ular specificity and sensitivity. Although not discussed here, it is possible to probe phenomena associated with the interphase of the electrode surface. Examples are the evaluation of optical constants of the electrode surface,[58,59] the observation of surface adsorption of anions and Pb^{2+} complexes on a Hg–Pt OTE,[19] the study of organic adsorption by internal reflection spectroscopy,[60,61] and protein adsorption on Ge OTE by infrared internal reflection spectroscopy.[20] The main utility of OTE will undoubtedly be to assist in the elucidation of electrode mechanisms and the evaluation of associated kinetics of homogeneous reactions. We hope that chemists with interests in organic, inorganic, and biochemical redox systems will be encouraged to use spectroelectrochemistry. Perhaps this Account will stimulate them to try.

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Reactions on Single-Crystal Surfaces

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Reactions that require catalysis by solid surfaces have importance obvious to every chemist. They have been studied a great deal, but true understanding of just what occurs at the surface has been frustrated by difficulties in characterizing the active surfaces or in observing what happens to them as they react or catalyze a reaction.

In recent years it has been possible to obtain fundamental information about events that occur at reactive surfaces by employing techniques that are mostly new. In this work single crystals of metals are sliced so as to expose crystal faces of well-defined atomic arrangement. These faces are scrutinized by physical methods to determine surface structure and composition. A gaseous reactant can then be admitted and the kinetics of its reactions with the surface or as catalyzed by it can be studied. Finally, the very same surface can be examined during or after the reaction in order to see what changes have occurred.

The primary aim of such research is to uncover the elementary steps of surface chemical reactions. Surface reactions or catalyzed surface reactions take place under conditions of atom transport. Molecules impinge, adsorb, react on solid surfaces, and form intermediates of various lifetimes, and then the products desorb into the gas phase.

However, many of the techniques that are used to study the atomic and electronic structure of adsorbed surface species are static in nature, for example, low-energy electron diffraction (LEED) and electron or infrared spectroscopy of adsorbed molecules. Possibly static experiments that investigate the properties of adsorbates do not sense the same species that are present under conditions of atom transport. Therefore, it is of great value to combine studies of surface structure and composition with kinetic studies of reaction rate and reaction path.

In recent years there has been intensive effort in my laboratory and in others to develop techniques that permit monitoring the rates of reactions on well-characterized single-crystal surfaces of small area.[1,2] Surface reactions of low reaction probability (less than 10^{-3}) can now readily be studied on single-crystal surfaces of area approximately 1 cm^2 where the surface structure and composition is determined by LEED and Auger electron spectroscopy.

Atomic Structure of Crystal Surfaces

A solid surface is represented schematically in Figure 1. The surface is heterogeneous. There are several atomic sites that are distinguishable by the number of nearest neighbor atoms surrounding them. Atoms in terraces have the highest coordination number while adatoms, which stand singly atop a lower layer, have the lowest. Experimental evidence for the presence of these surface sites comes mostly from LEED and field ion microscopy. Atoms in terraces, in steps, and in kinks are the most numerous ($\sim 10^{14} \sim 10^{15}$ atoms/cm^2) while the concentrations of the other kinds of surface sites are orders of magnitude smaller near equilibrium.

We can vary the relative numbers of terrace, step, and kink atoms by cutting a single crystal in various directions. Figure 2 shows LEED patterns and schematic diagrams for three representative Pt surfaces that were cut in different crystallographic orientations. One of the surfaces exhibits a diffraction pattern that indicates most of the surface atoms to be in terrace positions. The second surface (Figure 2b) has steps of atomic height, 6-atom spacings apart, on the average. Stable stepped

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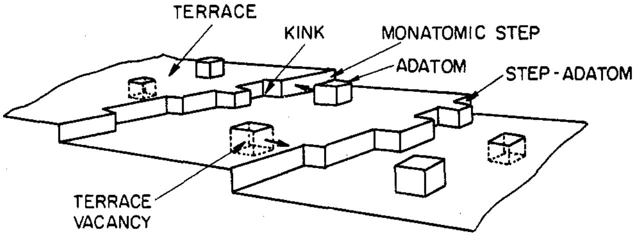
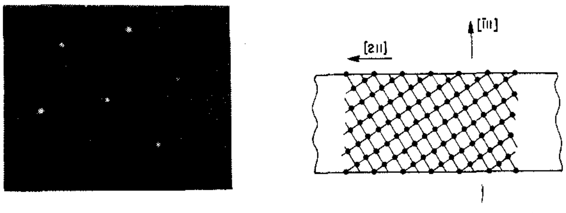
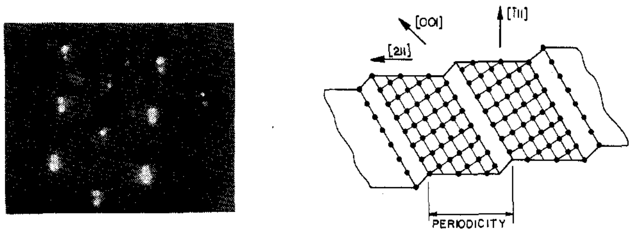


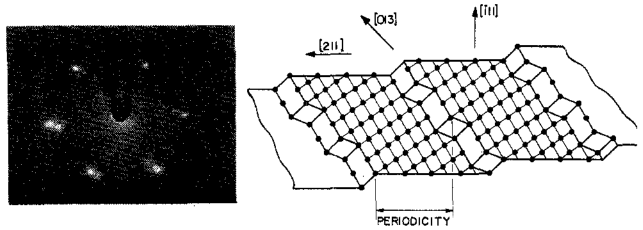
Figure 1. Model of a solid surface.



a) Pt-($\bar{1}$11)



b) Pt-($\bar{5}$57)



c) Pt-($\bar{6}$79)

Figure 2. Scheme of three representative platinum crystal surfaces: (a) (111) surface containing less than 10^{12} defects/cm^2; (b) (557) surface containing 2.5×10^{14} step atoms/cm^2 with an average spacing between steps of six atoms; (c) (679) surface containing 2.3×10^{14} step atoms/cm^2 and 7×10^{13} kink atoms/cm^2 with an average spacing between steps of 7 atoms and between kinks of 3 atoms.

surfaces with 20% of the surface atoms in step positions have been prepared. The third surface in Figure 2 is also stepped but is cut in such a way that there are many kinks in each step.

The chemical bond-breaking activity and the reactivity of these various surface sites are very different from each other. Thus cutting crystals in different crystallographic directions to change the relative numbers of terrace, step, and kink atoms changes markedly the reactivity of the surface.

Molecular Beam–Surface Scattering

The geometry of a molecular beam scattering experiment is shown in Figure 3. A well-collimated molecular beam of the reactant gas or gas mixture is scattered from the crystal surface, and the products that leave the surface at a given solid angle are detected by mass spectrometry. By rotation of the mass spectrometer around the sample, the angular distribution of the scattered products can be determined. If the incident molecular beam is chopped at well-defined frequencies, the time of flight of the incident molecules between the chopper and the detector can be determined by phase-shift measurements. This information yields the residence time of the molecules on the surface. Chopping the product molecules that desorb from the surface permits determination of their velocity.

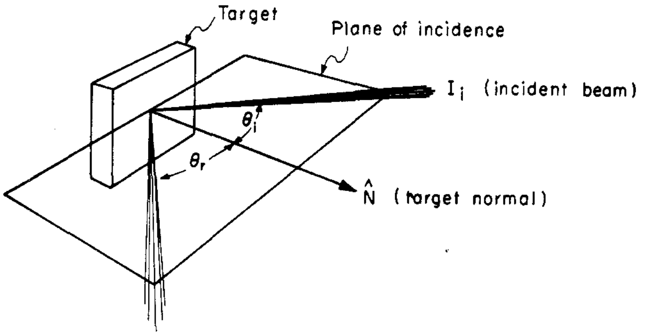


Figure 3. Scheme of the molecular beam–surface scattering experiment.

The experimental variables of the system are the temperature, atomic structure, and composition of the surface and the velocity and angle of incidence of the molecular beam. In reactive scattering experiments, the mass spectrometer detects the product distribution and rates of formation of product molecules (reaction probabilities) as a function of the system variables. From the dependence of the reaction rate on the incident beam velocity (or beam temperature) the activation energy for adsorption (if any) is determined. From the surface temperature dependence of the rate, the activation energy of the surface reaction is obtained. The surface residence time of the molecules and the kinetic energy and angular distribution of the products reveal the nature of energy transfer during the gas–surface interaction.[3,4]

Reactive scattering studies may be divided into two groups: (1) the reaction takes place on the surface under the catalytic influence of surface atoms that are not present among the reactants and products (for example, $A_{2(gas)} + B_{2(gas)} \xrightarrow{\text{surface}} 2AB_{(gas)}$); (2) the surface atom, S, is one of the reactants ($A_{2(gas)} + S = SA_{2(gas)}$). Only a few of each type have yet been investigated, but they are very informative.

In most of our studies the angular distribution of the beam scattered from the surface is measured as a function of the system variables, not the velocity distribution. (However, a new generation of equipment will soon be available to measure both the angular and velocity distributions.) Two important features of the distribution are generally discussed: the angle of the intensity maximum of the scattered beam with respect to the angle of the incident beam and its peak width at half-maximum. Most measurements are in plane, which means that the angular distribution is measured in the plane defined by the incident beam and the surface normal.

If the scattered beam has maximum intensity at angle θ_R, being equal to the angle of incidence of the incoming beam θ_I (both being measured with respect to the surface normal), the scattering is said to be specular. If θ_R is between θ_I and the surface normal, the scattering is called subspecular. If θ_R is larger than θ_I, the scattering

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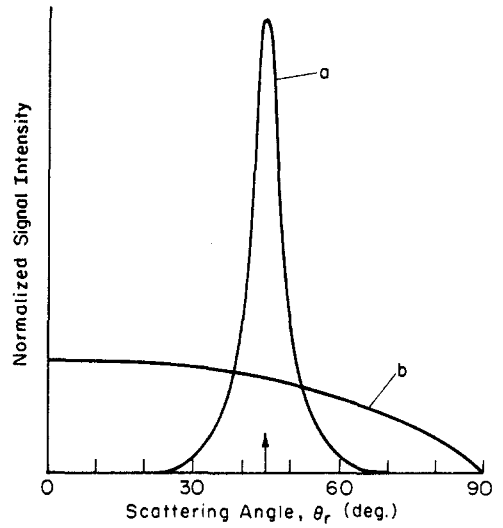

Figure 4. (a) Angular distribution of highly specularly scattered beam. Arrow indicates angle of incidence. (b) Scattered beam with cosine angular distribution.

is supraspecular. Typical specular distribution is shown in curve a of Figure 4. The angle of incidence is denoted by an arrow on the abscissa. It is customary to plot linear signal amplitude as a function of scattering angle, although polar plots are sometimes used. In order to compare data from different experiments the intensities are normalized by dividing by the maximum intensity of the incident beam. If the particles emitted had been completely equilibrated with the surface, a cosine distribution would have been obtained, as shown in curve b of Figure 4.

H_2–D_2 Exchange on Surfaces. This surface reaction has been studied in some detail on several crystal surfaces. The results indicate the types of experimental information that become available from these investigations.

One of the fundamental questions of heterogeneous catalysis is how surfaces lower the activation energy for simple reactions on an atomic scale so that they proceed readily on the surface while the same reaction in the gas phase is improbable. The reaction of hydrogen and deuterium molecules to form hydrogen deuteride is a simple reaction that takes place readily on metal surfaces even at temperatures below 200 K. The same reaction is completely inhibited in the gas phase by the large dissociation energy of H_2 or D_2 (103 kcal/mol). Even when the H_2 molecule is dissociated, the successive atom–molecule reaction ($H + D_2 = HD + D$) in the gas phase still has a potential energy barrier of roughly 10 kcal/mol.

The H_2–D_2 exchange reaction was studied by Bernasek et al.,[5] who used platinum single-crystal surfaces of high step density as well as surfaces with most atoms in terrace sites. Under the conditions of their experiments, which put strict limitations on the residence time of the detected molecules, no formation of reaction product HD could be detected to have occurred on the terrace crystal face. However, the reaction product formed readily on the stepped surface. The integrated reaction probability (defined as total desorbed HD flux divided by H_2 flux incident on the surface) was approximately 10^{-1} from the stepped surface while HD formation was below the limit of detectability on the terrace (reaction probability less than 10^{-5}).

Stepped crystal surfaces have an ordered arrangement of atomic steps (of one atom heights) separated by terraces. Thus, atomic steps at the platinum surface must play controlling roles in dissociating the diatomic molecules.

Figure 5 shows the scattering distributions from both the terrace and the stepped platinum surfaces. Varying the chopping frequency of the incident molecular beam has revealed HD resident times of about 25 ms and longer on a stepped platinum surface at 700 K surface temperature. Such a long residence time should result in complete thermal equilibration between the surface and the reaction products. Indeed, it was found by experiments that the desorbing HD beam exhibits cosine angular distribution, as seen in Figure 5.

The experiment was carried out either by employing a beam of one of the hydrogen isotopes while maintaining a constant pressure of the other in the ambient or by using a mixed beam. The pressure dependence of the exchange reaction (first order in incident D_2 beam flux and one-half order in H_2 that is in the ambient) indicates than an atom–molecule reaction or possibly an atom–atom reaction on the surface is the rate-limiting step. The absence of beam kinetic energy dependence of the rate indicates that the adsorption of hydrogen does not require activation energy. The surface is able to store enough atoms to react with the molecules by a two-branch mechanism. The rate constants for the H_2–D_2 reaction were also determined under conditions of constant hydrogen atom coverage. The rate-determining step below 700 K appears to be diffusion of D_2 molecules on the surface to a step site where HD is formed by a three-center or a two-center reaction (subsequent to D_2 dissociation at the step). At higher temperatures the reaction between adsorbed H atoms and incident D_2 gas molecules competes with the low-temperature branch. The catalytic action of platinum for the exchange reactions stems from its ability to adsorb and dissociate hydrogen molecules with near-zero activation energy and to store atomic hydrogen on its surface, thereby converting the gas-phase molecule–molecule reaction to an atom–molecule or atom–atom reaction of low activation energy.

The H_2–D_2 exchange reaction has also been studied by Palmer,[6] Stickney,[7] and Balooch[8] and their coworkers on a variety of metal surfaces. On copper, in contrast to platinum, the adsorption of H_2 or D_2 is an activated process, with activation energy about 5 kcal/mol.[8] A current objective in several laboratories is to measure the velocity of the products scattered from metal surfaces as well as their angular distribution, in order to determine the nature of energy transfer between the HD product molecules and the surface prior to desorption.

Surface Reactions of Other Small Molecules, Dissociation Reactions, and Reactions between Gases and Solid Surfaces. The surface reactions between O_2,[9,10] CO,[11] H_2,[12] NH_3,[13] and C_2H_4[14,15] on a va-

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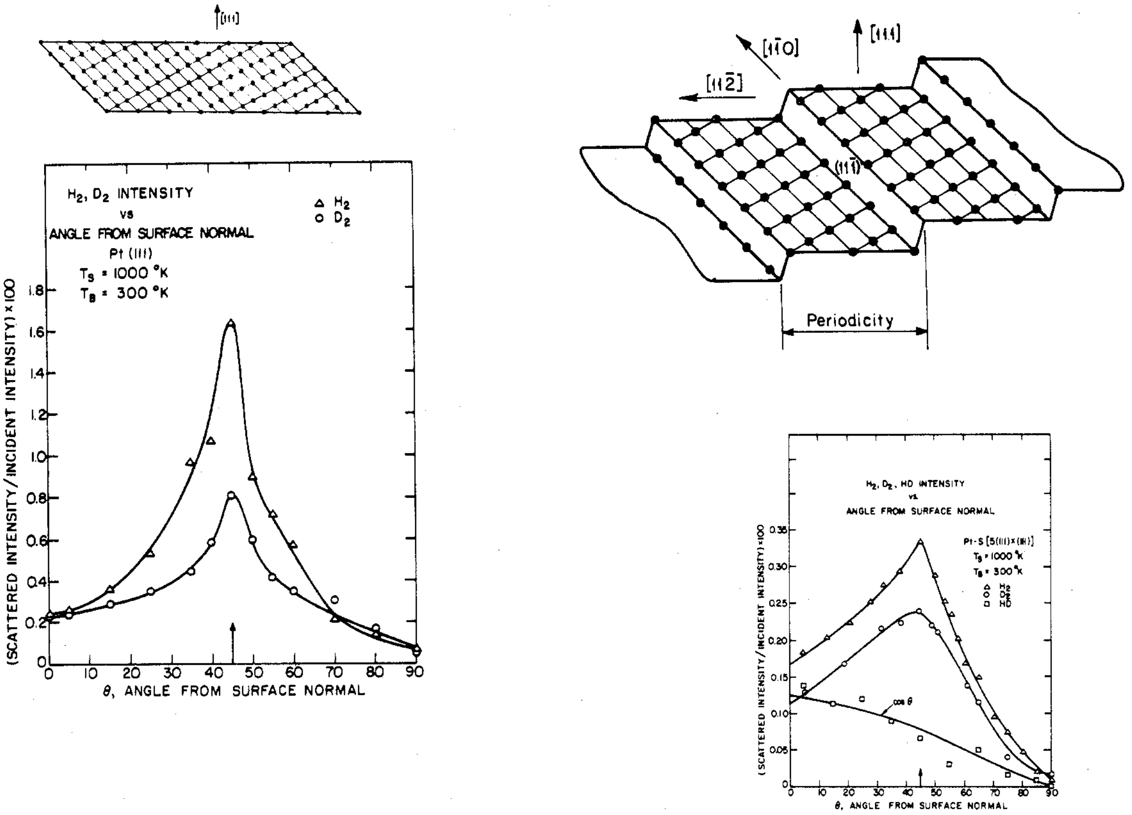

Figure 5. (a, left) Angular distribution of H_2 and D_2 scattered from Pt(111) single crystal (HD signal is undetectable). (b, right) Angular distribution of H_2, D_2, and HD scattered from a stepped Pt single crystal. Schematic diagrams of the surfaces are shown above the figures.

riety of metal surfaces have been studied. The dissociation of H_2,[16,17] N_2O,[18,19] and HCOOH[20] have also been studied by molecular beam scattering. Also, for reactions with the surface as a reactant, several molecular beam–surface studies have provided kinetic information.

In Table I we list preexponential factors, activation energies, and reaction probabilities for surface reactions that have been studied by molecular beam scattering techniques and where such data were reported. Table II lists similar data for other gas–surface reactions (see ref 21–28). Most of the tabulated surface reactions have low preexponential factors. Although it has long been known that surface reactions have rate constants with low preexponential factors, theoretical explanation has been lacking.

Surface diffusion is often suggested to be the slow step in surface reactions either between two adsorbates or between the adsorbate and the solid. Possibly the low preexponential factor for most surface reactions is due to molecular processes that are associated with the motion or reaction of diffusing atoms or molecules. Theoretical investigations of adsorption processes and surface reaction rates would certainly be desirable.

The residence times, t, of the reacting molecules on the surface, that is, the times that elapse between incidence of the reactants and desorption of products, appear to be in the range of 10^{-1} to 10^{-4} s for the few reactions (all of them endothermic or athermic) for which these data have been determined. It appears that the desorption energy ΔH_s is sufficiently high to assure long residence times on the surface ($t = t_0 \exp[\Delta H_s/RT]$ as compared to the vibration times of surface atoms ($\sim 10^{-12}$ s). As a result, spectroscopic probes of many types may be used to study the properties of reaction intermediates under steady-state reactant flux conditions at low pressures (less than 10^{-3} Torr).

The exothermic reactions that have been studied (the reaction of N_2O with carbon on the surface and HCOOH decomposition) showed evidence for direct scattering of the product molecules (NO) and for a low surface residence time of the reactant (HCOOH). It is probable that, in proper experimental circumstances, much of the available chemical energy is transferred to product molecules that will scatter as internally excited species and/or with high velocity. The partitioning of available chemical energy between the surface atoms and the products is under investigation at present in our laboratory through studies of the recombination of H and O atoms on solid surfaces.

Studies of Catalytic Reactions

The purpose of these investigations is to understand the mechanism of catalyzed surface reactions on the

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Table I

Preexponential Factors, Activation Energies, and Reaction Probabilities for Several Surface Reactions Studied by Molecular Beam Scattering

Reaction	A^a	E_a, kcal/mol	Reaction probability
$H + D_2 \xrightarrow{Pt} HD$ (<600 K)[5]	2×10^5 s^{-1}	4.5	$\sim 10^{-1}$
$H + D_2 \xrightarrow{Pt} HD$ (>600 K)[5]	1×10^2 s^{-1}	0.6	$\sim 10^{-1}$
$D + O_2 \xrightarrow{Pt} D_2O$ (700 K)[9]		12	
$CO + O \xrightarrow{Pt} CO_2$ (700 K)[10,11]		20	$\sim 10^{-3}$
$C_2H_4 + O_2 \xrightarrow{Ag} CO_2$ (800 K)[14,15]		8	$<10^{-2}$
$2H \xrightarrow{\text{graphite}} H_2$ (800–1000 K)[16]		15.9	10^{-3}–10^{-2}
$H_2 \xrightarrow{Ta} 2H$ (1100–2600 K)[17]	1×10^{-2} cm^2/atom-s	75	4×10^{-1}
$HCOOH \xrightarrow[\text{decomp}]{Ni} CO_2$ (<455 K)[20]	10^{12} s^{-1}	20.7	
$HCOOH \xrightarrow[\text{decomp}]{Ni} CO_2$ (>455 K)[20]	5.8×10^{13} s^{-1}	2.5	~ 0.9

[a] For bimolecular surface reactions, the preexponential factors also include the surface concentration of one of the reactants that is held constant during the experiments. These surface concentrations may vary in the range of 10^{-2}–1 monolayer (10^{13}–10^{15} molecules/cm^2).

atomic scale. Studies involve steady-state or time-dependent measurements of the reaction rate and product distribution using catalyst surfaces with well-characterized atomic structure and chemical composition. In contrast to molecular beam studies, multiple collisions of the reactants and products with the surface are allowed. By systematically changing the structure and/or the composition of the surface, the relationship between these parameters and the reactivity is established.[29] Using a single-crystal surface, one can make good use of LEED to characterize the atomic surface structure while Auger electron spectroscopy reveals the presence of impurities or the surface composition of multicomponent systems (alloys, oxides), whether the surface is crystalline or not.

Of course, studies of this type, using single crystals and low reactant pressures (less than 10^{-3} Torr) so that the structure and composition can be monitored continuously by electron beam scattering (long mean-free-path conditions), are far removed from the catalytic reaction conditions utilized in chemical technology. Usually small catalyst particles, 20–150 Å in size, dispersed on a high surface area support (such as oxides or oxyhydrides of aluminum or silicon) are used at pressures of 1 to 100 atm to achieve large contact area and optimum reaction rates (that are proportional to the surface area). Studies at low pressures or on crystal surfaces can be related to the behavior of conventional catalytic systems as follows:

surface reactions at low pressures
($\sim 10^{-4}$ Torr) on crystals
⇄ surface reactions at high pressures
($\sim 10^3$ Torr) on crystals
⇄ reactions on dispersed catalyst particles

First the reaction is studied at low pressure to establish correlation between reactivity and surface structure and composition. Then the same catalytic reaction is studied at high pressures (1–100 atm) and the pressure dependence of the reaction rate using the same sample is determined over the nine orders of magnitude range. Then the rates and product distributions determined at high pressures on single-crystal surfaces are compared with the reactivity of polydispersed small particle catalyst systems. Our experiments indicate that small surface area (approximately 1 cm^2) single-crystal catalyst samples can readily be used in studies as long as the reaction rate is greater than 10^{-6} product molecule surface atom^{-1} s^{-1}. The rate so defined is commonly called "turnover number" in the field of catalysis. Most of the important catalytic reactions—hydrogenation, dehydrogenation, oxidation, isomerization, dehydrocyclization, hydrogenolysis—usually have rates greater than the detection limit even at low pressure.[30]

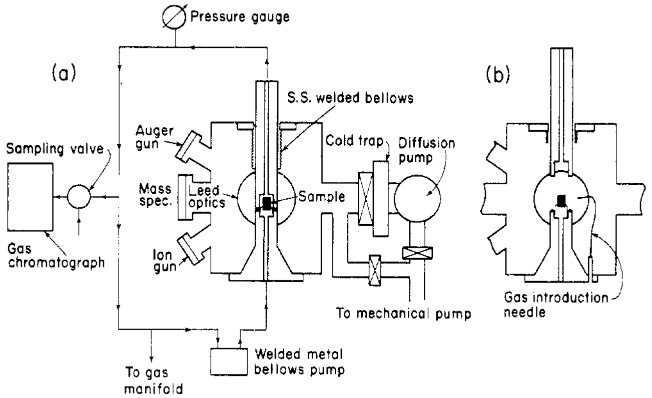

Figure 6. Scheme of the apparatus to study catalyzed surface reactions on small area crystalline surfaces at both low pressures (10^{-6}–10^{-4} Torr) and at high pressures (1–10^4 Torr).

We have recently developed new instruments for in situ studies of the reactivity of crystal surfaces at both low and high pressures. The scheme of one of these apparati is shown in Figure 6. At low pressures (10^{-7}–10^{-4} Torr), the reaction rate and product distributions are monitored by a quadrupole mass spectrometer while the surface structure and composition are determined by

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Table II
Preexponential Factors, Activation Energies, and Reaction Probabilities for Several Solid–Gas Reactions Studied by Molecular Beam Scattering

Reaction	A^a	E_a, kcal/mol	Reaction probability
$C + O_2 \xrightarrow{1000-2000\ K} CO$[22]	$2.5 \times 10^7\ s^{-1}$	30	$10^{-3}-10^{-2}$
$C + O_2 \xrightarrow{1000-2000\ K} CO$[22]	$3 \times 10^{12}\ s^{-1}$	50	$10^{-3}-10^{-2}$
$C + 4H \xrightarrow{500-800\ K} CH_4$[25]	$1.27 \times 10^{-18}\ cm^4/atom\text{-}s$	3.3	$10^{-3}-10^{-2}$
$2C + 2H \xrightarrow{>1000\ K} C_2H_2$[25]	$1.59\ cm^2/atom\text{-}s$	32.5	$10^{-3}-10^{-2}$
$Ge + O_2 \xrightarrow{750-1100\ K} GeO$[23]	$10^{16}\ s^{-1}$	55	2×10^{-2}
$Ge + O \xrightarrow{750-1100\ K} GeO$[24]	$10^{16}\ s^{-1}$	55	3×10^{-1}
$Ge + O_3 \xrightarrow{750-1100\ K} GeO$[26]	$10^{16}\ s^{-1}$	55	5×10^{-1}
$Ge + Cl_2 \xrightarrow{750-1100\ K} GeCl_2$[27,28]	$10^7\ s^{-1}$	25	3×10^{-1}
$Ge + Br_2 \xrightarrow{750-1100\ K} GeBr_2$[28] $\searrow GeBr_4$	$10^7\ s^{-1}$	20	3×10^{-1}
$Si + Cl_2 \xrightarrow{1100-1500\ K} SiCl_2$[28]	$10^8\ s^{-1}$	40	3×10^{-1}
$Ni + Cl_2 \xrightarrow{900-1400\ K} NiCl$[21]	$10^7\ s^{-1}$	30	8×10^{-1}

[a] For bimolecular reactions, the preexponential factor also includes the surface concentration of one of the reactants that is held constant during the experiments.

LEED and Auger electron spectroscopy, respectively. Then a small cup (total volume approximately 20 cm^3) is placed around the crystal sample to isolate it from the rest of the chamber that can be pressurized to over 100 atm, if desired, using the mixture of gaseous reactants. The high-pressure reaction chamber is connected to a gas chromatograph that serves to monitor both rate and product distributions. The structure and composition are determined in situ by LEED and Auger before the high-pressure experiment and after, once the cup is removed.

The crystal sample may be heated during both low- and high-pressure experiments, and a pressure of 10^{-8} Torr can be maintained outside the pressurized cup in the reaction chamber. The effect on reactivity of adding an impurity or a second constituent (alloying) to the surface can also be studied in this system. The second constituent may be vaporized at low ambient pressure onto the surface of the crystalline sample from a vapor source until the desired surface composition is obtained. The crystal surface can be cleaned by ion bombardment that is also available as an attachment on the reaction chamber. Most of our low- and high-pressure studies of catalytic reactions were carried out on platinum surfaces.

Catalysis of Hydrocarbon Reactions by Platinum. *A. Active Sites on Platinum Surfaces.* Three types of Pt surfaces which are distinguishable by their reactivity are shown schematically in Figure 2. The platinum surface where most atoms are located in the terrace has a very low density of surface imperfections (less than 10^{12}/cm^2) as compared to the number of surface atoms (1.5×10^{15} atoms/cm^2). The stepped platinum surface is characterized by a stable surface structure with about 20% of the surface atoms in steps of monatomic height. The third platinum surface must have, besides high step density, a high density of kinks in the step. These atomic surface structures are obtained by cutting the crystal in the proper crystallographic orientations.

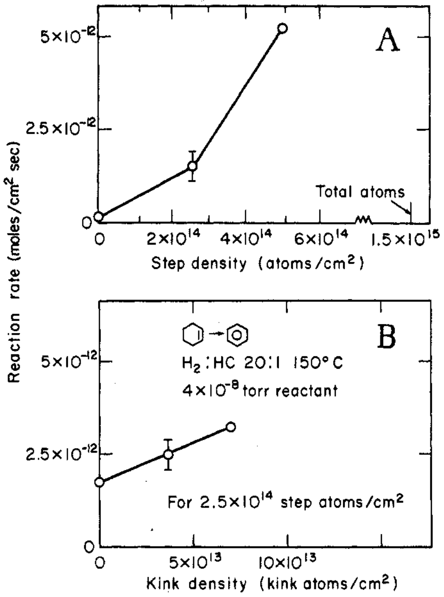

Figure 7. Initial rate of cyclohexene dehydrogenation to benzene on platinum single-crystal catalysts as a function of (A) increasing step density and (B) increasing kink density at constant step density. The reaction conditions are 5×10^{-8} Torr of cyclohexene, 1.0×10^{-6} Torr of hydrogen, and 423 K catalyst temperature.

The thermal stability of the various stepped and kinked platinum surfaces has been systematically investigated, and the relative stability as a function of crystal orientation and relative activity in various hydrocarbon reactions has been determined.[31] The surface sites on the different Pt surfaces are distinguishable by their coordination number, i.e., the number of nearest neighbors, ranging from kink atoms with only six nearest neighbors to atoms in the hexagonal orientation terraces with nine nearest neighbors.

Dehydrogenation of cyclohexane or cyclohexene to benzene occurs only on stepped platinum surfaces at an appreciable rate.[30] Figure 7 shows the step and kink density dependence of the rate of cyclohexene dehy-

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(31) D. W. Blakely, Ph.D. Thesis, University of California, Berkeley, 1976.

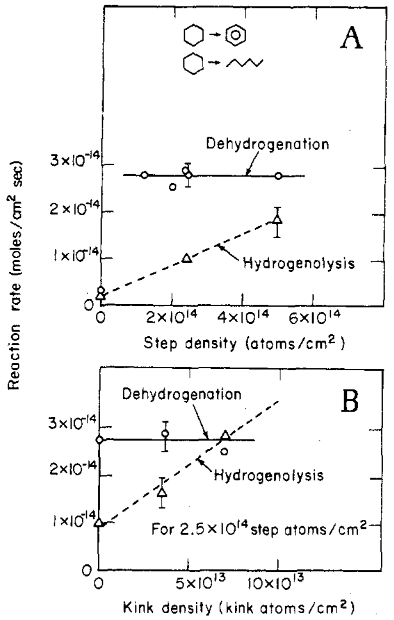

Figure 8. Initial steady-state rates of cyclohexane dehydrogenation to benzene (○) and hydrogenolysis to n-hexane (△) on platinum single crystal catalysts as a function of (A) increasing step density and (B) increasing kink density at constant step density of 2.4×10^{14} step atoms/cm^2. The reaction conditions are 5×10^{-8} Torr of cyclohexane, 1.0×10^{-6} Torr of hydrogen, and 423 K catalyst temperature. The rate of dehydrogenation is constant at 2.8×10^{-14} mol cm^{-2} s^{-1} with steps present but is less (0.3×10^{-14} mol cm^{-2} s^{-1}) on the (111) surface (near zero step density). The rates of hydrogenolysis per surface sites are the slope of the lines representing hydrogenolysis and are 3×10^{-28} mol (kink atom)$^{-1}$ s^{-1} and 4×10^{-29} mol (step atom)$^{-1}$ s^{-1}.

drogenation to benzene to demonstrate this effect. While the rate increases markedly with increasing step density (Figure 7A), it is relatively unaffected by changes of kink density (Figure 7B).

The rate of cyclohexane dehydrogenation to benzene is constant as long as there are steps on the catalyst surface, but it is almost an order of magnitude lower on the Pt(111) surface, as seen in Figure 8A. Thus atomic steps appear to be preferred surface sites for breaking H–H and C–H bonds[29] (H–H bond breaking has been studied by the H_2–D_2 exchange[11] described above).

Cyclohexane undergoes both dehydrogenation and hydrogenolysis on the stepped Pt surfaces. The relative rates of these two reactions can best be monitored by the ratio of benzene to n-hexane in the reaction product. As is demonstrated in Figure 8, the rate of benzene production is independent of step and kink density while n-hexane production increases slowly with step density (Figure 8A) and rapidly with kink density (Figure 8B). The rate of cyclohexane hydrogenolysis to n-hexane per kink site is determined by the slope of the line in Figure 8B representing hydrogenolysis and is 3×10^{-28} mol of n-hexane (kink atom)$^{-1}$ s^{-1}. This is almost an order of magnitude higher than the slope in Figure 8A, which is 4×10^{-29} mol of n-hexane (step atom)$^{-1}$ s^{-1}. The observed low hydrogenolysis activity on the type of stepped surfaces represented by Figure 8A may be caused by some thermally generated kinks in the steps. The formation of n-hexane and other hydrogenolysis products must result from C–C bond scissions. It appears that kinks are very effective in breaking C–C bonds as well as C–H and H–H bonds. Thus we have been able to identify two types of low coordination number active sites on platinum surfaces: steps with C–H and H–H bond-breaking activity and kinks in steps with C–C, C–H, and H–H bond-breaking activity.

B. The Carbonaceous Overlayer. During studies of hydrocarbon reactions on the various platinum surfaces, the catalyst surfaces are always covered with a carbonaceous overlayer as determined by Auger electron spectroscopy.[30,32] The coverage is almost independent of the pressure in the range of 10^{-6}–10^3 Torr but varies markedly with temperature and the molecular weight of the saturated hydrocarbon reactant molecules. The higher the temperature and the reactant molecular weight, the higher the coverage reaching monolayer amounts for cyclohexane at 725 K and for n-heptane at 575 K. Unsaturated hydrocarbons, such as ethylene or benzene, form complete monolayers at all temperatures, pressures, and double layers under certain conditions. The reactant dissociates and the overlayer consists of partially dehydrogenated species. This carbonaceous overlayer may be ordered or disordered depending on the platinum surface structure, the nature of the reactant, and the hydrogen to hydrocarbon ratio during the reaction.

Several reactions are sensitive to the presence of ordering in the overlayer. Cyclohexene conversion to benzene is poisoned unless the overlayer is ordered and n-heptane to toluene conversion occurs only in the presence of an ordered overlayer. Other reactions, like the hydrogenolysis of cyclohexane, occur readily even in the presence of a disordered overlayer.

The adsorption of hydrocarbons on the (111) and (100) platinum surfaces has been studied by LEED.[33] These studies indicate the organic molecules are stable on these flat, terrace surfaces; they do not undergo dehydrogenation or chemical rearrangements readily in the temperature range 300–600 K and at low adsorbate pressures (~10^{-4} Torr). Thus, while such low index platinum surfaces are excellent for studies of the surface structures of adsorbed molecules, they are poor catalysts since they are not likely to break C–H and C–C bonds under catalytic reaction conditions. The distinctly different chemisorption and catalytic characteristics of stepped platinum surfaces can be explained by considering the interplay of four competing processes: (1) dehydrogenation, (2) decomposition of the organic molecules, (3) nucleation and growth of carbonaceous overlayers, and (4) rearrangement of the platinum substrate in some cases by facetting.[34] The effect of increased partial pressure of hydrogen over the surface is to retard decomposition so that processes 1 and 3 may predominate on a stepped single-crystal surface.

Catalytic Studies at High Pressures on Crystal Surfaces. The hydrogenolytic ring opening of cyclopropane to form propane, the dehydrogenation of cyclohexane to cyclohexene and benzene, and the dehydrocyclization of n-heptane to toluene have all been studied at high as well as low pressures on crystal surfaces. Table III compares the rates of these reactions at high and low pressures at 300 °C (see ref 30, 32, 35, 36). The rates increase three to five orders of magnitude when the pressure is increased by eight to nine orders of magnitude. Studies of the pressure dependence of

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(32) B. Lang, R. W. Joyner, and G. A. Somorjai, *Proc. R. Soc. London, Ser. A*, **331**, 335 (1972).

(33) J. L. Gland and G. A. Somorjai, *Surf. Sci.*, **41**, 387 (1974).

(34) K. Baron, D. W. Blakely, and G. A. Somorjai, *Surf. Sci.*, **41**, 45 (1974).

(35) R. Herz, D. W. Blakely, and G. A. Somorjai, *J. Catal.*, in press.

(36) D. R. Kahn, E. E. Petersen, and G. A. Somorjai, *J. Catal.*, **34**, 294 (1974).

Table III
Initial Reaction Rates (Product Molecules/Surface Atom-s) of Hydrocarbon Reactions on Platinum Crystal Surfaces at 300 °C at Low and at High Reactant Pressures

Reaction	High pressure[a]	Low pressure[b]
$C_6H_{12} \rightarrow C_6H_6$[30,35]	3	6.3×10^{-5}
$C_6H_{12} \rightarrow C_6H_{10}$[30,35]	2×10^{-2}	2.0×10^{-5}
$C_6H_{10} \rightarrow C_6H_6$[30,35]	100	4×10^{-3}
n-Heptane → toluene[32,35]	10^{-2}	10^{-5}
n-Heptane → methylcyclohexane[35]	10^{-1}	
Cyclopropane → propane[35,36]	150	10^{-3}

[a] Total pressure 215 Torr; reactant pressure 15 Torr. [b] Total pressure 8×10^{-7} Torr; reactant pressure 4×10^{-8} Torr.

Table IV
Classification of Reactions by Step Density and Carbonaceous Overlayer Dependence[30]

Step Structure Sensitive		Step Structure Insensitive, overlayer structure insensitive
Overlayer structure sensitive	Overlayer structure insensitive	
Cyclohexene → benzene	Cyclohexane → n-hexane	Cyclohexane → cyclohexene
n-Heptane → toluene		Cyclopropane → propane

these various reaction rates will help us to decipher the mechanism at both low and high pressures and how they correlate to each other.

So far only for the hydrogenolytic cyclopropane ring opening has a reaction on platinum crystal surfaces been compared with that on polydispersed supported platinum catalysts.[36] The rates obtained on stepped platinum single-crystal surfaces were identical with published values for this reaction on supported platinum particles. This significant result supports the contention that well-defined single-crystal surfaces are excellent models for polycrystalline supported metal catalysts. It also tends to verify the hypothesis that the cyclopropane hydrogenolysis is a structure-insensitive reaction.[37] If the atomic surface structure played a significant role in determining the reactivity, the platinum single-crystal surface would not necessarily give the same result as a polydispersed particle system in which particles have a variety of atomic structures available simultaneously.

Structure Sensitivity of Catalytic Reactions. The rates of some catalytic reactions in polydispersed supported systems change by orders of magnitude upon changing the catalyst particle size. For other reactions, reaction rate is independent of the catalyst particle size. These two groups are called "structure-sensitive" and "structure-insensitive" reactions, respectively.[37] This classification can now be expanded to separate those reactions that exhibit step or kink sensitivity into one group and those that are sensitive to the structure of the overlayer into another. This is shown in Table IV. It will be of great interest to find the proper place in this classification for other hydrocarbon reactions (isomerization, hydrogenation, and oxidation) as more experimental data become available.

Studies to correlate reactivity with platinum surface structure and composition indicate that an active crystal surface must be heterogeneous. The heterogeneity involves the presence of various atomic sites that are distinguishable by their number of nearest neighbors, atoms in terraces, in steps, and in kinks, and also variation in surface chemical composition. A model that depicts the active platinum surface is shown schematically in Figure 9. Part of the surface is covered with partially dehydrogenated carbonaceous overlayer, ordered or disordered, from which platinum atom clusters protrude. These are the platinum atoms in steps and at kinks that are active in various C–C, C–H, and H–H bond-breaking activity. Perhaps because of the ease of dissociation and higher binding energy of hydrogen at steps, these sites and their vicinity remain clean and represent areas of high reaction rate. The species that form as a result of bond scission at these clusters may rearrange and then diffuse onto the terrace that is covered with the carbonaceous overlayer. Ultimately, rearrangement takes place on the ordered carbonaceous overlayer prior to desorption. The heat of desorption should be lower on the portion of the surface that is covered with the overlayer than at an exposed step.

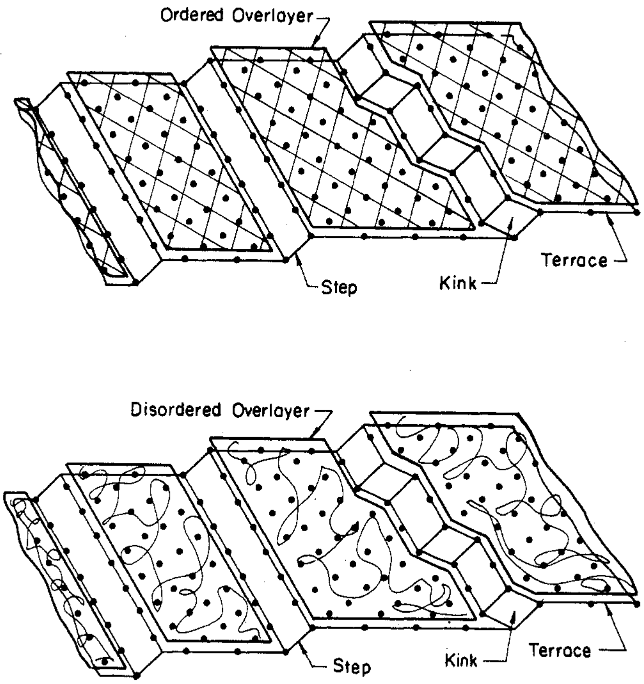

Figure 9. Model of the active platinum catalyst surface with a full carbonaceous overlayer showing exposed catalytic bond-breaking sites.

The discovery that kink sites in steps are effective in breaking C–C bonds as well as C–H and H–H bonds, thereby initiating hydrogenolysis reactions, may also explain the effect of trace impurities or second component metals that introduce selectivity. Since these kink sites have fewer nearest neighbors than steps or terrace

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(37) M. Boudart, A. Aldag, J. E. Benson, N. A. Dougerty, and C. G. Harkins, *J. Catal.*, **6**, 92 (1966).

sites, they are likely to bind impurities or other metal atoms with stronger chemical bonds. Thus, these sites are readily blocked by impurities. As a result, selective poisoning of hydrogenolysis may be obtained by minute concentrations of well-chosen impurities or other metal components.

Poisoning of Catalytic Surfaces. It is well known that many surface reactions are inhibited by very small amounts of impurities. Estimates based on experimental data are that each impurity may render five to ten metal atoms ineffective. Impurity atoms may inhibit catalytic reactivity in two ways. They may block crucial active sites necessary to break a certain chemical bond.[38] (For example, by blocking kink sites, the C–C bond-breaking activity of platinum surfaces may be removed.) Poisoning by this mechanism should be a general phenomenon applicable to a wide range of catalyst materials.

In a second mechanism for poisoning, foreign atoms that adsorb on a crystal surface may lower the surface free energy. If the adsorbed impurity changes the surface free energy of the various crystal planes by different amounts, it can induce rearrangements of the surface structure to form crystal planes that have lower surface free energy in the presence of the adsorbed impurity than the crystal planes that bound the clean solid.[39] In general, surfaces that exhibit the highest atomic densities have the lowest surface free energies. The ratio of surface free energies of these various high density surfaces is 0.9–0.95 for typical metal surfaces.

Schmidt and Luss[40] have reported that platinum wires used in the catalytic oxidation of ammonia have recrystallized in the presence of H_2S gas in the feed. Electron microscopy studies showed that a wire surface that was composed of predominantly hexagonal orientation crystal planes (111) restructured in the presence of H_2S to crystal planes of square orientation (100). It appeared that adsorption on sulfur lowers the surface free energy of the (100) crystal face of platinum more than that of the (111) face because sulfur bonds differently to the two crystal faces. The surface free-energy difference provides the driving force for surface diffusion-controlled recrystallization. The experimental information that is available from studies of silver and nickel surfaces[41,42] as well as the results on platinum surfaces mentioned above indicate that the (100) crystal face of face-centered cubic solids is stabilized in the presence of sulfur with respect to the (111) face. Since poisoning of catalytic reactions as a function of time occurs in many important catalyst systems, a better understanding of the mechanism of this phenomenon on the molecular level would be of great importance.

Some Outstanding Problems in Catalysis. Both molecular beam–surface scattering studies and studies of catalytic surface reactions are in their infancy. It is not difficult to identify a few experimental and theoretical problems of outstanding importance in these areas. It would be important to study exothermic surface reactions by molecular beam scattering to determine how the available chemical energy is partitioned between the surface atom and the various degrees of freedom (translation, rotation, vibration) of product molecules. Studies of reactive scattering should be carried out to identify the surface sites where various chemical bonds, C–H, C–C, C–O, N–N, etc., are broken on various metallic as well as oxide surfaces. Catalytic studies should explore the mechanism, on the molecular scale, of the carbon monoxide–hydrogen reactions on a variety of transition metals and oxide and sulfide surfaces, since $CO + H_2$ mixtures will become available from coal gasification in large quantities as raw materials for many chemical technologies.

The oxidation of ethylene on silver and other selective catalytic oxidation reactions that take place on oxide surfaces should be explored with use of single crystal surfaces. The small preexponential factor of surface reactions should be subjected to theoretical scrutiny. Energy surface calculations of surface chemical reactions using simplified models to represent the surface would be of great value. Calculations to explain the different chemistry (bond breaking activity) associated with surface sites (steps and kinks) of low coordination number for platinum and for perhaps other transition metal surfaces would help to explain the nature of heterogeneous catalysis. The properties of the partially dehydrogenated carbonaceous overlayers and the bonding of adsorbates to the metal through this layer are likewise important problems to study.

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(39) G. A. Somorjai, *J. Catal.*, **27**, 453 (1972).

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