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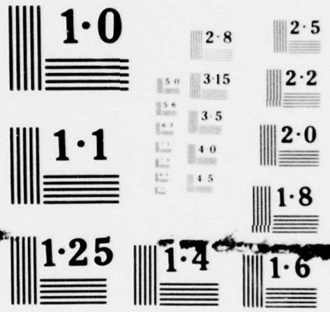

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The full potential of modern surface analysis techniques are beginning to be realized in studies of the chemical behavior of surfaces. Single crystal surfaces are often very active catalysts and are, thus, ideal substrates for studies of "model" reactions using molecular beams. Subsurface oxygen has been found to have a significant effect on the catalytic activity of several transition metals including nickel, cobalt, platinum, and rhodium.

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October 20, 1977

TECHNICAL REPORT

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MOLECULAR BEAM STUDIES OF MODEL CATALYTIC CHEMICAL REACTIONS

Of the many areas of interest to chemists and physicists, the field of heterogeneous catalysis has proven to be one of the most intractable to both experimental and theoretical investigation. In recent years the field has tended to become more multidisciplinary and most basic heterogeneous catalysis research is now considered a subset of the new field of "surface science." Whereas, much of our present understanding of the interactions of atoms, molecules and ions is the result of beam-type experiments in the gas phase, it is only recently that molecular beam studies of chemical interactions with surfaces have been undertaken with any degree of success. The technique is a powerful but specialized one that requires stringent experimental control of the surface as well as of the reacting species. This requires the use of clean, well defined, single crystal surfaces as the catalytic substrate.

The essence of a molecular beam experiment involves generating a well defined flux of atoms or molecules which, in catalysis studies, is directed onto a test surface. Reactions between two species can be studied by mixing two reactants in the beam, or by introducing a second reactant as an uncollimated gas at low pressures (below 10^{-4} torr) over the surface.

Many beam experiments are performed using simple Knudsen cell or effusive beam sources, but modern "supersonic nozzle" sources offer many advantages. The supersonic nozzle source operates by expanding a high pressure gas adiabatically through a tiny orifice, thereby obtaining a nearly monoenergetic beam. By "seeding" heavier gases in a lighter, faster moving gas like He, the nozzle source is capable of generating kinetic energies up to about 10 eV. Additional benefits of the supersonic nozzle are increased beam flux and a degree of control over the internal energies (vibrational and rotational) of the beam, independent of its translational energy. Early nozzle source systems required tremendously large vacuum pumps to handle the large gas loads they produced, but today's well designed system can be adequately pumped by a 6" or smaller diffusion pump.

Surfaces suitable for beam studies can be obtained by starting with bulk single crystals that are mechanically and chemically polished, then placed in ultra-high vacuum where they are cleaned by sputter etching, usually with argon ions at energies of a few kilovolts. Single crystal surfaces for beam studies can also be produced *in situ* by the epitaxial growth of vacuum evaporated films on crystalline substrates such as cleaved mica or alkali halides. After preparation, crystal surfaces are usually analyzed for chemical composition using Auger electron spectroscopy (AES) and/or X-ray or ultraviolet photoelectron spectroscopy (XPS, UPS) and the surface lattice geometry studied using low energy electron diffraction (LEED). These surface-sensitive probes are now part of the standard repertoire of surface science and their off-the-shelf commercial availability has given great impetus to this field in recent years.

While LEED provides a means of determining the repeated geometrical arrangements of atoms (including adsorbates) on the surface, random topological features such as steps, kinks and other faults and defects that vary from the ideal regular surface array can be investigated more readily by means of thermal energy atom scattering (TEAS). By comparing the scattering intensities of atoms such as helium, a measure of the atomic scale smoothness of the surface can be obtained. Like x-rays, the wavelength of thermal energy helium atoms is less than one angstrom, so that diffraction of He atoms from surfaces can also sometimes be observed.

Such diffraction was first observed as intense peaks in the scattering of He and H_2 from cleaved LiF surfaces by Estermann and Stern in Germany only shortly after Davisson and Germer first observed particle/wave effects in the scattering of electrons. On metal crystal surfaces the interaction potential energy variation across the surface is typically much less than on ionic crystals like LiF, so that these surfaces look much smoother to the incident atoms. However, it has been possible to observe helium and hydrogen diffraction from tungsten, tungsten carbide, and, very recently, from Ag(111)(1) surfaces. Since thermal energy atoms do not penetrate the surface they are an ideal surface probe and (TEAS) promises to become an increasingly important quantitative technique for probing surfaces. Surface structure, phonon spectra, and adsorbate coverages are currently being studied in several laboratories using this techniques.

In our laboratory we are using molecular beam techniques to study simple, surface catalyzed chemical reactions with the hope of understanding more completely the various steps involved in the reaction path, i.e., chemisorption, surface diffusion, recombination and desorption. Most of this work has been done on epitaxially grown single crystal films produced *in situ*. We have been able to prepare a variety of single crystal metal surfaces, including Pt, Ag, Au, Ni, Co, Fe, Pd, Al, Mg and Cu, by vacuum evaporation onto cleaved mica substrates. These films can be routinely prepared once the proper "recipe" has been determined, i.e., deposition rate, and substrate temperature. Epitaxial films are usually limited to one, or possibly two, crystal faces because the thermodynamics of crystal growth favor the minimum free energy surface. For example, face centered cubic (FCC) metals like Pt, etc., grow with the (111) surface exposed. However, minimum energy surfaces also predominate on polycrystalline materials, so they are often the most relevant in terms of characterizing the catalytic activity of the material. By varying the crystal growth parameters, polycrystalline or even amorphous films can also be obtained. This ability to vary the surface structure is important since some catalytic reactions have been found to be structure sensitive. For example, the dissociative chemisorption of oxygen and hydrogen on platinum has been studied extensively by molecular beams and other modern techniques. Somorjai and co-workers at Berkeley have shown, for example, that the surface "steps" provide sites that are more active for both oxygen and hydrogen chemisorption.(2) The theoretical explanation of this observation has focused on the degree of coordination of the surface atoms, i.e., the number of nearest neighbors, and the resulting changes in the electronic structure of the more exposed atoms at step sites.(3) Although the idea of localized active sites is an old one in catalysis, modern experimental surface techniques now allow investigators to begin to identify the nature of these sites and the particular role they play in the reaction path.

The question of the relevance of molecular beam and other experiments carried out at very low pressures, 10^{-10}-10^{-5} torr, to the "real" world of high pressure commercial processes, is often raised. In reply to this question there are several important facts that can be cited in support of work at low pressures. First, with surface reactions the relevant parameter is the surface coverage which usually has a very mild dependence on pressure. Second, when the kinetics of the reaction are optimized, the rapid removal of reactants keeps surface coverages quite low, sometimes less than a monolayer at high pressures. Last, and most convincing, the kinetics of fundamental catalytic reaction steps measured on clean, single crystal surfaces described, in a number of cases, the behavior observed at pressures above one atmosphere.

One important feature of molecular beam studies of surface reactions is the sensitivity limit of the technique. Although sensitivity varies with the particular geometry employed, the lower limits of detection usually fall in a range corresponding to a reaction probability per incident beam molecule of about 10^{-4}. Althought this may sound quite low, this reaction probability is actually enormous when compared with the activities of typical industrial catalysis. In terms of the more familiar "turnover number," $N = \frac{\text{reactions}}{\text{surface atom-sec}}$, introduced by Boudart for comparison of specific catalytic activities, values of N for industrial type catalysts are often less than unity, while a reaction probability per collision of 10^{-4} corresponds to values of N at atmospheric pressure in the range of 10^4-10^5.

Fortunately, we have found that many reactions involving the small, simple molecules preferred for molecular beam studies of model catalytic reactions proceed at readily detectable rates on single crystal transition metal surfaces. Molecular beam studies of simple catalytic reactions have been used to obtain important information on the interaction of species such as H_2, O_2, CO, CO_2, CH_4, C_2H_x, H_2O and their isotopes with single crystal surfaces of platinum, nickel, iron, cobalt and silver, and survey investigations indicate that many other gas-surface systems are also amenable to study using beams.

Our molecular beam studies have produced several surprises which have forced us to re-evaluate some of the traditional assumptions of catalysis. One such surprise was the discovery that molecules produced in surface reactions often desorb with energies that are quite unrelated to the surface temperature. One striking example of this phenomenon is the desorption of CO_2 from platinum surfaces where the molecule has been observed to desorb with a kinetic energy excess of about 7 kcal/mole.(4) This is roughly equivalent to a gas temperature of 3500°K, although, since the energy distribution is not Maxwellian, the term "temperature" is used rather loosely. A similar behavior has also been observed when hydrogen desorbs from platinum, nickel and copper surfaces.(5) Internal energies can also be similarly non-equilibrium following desorption of molecules from surfaces.(6) Now that the reasons for this behavior are beginning to be understood it appears that "non-equilibrium" desorption of reacted species is actually a fairly common phenomenon. For further theoretical and experimental details the reader should peruse the articles cited above. One consequence of these findings is that we must now reexamine the various chemical rate theories which generally assume that reactions proceed through a series of isothermal steps. It now seems possible that many chemical steps proceed very nearly adiabatically just like the chemical transitions that occur during desorption and chemisorption of gases on surfaces. Significant changes in chemical rate theory will inevitably occur if this indeed proves to be the case.

Another important result of beam studies of the kinetics of surface reactions concerns the relationship of the mechanism to the kinetics of these processes. Traditionally, chemists have considered essentially just two basic mechanisms for the chemical interaction of molecules on a surface. The first or Langmuir mechanism assumes that both interacting species adsorb onto the surface and then interact chemically as one or both species migrate across the surface. Rideal proposed an alternate reaction mechanism in which just one species is adsorbed and interacts more directly via impact with another species from the gas phase. The kinetics of these two cases have been discussed for many years in various papers and texts on the subject. However, in doing careful kinetic experiments on model catalytic reactions, it has become clear that it is often not possible to distinguish these two mechanisms from the kinetics alone. For example, in the much studied case of CO oxidation on platinum there are temperature/pressure regimes where the reaction is best described by Rideal kinetics even though more direct beam evidence indicates that the reaction proceeds via the interaction of rapidly diffusing surface CO with tightly chemisorbed oxygen atoms; i.e., the classic Langmuir mechanism. Actually, this is but one example of a rather general problem in chemical kinetics. Indeed, by choosing the appropriate rate limiting steps almost any reaction model can be made to yield the observed kinetics. This underlines the need for the kind of direct experimental evidence regarding chemical reaction paths that molecular beam experiments provide.

Our most recent experiments with molecular beams have been studies related to methanation synthesis from H_2/CO mixtures over nickel, cobalt and iron catalysts.(7) During the course of this work it was found that the activities of nickel and cobalt could be enhanced dramatically by the introduction of small amounts of subsurface oxygen to the catalyst. This can be accomplished by heating the catalyst in oxygen followed by mild reduction in hydrogen below $600^{o}K$. This procedure products subsurface oxygen which is stable in H_2/CO mixtures up to $\sim 600^{o}K$. For nickel, the increase in methanation activity, compared with the clean surface, is more than an order of magnitude while, with cobalt, the activity increases more than two orders of magnitude. The activity of iron, on the other hand, decreases when oxygen is introduced into the surface lattice. Other workers have noted an increase in the methanation activity of rhodium with oxygen treatment(8) and surface oxygen is suspected of playing an important role in the catalytic activity of platinum as well.(9) By noting subtle changes in the electronic properties of these surfaces that result from the introduction of oxygen into the surface lattice using, for example, photoelectron spectroscopy, it may be possible to identify the physical interaction that is responsible for the high catalytic activities of these surfaces.

In addition to the oxygen enhancement effect, the molecular beam experiments give strong, albeit indirect, evidence that the methanation proceeds via a labile surface carbon intermediate, at least on the active, oxygen treated surfaces. Several other workers have also reached similar conclusions in recently published work.(10) Thus, it appears that the old "carbide" theory that lost favor as the mechanism in Fischer-Tropsch synthesis may experience a revival as the dominant mechanism in methanation synthesis. However, this issue is far from resolved and alternate mechanisms involving intermediates such as CHO and CHOH are not without their proponents. Ultimately, this and other problems in catalysis will be resolved, not by deductions based on the kinetics of the overall reaction, but by direct observation of surface chemical intermediates using the various spectroscopies now available for this purpose.

Those of us working in the field of surface science are particularly aware of the development during the last decade of an unprecedented number of new tools for surface investigation. The full utilization of these techniques has been a slow process requiring the collective efforts of many researchers, each contributing to the various technical and theoretical problems associated with each technique. The collective expertise that now exists with the various complementary surface investigative techniques such as LEED, AES, UPS, XPS (or ESCA) and, of course, molecular beams is now beginning to be applied in earnest to significant problems in catalysis and other surface related areas. The indications from this vantage point are that the field is just beginning a period of unprecedented productivity. The implications for catalysis and other surface related technologies are enormous.

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