydrogenolysis) both the catalyst surface structure and hydrogen transfer via the strongly held carbonaceous deposit play important catalytic roles. Thus, the reaction conditions are adjusted to continuously expose some of the bare metal sites to the incoming reactants that also migrate onto the strongly held deposit to participate in chemical interactions at both sites 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 (Figure 1).

c.) The Oxidation State of Surface Atoms

There are several experimental studies published in recent years that indicate the importance of oxidation states other than the zero valent
metallic state for catalyzed reactions. During the hydrogenation of carbon monoxide over rhodium, rhodium was reported to yield predominantly \( \text{C}_2 \) oxygenated products, acetaldehyde and acetic acid, when prepared under appropriate experimental conditions.\(^{(21)}\) Our studies using unsupported polycrystalline rhodium foils have detected mostly methane along with small amounts of ethylene and propylene under very similar experimental conditions. This product distribution was identical to that obtained by others over supported rhodium catalysts along with the activation energies for methanation about 24 kcal per mole that we both found.\(^{(21)}\) It appears that most of the organic molecules form following the dissociation of carbon monoxide, by the rehydrogenation of \( \text{CH}_x \) units in the manner similar to alkane and alkene production from \( \text{CO}/\text{H}_2 \) mixtures over other more transition metal catalysts (iron, ruthenium, and nickel). However, when rhodium oxide (\( \text{Rh}_2\text{O}_3 \)) was utilized as a catalyst, large concentrations of oxygenated \( \text{C}_2 \) or \( \text{C}_3 \) hydrocarbons were produced including ethanol, acetaldehyde and propionaldehyde.\(^{(21)}\) Furthermore, the addition of \( \text{C}_2\text{H}_4 \) to the \( \text{CO}/\text{H}_2 \) mixture yielded propionaldehyde indicating the carbonylation ability of \( \text{Rh}_2\text{O}_3 \). Under similar experimental conditions over rhodium metal, \( \text{C}_2\text{H}_4 \) was quantitatively hydrogenated to ethane and carbonylation activity was totally absent. Clearly, higher oxidation state rhodium ions are necessary to produce the oxygenated molecules. Similar behavior was exhibited by molybdenum. The metal produced methane and other two or three carbon containing alkanes or alkenes while molybdenum compounds that contain molybdenum ions in higher oxidation states produce alcohols from carbon monoxide and hydrogen. The marked change of selectivity in \( \text{CO}/\text{H}_2 \) reactions upon alteration of the oxidation state of the transition metal is due largely
to the change of heats of adsorption of CO and D_2(H_2) as the oxidation state of the transition metal ion is varied. The CO adsorption energy is decreased upon oxidation while the heat of adsorption of D_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, while 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 higher oxidation states of transition metal ion in the reducing reaction environment. It appears that the strong metal support interaction 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, as 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 shown by the catalytic cycle leading to the photocatalyzed dissociation of water on strontium titanate, SrTiO_3, surfaces. This is shown in Figure 12. 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 3.1eV or larger energy, electron-hole pairs are generated. The electron is utilized to reduce the Ti^{4+} to Ti^{3+} formal oxidation state. The electron vacancy
induces charge transfer from the hydroxyl group that produces OH radicals that
dimerize to $\text{H}_2\text{O}_2$ and splits off oxygen that evolves. The reduced Ti$^{3+}$
containing surface can now adsorb another water molecule that acts as an
oxidizing agent to produce Ti$^{4+}$ again and a hydroxylated surface, evolving
hydrogen in the process. (22) Clearly, changes of oxidation states of
transition metal ions are frequently indispensible reaction steps in catalytic
processes. (22)

We have thus identified several of the molecular ingredients 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, to establish direct correlation
between these molecular parameters and the catalytic behavior eluded the
practitioners of catalysis in the past. Surface science has provided the
techniques for determination of the atomic structure, composition and
oxidation state of surface atoms, and adsorbed molecules in the monolayer and
when combined with studies of the kinetic parameters of catalytic reactions
(rates, selectivities, activation energies) the all important correlations
between the molecular ingredients on the catalyst surface and the high
pressure catalytic reaction behavior could be established.
Surface Science Studies of High Surface Area Catalyst Systems

There are many catalyst systems that demand the investigation of the high surface area catalysts directly instead of the use of model low surface area systems. One of these is the zeolites, (23) high surface area alumina silicates (Figure 13) with pores of molecular dimensions. These are the highest volume catalysts used in the chemical and petroleum technologies for alkylation, cracking, hydrocracking, isomerization, cyclization and dehydrocyclization. Solid state NMR, X-ray photoelectron spectroscopy (XPS) and extended X-ray adsorption fine structure (EXAFS) studies using high intensity synchrotron radiation along with a variety of chemical probes were found eminently successful to determine the structure and composition of these crystalline materials. Metal-oxide catalyst systems that consist of metals dispersed as small particles on high surface area oxide supports (alumina, silica, titanium oxide, zirconia, lanthanum oxide, magnesium oxide,) have also been studied extensively by surface science. Molecular level scrutiny reveals not only the atomic structure and size of the metal particles and the pore structure of the oxides but also their nucleation in solution as clusters and their growth that controls 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.

Studies of New Reactions

The tools of surface science were first employed to understand, in molecular detail, the working of catalysts that are important in technology. These included platinum that is used to produce high octane gasoline because of its superior 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. 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, commonly called "promoters", that when also co-adsorbed on the surface improve catalytic rates and selectivities to produce the desired molecules only, has been unravelled in many cases. Alkali metals, halogens and other transition metals that are used as alloying agents were among the promoters that were subjected to detailed surface science studies. The important role of the high surface area oxides support to stabilize the structure and oxidation states of transition metal catalysts or modify their chemistry was uncovered. By appropriate variation of the composition or structure and additives, the catalytic behavior could be systematically modified to produce new generations of more selective, active and longer life catalysts. Thus, surface science converted the technology of catalyst fabrication to high technology. Examples of new high technology catalyst systems are the new generations of catalytically superior zeolites with high Si/Al ratio. This research made possible the discovery of new zeolite systems
that are made of aluminum phosphates. It appears that the production of crystalline solids of various chemical compositions that contain channels of molecular dimensions, similar to that of the alumina silicates, can be attained. The catalytic converter on automobiles is another example of the development of a surface science based, successful high technology that cleaned up the automobile exhaust. New generations of platinum, silver and molybdenum catalysts have appeared of higher selectivity and useful life.

The energy crisis accelerated the development of new chemical technologies that produce chemicals and fuels from carbon monoxide and hydrogen. Surface science has been utilized extensively in this research as shown clearly by the many research papers that were published in the Journal of Catalysis, Surface Science and the Journal of Physical Chemistry, just to name a few frequently used journals. The strong metal-oxide support interaction was uncovered to have beneficial effects on controlling the oxidation state and the surface structure of catalysts. Surface compounds that were formed from two or more metals with unusual thermodynamic and catalytic properties were discovered (often called bimetallic clusters).

Surface science is increasingly being employed to develop catalysts for carrying out new reactions that have not received attention before. These include the photocatalyzed 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.
There is a large number of academic institutions with strong focus in surface science and catalysis. There is also strong industrial participation in the research of these newly formed centers that educate new generations of scientists and engineers in this sub-discipline of chemistry.

Surfaces are not only used as active agents (catalysts for example) but also for passivation to inhibit chemical or mechanical damage to the solid. They are the first line of defense of the condensed phase against external attack like chemical corrosion or high energy radiation. The development of adhesion and lubrication science and the science of passive coatings to prevent chemical or mechanical damage will benefit greatly from molecular level surface science studies.

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

It appears that as catalysis based technologies are converted to high technology, 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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**FIGURE CAPTIONS**

Figure 1. Idealized atomic surface structures for the flat (100) fcc (a) and (111) fcc (b) crystal faces, the rough (111) bcc (c), (1121) hcp (d) and (1120) hcp (e) crystal faces and for some of the stepped (f) and kinked (g) fcc crystal faces.

Figure 2a. Schematic representation of relaxation at the surface; a contraction of the interlayer distance as compared to that in the bulk.

Figure 2b. Structure of the reconstructed (100) crystal face as solved by surface crystallography.

Figure 2c. Top and side views of ideal, bulk-like Si(100) at the left and the reconstructed real Si(100) surface at the right. Layer-spacing contractions and intralayer atomic displacement relative to the bulk structure are given. Shading differentiates surface layers.

Figure 3. 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.

Figure 4a. Top site bonding structure of carbon monoxide on Ni(100) from low-energy electron diffraction and electron spectroscopy studies.

Figure 4b. Bridge site adsorption structure of carbon monoxide on Pd(100) at a half monolayer coverage.

Figure 4c. Structure determined by low-energy electron diffraction for a saturation coverage of carbon monoxide on Rh(111). Top and side views are shown. Large circles represent Rh atoms while smaller circles correspond to C and O atoms. Solid lines show the structure expected for hexagonal close-packing of the carbon monoxide while dotted circles depict the actual structure.

Figure 5. Isosteric heat of adsorption for CO on the Pd(111) crystal face as a function of coverage. (After H. Conrad, G. Ertl, J. Koch, and E.E. Latta, Surf. Sci. 43, 462 [1974]).

Figure 6. The surface structure of ethylidyne (bond distances and angles) is compared with several tri-nuclear metal cluster compounds of similar structure.

Figure 7. Schematic representation of the various organic fragments that are present on metal surfaces at higher temperature. The presence of CH, C₂, C₂H, CH₂, and CCH₃ species has been detected.
Figure 8. Thermal desorption spectra for hydrogen chemisorbed on flat Pt(111), stepped Pt(557), and kinked Pt(12,9,8) surfaces.

Figure 9. The remarkable surface structure sensitivity of the iron-catalyzed ammonia synthesis.

Figure 10. Proposed mechanism for the rapid, structure-insensitive hydrogenation of ethylene.

Figure 11. Model for the working platinum catalyst that was developed from our combination of surface studies using single crystal surfaces and hydrocarbon reaction rate studies on these same surfaces.

Figure 12. A proposed mechanism for the photodissociation of water over TiO₂ and SrTiO₃ surfaces.

Figure 13. Two recently synthesized zeolites with large silicon to aluminum ratios.
### TABLE 1

**FREQUENTLY USED TECHNIQUES OF SURFACE SCIENCE FOR STUDIES OF CATALYSTS**

- **ELECTRON SCATTERING**
  - Electron Spectroscopies (XPS, HREELS, AES)
  - Low Energy Electron Diffraction (LEED)
  - Electron Microscopy

- **PHOTON SCATTERING (HIGH AND LOW INTENSITIES)**
  - Spectroscopies (IR, FTIR, Raman, Solid State NMR, ESR, EXAFS, NEXAFS, Laser techniques)
  - Grazing angle X-ray Diffraction

- **MOLECULE AND ION SCATTERING**
  - Molecular Beam-surface interaction
  - SIMS, ISS

- **OTHER TECHNIQUES**
  - Radiotracer labeling
  - Mossbauer spectroscopy
  - Thermal desorption
Fig. 1f

fcc (977)  fcc (755)  fcc (533)
fcc (100): buckled hexagonal top layer

two-bridge  top/center

Fig. 2b
Si (100)

ideal

Si (100)
p (2x1)

Fig. 2c
Fig. 3
Ni (100) + c (2×2) CO

Fig. 4a
Pd (100) + (2√2×√2) R 45° 2 CO

Fig. 4b
Fig. 4c
Fig. 5

E_{ad} [kcal/mole] C \((4 \times 2) 45^\circ\)

XBL 7911-12823
Different ethylidyne species: bond distances and angles
($r_C = \text{carbon covalent radius}; \ r_M = \text{bulk metal atomic radius}$)

<table>
<thead>
<tr>
<th>Species</th>
<th>C [Å]</th>
<th>m</th>
<th>$r_M$</th>
<th>$r_C$</th>
<th>$\alpha$ [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co$_3$ (CO)$_9$ CCH$_3$</td>
<td>1.53 (3)</td>
<td>1.90 (2)</td>
<td>1.25</td>
<td>0.65</td>
<td>131.3</td>
</tr>
<tr>
<td>H$_3$ Ru$_3$ (CO)$_9$ CCH$_3$</td>
<td>1.51 (2)</td>
<td>2.08 (1)</td>
<td>1.34</td>
<td>0.74</td>
<td>128.1</td>
</tr>
<tr>
<td>H$_3$ Os$_3$ (CO)$_9$ CCH$_3$</td>
<td>1.51 (2)</td>
<td>2.08 (1)</td>
<td>1.35</td>
<td>0.73</td>
<td>128.1</td>
</tr>
<tr>
<td>Pt$^+$ (111) + (2 × 2) CCH$_3$</td>
<td>1.50</td>
<td>2.00</td>
<td>1.39</td>
<td>0.61</td>
<td>127.0</td>
</tr>
<tr>
<td>Rh (111) + (2 × 2) CCH$_3$</td>
<td>1.45 (10)</td>
<td>2.03 (7)</td>
<td>1.34</td>
<td>0.69</td>
<td>130.2</td>
</tr>
<tr>
<td>H$_3$C - CH$_3$</td>
<td>1.54</td>
<td></td>
<td></td>
<td>0.77</td>
<td>109.5</td>
</tr>
<tr>
<td>H$_2$C = CH$_2$</td>
<td>1.33</td>
<td></td>
<td></td>
<td>0.68</td>
<td>122.3</td>
</tr>
<tr>
<td>HC = CH</td>
<td>1.20</td>
<td></td>
<td></td>
<td>0.60</td>
<td>180.0</td>
</tr>
</tbody>
</table>

Fig. 6
Fig. 8
Fe

(III)

C₄ (SOLID)  C₇ (DOTTED)

(100)

C₄ (SOLID)  C₈ (DOTTED)

(110)

C₆ (SOLID)  C₈ (DOTTED)

NH₃ SYNTHESIS YIELD (a.u.)

Fig. 9
PROPOSED MECHANISM FOR ETHYLENE HYDROGENATION

Fig. 10
MODEL FOR THE WORKING PLATINUM CATALYST

3D Carbon Island

Carbonaceous Overlayer

Uncovered Ensemble Of Pt Sites

Fig. 11
\[
\begin{align*}
\text{OH}^- \quad \text{Ti}^{4+} \quad \text{O}^2- \quad \text{Ti}^{4+} \\
\text{Ti}^{3+} \quad \text{O}^2- \quad \text{Ti}^{3+} \\
\text{Ti}^{3+} \quad \text{O}^2- \quad \text{Ti}^{3+} \\
\text{H}_2\text{O}_2 \quad \text{H}_2\text{O} \quad \text{Ti}^{4+} \quad \text{O}^2- \quad \text{Ti}^{4+} \quad \text{H}_2
\end{align*}
\]

Van Damme and Hall, JACS 101 4373

Fig. 12
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