29 October 1982, Volume 218, Number 4571 **SCIENCE**

Surface Science of Heterogeneous Reactions

John M. White

Summary. Some of the present and future directions for surface science as a growing and naturally interdisciplinary subject are reviewed. Particular attention is given to surface reaction chemistry as it is related to heterogeneous catalysis, a subject area where there are abundant opportunities for detailed measurements of structure and dynamics at the molecular level.

The study of interfaces, with their interesting and significant physical and chemical processes, is an old discipline which has recently reawakened. To appreciate the role of interfaces in many phenomena one need only recognize that, in any multiphase system, communication between the bulk phases occurs through the surfaces that connect them. Even when these surfaces comprise a small fraction of the total volume of the system, they may have a dominant effect, as in grain boundary segregation and fracture of steels and in Schottky-barrier electronic devices. When the surface-to-volume ratio of a system is large, the physical and chemical properties of the system reflect, in large measure, the surface properties. Examples include clays, porous membranes in living systems, dispersed metals in heterogeneous catalysis, thin and narrow electronic devices, and colloids. This article is focused on chemisorption and reactions on well-characterized surfaces.

The vigorous growth of this kind of surface science research over the past 15 years is indicated by the increased number of journal pages devoted to this field and of professional meetings where this area is represented. *Surface Science*, one of the discipline's major journals, has grown eightfold since 1964, and the American Vacuum Society's annual meeting, long a major surface science forum, now has an almost overwhelming number of contributed papers. Interest in surface chemistry, discussed earlier by Somorjai (*1*), continues to grow and there are numerous exciting unexplored areas. In many respects we are just beginning to chart this dimension of the material world. In this article I give my own views, as a chemist interested in reaction dynamics and surface analysis, about some of the more promising directions for future research.

Opportunities for Surface Science

The opportunities in experimental surface science derive in no small measure from a developing arsenal of probes: electron guns, atom guns, neutron guns, ion guns, and photon guns have been fired at surfaces to eject or scatter electrons, ions, photons, and neutral particles in almost every conceivable combination in one or another experiment. The number of techniques, about 80 in 1978 (*2*), continues to increase.

Because even the simplest surface chemical reactions—for example, chemisorption bond formation or atom recombination at a single-crystal metal surface—are very complex at the molecular level, understanding at this level requires the application of many complementary experimental and theoretical tools. Detailed information, both structural and kinetic, is required.

Surface Structure

As in all of chemistry and solid-state physics, atomic and electronic measurements lie at the heart of a satisfying description of surface structure. Processes that occur at surfaces are described in terms of the time evolution of reactant, product, and intermediate structures. Without definition of surface structures in terms of equilibrium bond lengths and bond angles as well as the potential energy functions that describe their variations, an adequate description of reactions at the molecular level is impossible. In the language of the chemist, structure and reactivity (or function) are intimately related, and an understanding of reactivity generally follows an understanding of structure.

Along with atomic structure, the surface electronic structure is important for an understanding of surface reactions. Bulk electronic structure determination, one of the central subjects of solid-state physics, is one base from which to work toward the surface. Molecular electronic structure determination, a hallmark of physical chemistry, is another. Both views are often helpful, as in the study of chemisorption and heterogeneous catalysis. This illustrates one of the distinguishing features of research in surface science—its naturally interdisciplinary character.

Electron Spectroscopies

Several recent articles have summarized some of the approaches used to determine surface structure (*3*). I will mention only briefly some of the topics covered there: ultraviolet photoelectron spectroscopy (UPS), x-ray photoemission spectroscopy (XPS), low-energy electron diffraction (LEED), x-ray absorption fine structure (EXAFS), Bragg diffraction, photoelectron diffraction, stimulated desorption, helium beam scattering, and Rutherford scattering.

The author is a professor of chemistry and chairman of the Department of Chemistry, University of Texas, Austin 78712.

0036-8075/82/1029-0429$01.00/0

The traditional method for determining surface structure is LEED. In a few cases it has provided local atomic structures, but progress has been slow and the method is limited to ordered structures. With the development of synchrotron sources, several new photon-based methods have emerged. Among the more promising is a surface version of x-ray absorption fine-structure spectroscopy known as SEXAFS (*4*). A major advantage of the fine-structure method is that it does not require long-range order, which is necessary in LEED. Consequently, amorphous materials, such as many catalysts, can be examined successfully. In view of the great practical importance of such materials, we can expect an expanding role for these measurements and they should become a standard part of catalyst characterization.

While EXAFS and SEXAFS will provide important insights into the structures of amorphous materials, an important question is left unanswered: How do small concentrations of special active sites participate in surface reactions? What we need are site-specific and atom-specific probes that are capable of detecting very small concentrations. Among the more promising techniques are photon- and electron-stimulated desorption (PSD and ESD) (*3, 5, 6*).

Another approach, based on line shapes of Auger electron emission, is being pursued experimentally and theoretically with the goals of "fingerprinting" and interpreting the local electronic structure around a chemisorbed atom. In this work, the familiar chemical concepts of orbital hybridization and polarization play a central qualitative role. Auger spectra are now available for a series of hydrocarbons in the gas and solid phases and clearly show different carbon atom Auger [C(KVV)] "fingerprints" depending on the hybridization of s and p orbitals at the probed atom (*7*). There is considerable interest in extending this work to monolayer and submonolayer amounts of hydrocarbons and other small fragments of catalytic interest. Examples include the distinction between carbide and graphite formed on Ni(100) during methanation studies (*8*), the structure of ammonia on aluminum and oxidized aluminum (*9*), and the C(KVV) line shape for carbon monoxide on hydrogen-covered Ni(100) (*10*). Extension of this work to other fragments and organometallic compounds is a very promising area of research in surface chemistry, particularly in relation to the identification and kinetics of surface species formed during reactions.

Optical and Magnetic Spectroscopies

An important problem for surface science is the measurement of surface structure at the interface between a solid and a high-pressure gas or liquid under reaction conditions. Except with very special apparatus, it is not possible to use electron spectroscopy for such measurements because the scattering length becomes short compared to the analyzer dimensions and the electrons lose their atom-specific initial kinetic energies. Optical and magnetic spectroscopies are ideally suited to this kind of measurement and have long been used to characterize samples with high surface areas. Single-crystal work, which should provide benchmarks for our understanding of surface species and processes at the molecular level, is meager and is not yet possible with nuclear magnetic resonance (NMR) and electron spin resonance (ESR) spectroscopies. A recent review emphasizing the detection of chemisorbed species and substrate surface properties notes the complexity of NMR experiments even on samples with high surface areas (*11*). The major difficulties are traceable to the large line widths of the spectra, which reduce resolution and signal-to-noise ratio.

Although infrared studies of single-crystal surfaces exist, they are limited to a few systems, mainly involving chemisorbed CO (*12*). A very important prospect for surface science is the development of routinely applicable infrared instrumentation capable of detecting submonolayer amounts of species chemisorbed on single-crystal surfaces (*13*).

Like infrared measurements, surface Raman spectroscopy provides vibrational data, but it may be even more generally applicable to liquid-solid and high-pressure gas–solid interfaces because the exciting light can be turned into a region where the gas or liquid does not absorb. In surface-enhanced Raman spectroscopy, signals up to six orders of magnitude larger than expected on the basis of ordinary Raman scattering cross sections are observed (*14*). Equally exciting has been the prospect of measuring, with a good signal-to-noise ratio, the ordinary Raman spectra of submonolayer coverages of species on single-crystal surfaces. This has recently been realized for molecular and dissociated nitrobenzene on a very smooth, well-characterized surface of Ni(111), where the surface enhancement was less than a factor of 3 and, within experimental error, was not detectable (*15*). With this advance, the range of applicability of Raman spectroscopy was significantly expanded; enhancement is no longer necessary, and studies of single-crystal catalytic surfaces under reaction conditions, for example, are now within reach.

Besides infrared and Raman spectroscopy, high-resolution electron energy loss spectroscopy (HREELS) provides vibrational frequencies of species adsorbed at a surface (*16*). The resolution of this technique (30 to 40 cm^{-1}) is poor compared to that of infrared spectroscopy (1 cm^{-1}) and it cannot be applied at high pressures; however, it is more sensitive than infrared spectroscopy, particularly to low-frequency vibrations ($< 500\ \text{cm}^{-1}$), which include many adsorbate-substrate frequencies. Moreover, the most straightforward application of the technique is to species chemisorbed on single-crystal surfaces—just where some of the greatest limitations of infrared exist. Half-widths as low as 32 cm^{-1} for the elastically scattered beam are achievable with count rates suitable for detecting 0.05 monolayer of adsorbed species (*17*). With this resolution and sensitivity, adsorbed intermediates formed in chemical reactions can be detected and their structures determined. Adsorbate-adsorbate interactions can be probed and surface binding sites can be determined.

Reactions at Surfaces

The detailed study of reactions at surfaces is a formidable task even for the simplest systems. The complexity of the task becomes clearer when one considers the number of variables and the heterogeneity that must be controlled. For instance, gas-solid reactions may be heterogeneous in several ways:

1) In the usual sense, the systems are heterogeneous because two bulk phases, gas and solid, are present.

2) The surface itself is heterogenous, both intrinsically and extrinsically. Intrinsic heterogeneity involves such things as steps, kinks, and local impurities. Extrinsic heterogeneity is the result of reconstruction induced by the reaction.

3) There may also be significant heterogeneity in the adsorbed phase, particularly when two or more adsorbates are involved. In some cases coadsorption leads to homogeneous mixing, while in other cases the species are segregated. This kind of surface heterogeneity has implications for the kinetics of surface processes, as a full kinetic description requires knowledge of the coverage and organization of each adsorbed species.

Because of these complications, such precautions as controlling the gas-phase concentrations, the clean surface structure, and the bulk temperatures, although important, will often not be sufficient for an adequate kinetic description, even in an average, global sense. Useful empirical results can be obtained, but no satisfying molecular level description will emerge. It will seldom be possible to adequately describe surface reaction rates by using kinetic equations that are based on two-dimensional homogeneity.

Molecular Dynamics

We would like a molecular level description in which a system prepared in a fully specified initial quantum state is followed in time to a fully specified set of realizable final states. Such state-to-state molecular dynamics, long a goal of gas-phase molecular dynamics research, is not within reach, but it does give direction in the sense that many of the tools of gas-phase reactive molecular beam scattering and of pulsed laser excitation and detection can be carried over to surface dynamics research.

In applying reactive molecular beam scattering to the study of carbon monoxide oxidation, a modulated beam of CO molecules is directed at a well-characterized single-crystal surface and the scattered species, both reactive (CO_2) and nonreactive (CO), are detected as a function of angle with respect to the surface normal. From such studies, the mechanism of the reaction on palladium and platinum has been clarified (*18, 19*). Neither a direct reaction between gas-phase CO and adsorbed atomic oxygen nor a reaction from a weakly held physically adsorbed state of CO (Eley-Rideal mechanism) makes a significant contribution to the rate. Rather, the reaction occurs between chemisorbed CO and chemisorbed atomic oxygen, where the CO enters a strongly bound chemisorbed state (binding energy, 30 kilocalories per mole) before it reacts. This is known as the Langmuir-Hinshelwood mechanism. In addition to entering a chemisorbed state before reacting, the CO is very mobile under reaction conditions so that, once adsorbed, it can "search for" an oxygen atom with which to react. The detail provided by molecular beam scattering makes it a very promising technique for application to reactions that occur with a relatively high probability per collision. As noted above, the future of this approach lies in the not fully realizable direction of preparing beams of reactants in a single quantum state and detecting separately all of the quantum states of the products.

Fundamental aspects of the dynamics of surface reactions can also be probed by using laser excitation of reactants and laser detection of products. For example, the role played by the reactant's vibrational energy in dissociative chemisorption can be studied by laser excitation of a molecule before it collides with a surface or after it is physisorbed. The partitioning of energy between various modes of a molecule during desorption can be probed by using time-of-flight measurements to establish kinetic energy distributions and laser-induced fluorescence or infrared emission to monitor the energy in vibration and rotation. Exciting results have been obtained for a number of reactions, including CO oxidation and NO desorption. In the former case, molecular beam time-of-flight measurements show that CO_2 is desorbed from platinum with translational temperatures near 3000 K even though the surface temperature is around 700 K (*20*). Measurement of the infrared emission from CO_2 during desorption shows that vibrationally hot nascent molecules are formed (*21, 22*).

Because it is relatively easy to detect with laser-induced fluorescence and because its surface chemistry is of great interest, NO has been the subject of a number of studies on energy partitioning in scattering or desorption. Measurements of NO scattered from graphite-covered Pt(111) (*23*) and from Ag(111) (*24, 25*) show that rotational state populations can be described by Boltzmann-like distributions and that the degree of energy accommodation depends strongly on the nature of the surface. Recent measurements of NO being desorbed from Ru(001) in a temperature-programmed experiment are also described by a single rotational temperature (235 K) that is significantly lower than the surface temperature at the desorption maximum (455 K) (*26*).

Another promising research area involves the use of tunable high-intensity synchrotron light sources coupled with pulsed molecular beam–laser systems to perform real-time photoemission experiments on surface reactions. These experiments, and others like them, are important for testing theoretical models of surface processes because they provide considerable detail which acceptable candidates must reproduce or predict.

Theoretical studies of the dynamics of surface processes are in their infancy (*27*) but it is clear that the detailed dynamics often play an important role (*28*). Trajectory modeling of surface processes is now possible and provides some tantalizing insights.

Transient Kinetics

Low-pressure titration experiments, in which surface concentrations and product desorption rates are measured simultaneously, provide information on the reactivity of surface species and the operating mechanisms. For a kineticist, even a global description of a surface reaction involves equations containing surface concentrations, which, to be useful, must be measured under reaction conditions. In the case of carbon monoxide oxidation, much insight has been attained by such measurements (*29*), particularly as they complement molecular beam studies. Another example, the titration by hydrogen of oxygen chemisorbed on Ru(001), is characterized by rates that depend on the concentration and organization of the oxygen (*30*). Under some conditions a very long induction time is followed by a rapid reaction region and finally by a very slow reaction region. The interpretation, based on both kinetic and structural data, involves an island boundary reaction mechanism and both surface and subsurface oxygen. Because they are fast and relatively straightforward, such experiments will continue to be very useful in assessing the kinetics of a variety of reactions. For example, a standard test titration reaction can be used to investigate how the kinetics are altered by systematic changes in the substrate surface and surface concentrations of adsorbed species.

In much the same way, thermal desorption spectroscopy will continue to be a workhorse technique. There is an enormous literature on the thermal desorption spectroscopy of single adsorbates. When desorption occurs through several channels, including several products, such experiments provide valuable mechanistic information. For example, the decomposition pathways for several different small carbon-, hydrogen-, and oxygen-containing molecules have been mapped by measuring desorption peak temperatures, peak profiles, and peak areas for all the detectable products (*31*). Extension of this work to other surfaces and more complex adsorbates will supply kinetic information and point to conditions where direct spectroscopic examination of the surface should be particularly fruitful. However, one should be aware of the difficulties of interpreting measured and calculated thermal desorption parameters in terms of binding energies and preexponential factors.

Thermal desorption spectroscopy will be particularly helpful in the study of coadsorbed species. These measurements are valuable because many surface chemical reactions involve the adsorption of two or more gas-phase species. An example is the coadsorption of CO and H on single-crystal transition metal surfaces under conditions where reactions between the two species occur with low probability. Coadsorption on Ni(100) at 100 K leads to a homogeneous mixed surface phase, whereas on Ni(111) the CO and H tend to segregate (*32*). Warming of the Ni(100) substrate is accompanied by structural and phase transformations with and without desorption, indicating the diversity and richness of this relatively simple system even in the absence of extensive reaction. By using the thermal desorption data to point out interesting conditions, we have had considerable success in measuring the accompanying electronic structural changes (*33*).

An attractive feature of thermal desorption spectroscopy is its speed and simplicity. Other fast complementary methods, particularly those that are sensitive to surface rearrangements without desorption, will be very helpful. For example, we recently used temperature-programmed static secondary ion mass spectrometry (TPSSIMS) in a study of the behavior of water adsorbed on Pt(111) and showed (*34*) that desorbed ion fluxes, measured as a function of time while raising the substrate temperature, follow the normal thermal desorption spectra without the complicating background desorption effects that are found in normal thermal desorption experiments. Even more interesting is the detection of a low-temperature surface rearrangement which, on the basis of other spectroscopic work (*35*), is attributed to surface decomposition of water into adsorbed OH. As with normal thermal desorption spectroscopy, the major attractive feature of this approach is the ability to target particular conditions where other, more time-consuming spectroscopies will be particularly useful.

Surface Science and Catalysis

The connection between surface science and catalysis will continue to be vigorously pursued. This connection is not easy to make because of the vast pressure difference that exists between practical catalytic conditions and electron spectroscopic conditions of surface science. Moreover, the highly dispersed supported transition metal catalysts typical of industrial reactions are often significantly different from their single-crystal analogs. However, for some reactions the rates and activation energies for both types of catalysts have proved to be identical. A notable example is the methanation reaction over nickel (*8, 36*). At least for this case surface science experiments on single-crystal substrates which characterize the rates of production and reaction of surface carbide are directly relatable to the kinetics of methanation under practical conditions. These experiments and others like them (*37, 38*) involve measuring reaction rates at pressures of the order of 1 atmosphere with "before and after" electron spectroscopic analysis in ultrahigh vacuum. This technique and others, such as surface Raman spectroscopy, which bring together surface science and heterogeneous catalysis, will provide the experimental basis for many future investigations.

As another example of how surface science and heterogeneous catalysis can be connected, it is now possible to synthesize in situ thin metal oxide films which are suitable for electron spectroscopic and thermal desorption studies and which model high-surface-area materials typical of commercial catalysts. Controlled in situ deposition of transition metals accompanied by studies of chemisorption and reaction, all in the controlled environment of an ultrahigh-vacuum surface analysis chamber and an attached reaction chamber, will provide a detailed model study with clear connections to practical systems. With such information, the results of optical and magnetic spectroscopic studies at high pressure will be even more meaningful.

From a chemist's perspective, a major goal of surface chemical science is to systematize available reaction and structure data. Advances have been made in this area by both experimentalists and theorists. For instance, cluster calculations have shown how the properties of small particles of variable size compare with bulk properties (*39, 40*) and how some chemisorption and catalytic events can be understood (*41*).

For reactions, connections and generalizations can be sought in several directions both within surface science itself and between surface science and other areas of chemistry: for example, establishing conceptual linkages (or the lack of them) between homogeneous and heterogeneous catalysis (*42*), between small metal particles and macroscopic single crystals, and between acid-base concepts as applied to gas- and solution-phase species and to species attached to surfaces (*43*). Such linkages would enable us to build qualitative models that would be helpful in designing new catalytic systems on a less empirical basis. Coupled with this synthesis of experimental results, theoretical work aimed at a deeper understanding of the roles of electronic and structural factors will be of great utility.

The rational design of surfaces with desired catalytic properties is one of the outstanding goals of surface chemistry. It would be naïve to think that this goal is just around the corner or can be realized through the application of surface science, classical catalytic, or macroscopic electronic techniques alone. Skillful use of all kinds of data is called for and individuals and groups need to avoid narrow focusing. Surface science can contribute in the ways described above and in other ways—for example, in the analysis of new materials formed through novel synthetic routes such as ion implantation and pulsed laser heating, and in the detailed study of chemisorption and reactions on multimetallic systems with low surface areas (*44*).

Finally, surface photochemistry is an area of great interest, for example, in relation to the conversion of solar energy to electrical or chemical energy. Advances have been made in understanding photoassisted reactions (*45–49*) with materials such as platinum and titanium dioxide, which form an interesting supported system having novel metal-support interactions. Model studies of the adsorption of hydrogen and carbon monoxide on platinum vapor deposited on TiO and TiO_2 thin films show that more than three monolayers of platinum must be present before measurable chemisorption of either H_2 or CO occurs at 100 K (*50*). The utilization of surface science techniques in the study of these reactions is a straightforward extension of the methods described above; what one would like to do is investigate surface reactions that are under way in the presence of light.

Advances in surface chemical science depend on continued financial support for students and instrumentation in academic institutions. These and other constraints have been discussed briefly in a guest editorial in *Science* (*51*).

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52. I gratefully acknowledge the support of the National Science Foundation, the Office of Naval Research, the Robert A. Welch Foundation, and the Petroleum Research Fund of the American Chemical Society.

Molecular Biology of Learning: Modulation of Transmitter Release

Eric R. Kandel and James H. Schwartz

Behavior is modified by experience through two processes—learning, the acquisition of new knowledge about the environment, and memory, its retention. Depending on how long the change in behavior persists, the memory is termed short term (minutes to hours) or long term (days to years). The mechanisms by which learning is acquired and memory retained are central to both neurobiology and psychology. Despite its importance for neurobiology, learning has not been approachable with the techniques of cell biology until recently.

The ability to study learning on the cellular level results from the realization that it is a universal feature of nervous systems (*1*). Not only are all animals capable of elementary forms of learning, but several learning processes first described in mammals—for example, habituation, sensitization, and classical conditioning—occur in similar form in mollusks and other invertebrates (*1–6*). This suggests that the cellular mechanisms for these forms of learning are the same throughout phylogeny and therefore can be studied effectively in higher invertebrates. Some of these animals have nervous systems made up of larger (as large as 1000 micrometers) and fewer (10^5 to 10^6) neurons than are found in vertebrates (10 to 100 μm; 10^{12}).

The body of neurophysiological work on vertebrates and invertebrates carried out during the past half century has suggested that both learning and memory are somehow expressed through changes in nerve cells. Recent studies in the marine snail *Aplysia* and in several other higher invertebrates indicate that simple forms of associative and nonassociative learning occur at identified cellular loci, the synaptic connections between specific neurons (*7–9*). Memory persisting for weeks can result from changes in the strength of already existing contacts (*7, 10, 11*). Prolonged changes in synaptic strength can be achieved by changing the amount of chemical transmitter released by the presynaptic terminals of specific neurons (*9, 12*).

With the recognition that certain forms of learning can alter the strength of specific synaptic connections, comes the possibility of investigating the molecular basis of the learning by defining the biochemical mechanisms that underlie the persistent changes in transmitter release. Do these mechanisms require expression of specific genes that lead to the synthesis of entirely new proteins? Are there posttranslational modifications of already existing molecules that alter their activities? Or do learning and memory make use of both processes? The large size of the nerve cells of higher invertebrates and the ability to identify individual neurons have already permitted electrophysiological analysis of the synapses at which learning takes place. These experimental advantages now also promise to be useful for exploring the molecular mechanisms underlying learning because biochemical processes can be causally related to functional (plastic) changes in specific nerve cells, and these plastic changes in turn can be causally related to the behavioral modification.

The purpose of this article is to describe how a behavioral system in *Aplysia* can be used to examine the mechanisms of several forms of learning at different levels of analysis: behavioral, cell-physiological, ultrastructural, and

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Dr. Kandel is a professor of physiology and psychiatry and Dr. Schwartz is a professor of physiology and neurology, Center for Neurobiology and Behavior, College of Physicians and Surgeons of Columbia University, and the New York State Psychiatric Institute, New York 10032.