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REACTIONS ON SINGLE CRYSTAL SURFACES

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Introduction

Much of the research on clean solid surfaces is aimed at uncovering elementary steps of surface chemical reactions. Surface reactions or catalyzed surface reactions take place under conditions of atom transport. Molecules impinge, adsorb, react on these solid surfaces, form intermediates of various lifetimes, then the products desorb into the gas phase again. However, many of the experiments that study the atomic structure and the electronic structure of adsorbed surface species are static in nature; for example, low-energy electron diffraction, the electron or infrared spectroscopy of adsorbed molecules. It is not clear that the static experiments that investigate the properties of adsorbates are studying the same species that are present under conditions of atom transport; therefore, it would be of great value to combine studies of surface structure and composition with kinetic studies of reaction rate and reaction path.

Over the past several years there has been an intensive effort in my laboratory and in others to develop techniques that permit monitoring the rate of reactions on well-characterized single crystal surfaces of small area.^{1,2} Presently surface reactions of low reaction probability (less than 10^{-3}) can readily be studied on single crystal surfaces of area approximately 1 cm^2 where the surface structure and composition is determined by low-energy electron diffraction and Auger electron spectroscopy.

Perhaps one of the most powerful techniques in studies of surface chemical reactions is molecular beam surface scattering.^{3,4} We shall discuss this technique briefly below and then review the results of reactive scattering studies and the type of information that becomes

available from these investigations. Then we shall discuss studies of catalytic surface reactions that were carried out on crystal surfaces and the relationship of these studies to practical and technologically important catalyst systems. Finally, we shall review some of the important areas of research and the outstanding questions about the fundamental surface reaction steps that may be answered by experiment or theory.

MOLECULAR BEAM-SURFACE SCATTERING

The scheme of the molecular beam scattering experiment is shown in Figure 1. The well collimated molecular beam of the reactant gas or gas mixture is scattered from the crystal surface and the products that are desorbed 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 is 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. 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, 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 the

surface atoms that, however, are not present among the reactants and products (for example, $A_2(\text{gas}) + B_2(\text{gas}) \xrightarrow{\text{surface}} 2AB(\text{gas})$); 2) the surface atom is one of the reactants ($A_2(\text{gas}) + S = SA_2(\text{gas})$). Only a few of a multitude of possible reactions of these two types have been investigated. We shall review the various studies and the results that aid the unraveling of the nature of surface reactions.

Most studies measured the angular distribution of the beam scattered from the surface as a function of the system variables, not the velocity distribution (a new generation of equipment is becoming available presently that can 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 angle at which the scattered beam is maximum intensity θ_R (measured with respect to the surface normal) equals the angle of incidence of the incoming beam θ_I (also 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 is supraspecular. Typical specular distribution is shown in curve A of Figure 2. The angle of incidence is usually denoted by an arrow on the abscissa. It is also 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. In the case where the particles emitted from the surface are completely equilibrated with the surface, one obtains a cosine distribution as shown in curve B of Figure 2.

H₂-D₂ Exchange on Surfaces

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 one of the simple reactions that takes place readily on metal surfaces even at temperatures below 100 K. The same reaction is completely inhibited in the gas phase by the large dissociation energy of H₂ or D₂ (103 kcal per mole). Once the H₂ 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/mole. The H₂-D₂ exchange reaction was studied by Bernasek et al.⁵ using platinum single crystal surfaces of low and high Miller Index. Under conditions of the experiments which put strict limitations on the residence time of the detected molecules, the reaction product HD could not be detected from the (111) crystal face. However, the reaction product was readily detectable from the high Miller Index stepped surface. The integrated reaction probability (defined as total desorbed HD flux divided by H₂ flux incident on the surface) is approximately 10⁻¹ while HD formation was below the limit of detectability on the platinum (111) surface (reaction probability less than 10⁻⁵). High Miller Index single crystal surfaces are characterized by ordered arrangements of atomic steps

(of one atom height) separated by terraces of low Miller Index orientation. Thus, atomic steps at the platinum surface must play controlling roles in dissociating the diatomic molecules. Figure 3 shows the scattering distributions from both the (111) and the stepped platinum surfaces. Varying the chopping frequency of the incident molecular beam has yielded HD residence times of about 25 milliseconds on a stepped platinum surface at 700 K surface temperature. Such 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 3.

The pressure dependence of the exchange reaction indicates that 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 a sufficiently large concentration of atoms which 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 the diffusion of D_2 molecules on the surface to a step site that 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 an adsorbed H atom and an incident D_2 gas molecules competes with the low temperature branch. The catalyst action of the platinum surface for the exchange reaction is due to its ability to adsorb and dissociate hydrogen molecules with near zero activation energy and to store atomic hydrogen on the surface,

thereby converting the gas phase molecule-molecule reaction to an atom-molecule or an atom-atom reaction of low activation energy.

The H_2 - D_2 exchange reaction was also studied by Palmer et al.⁶ on platinum and nickel surfaces that were prepared as evaporated thin films. They observed angular distributions that are peaked near the surface normal following a cosine $^n\theta_R$ relationship, where θ_R is the angle of desorption from the surface relative to the surface normal. The value of n varies from 2.5 to 4.0 on the different surfaces studied. This angular distribution instead of cosine θ , indicates perhaps incomplete accommodation of the reaction product with the surface. The peaked angular distribution could be related to the presence of impurities such as carbon and sulfur contamination on the metal surfaces. There is evidence from the experiments of Stickney et al.⁷ that as the surface is cleaned of sulfur, oxygen or carbon, n approaches unity. Copper, on the other hand, shows noncosine angular distribution for scattered HD even from a clean surface. Unlike for platinum, the adsorption of H_2 or D_2 is activated on a copper surface. The activation energy of adsorption is about 5 kcal/mole as determined by Balooch et al.⁸ from the beam temperature dependence of the reaction probability. It would be of importance to measure the velocity of the scattered products in addition to their angular distribution in order to determine the nature of energy transfer between the HD product molecules and the surface prior to desorption. These studies are in progress in several laboratories.

Surface Reactions of Other Small Molecules

The oxidation of carbon monoxide has been studied on platinum surfaces by Palmer et al.,⁹ Bonzel and Ku¹⁰ and Bernasek and Somorjai.¹¹

It was observed that the oxidation reaction is strongly inhibited by carbon monoxide adsorbed on the surface. In fact the oxidation reaction is not observable when oxygen was incident from the molecular beam on a surface that was covered with carbon monoxide. The CO_2 product exhibits a non-cosine angular distribution indicating either excess energy or insufficient energy accommodation between the product molecules and the surface atoms prior to desorption. The chemical reaction between deuterium and oxygen to form D_2O occurring on the (111) platinum surface has been investigated by Smith and Palmer.¹² In these studies the molecular beam was D_2 and the oxygen was preadsorbed on the platinum thin film surface which was maintained in an oxygen ambient. The production of D_2 was studied as a function of D_2 flux and temperature, oxygen pressure, platinum surface temperature and the angle of incidence of the D_2 beam. The reaction rate was proportional to the second power of the D_2 pressure and the 0.8 power of the oxygen pressure. The adsorption of D_2 requires an activation energy of 1.8 kilocalories per mole. It is proposed that in the adsorbed state the reaction proceeds upon the collision of four adsorbed deuterium atoms with an adsorbed oxygen molecule or activated oxygen complex.

Nutt and Kapur¹³ reported on preliminary experiments involving the oxidation of ammonia using NH_3 and O_2 mixed molecular beams. The reaction products were N_2 , H_2O and NO in the temperature range of 600 - 1200 K, and the reaction probability is about 0.1 to 0.28. The oxidation of ethylene (C_2H_4) on silver surfaces was studied by Smith et al.¹⁴ The dominant reaction product was CO_2 . The surface temperature dependence of the CO_2 formation indicated an activation energy of 8 kcal/mole for

this surface reaction. The reaction probability was less than 10^{-2} at 820 K and poisoning of the surface reaction by carbon that builds up on the silver surface was inferred from the experimental data. The hydrogenation of ethylene was studied using the (111) crystal face of platinum.¹⁵ The reaction probability can be estimated to be about 10^{-4} in the range of 500 - 700°C. As a result, the formation of ethane could not be detected.

Reactive scattering studies with two or more reactants can be carried out either by using a mixed molecular beam or by preadsorbing one of the reactants on the surface and monitoring the reaction between one of the reactants in the molecular beam and the other reactant that was adsorbed. Although detailed comparisons between the two modes of reaction have not been made as yet, it is likely that the surface reaction kinetics may change as the reaction conditions are varied in this manner.

Dissociation Reactions

The dissociation of H_2 on tungsten surfaces was studied by Smith and Fite¹⁶. The reaction probability was about 0.3 at 3000 K. The angular distribution of H atoms was cosine-like indicating thermal equilibration between the hot surface and desorbing H atoms. This was also corroborated by a long residence time, 280 μ sec that was measured. The dissociation of H_2 on tantalum surfaces was studied by Krakowski et al.¹⁷ in the temperature range of 1100 - 2600 K. Reaction probability increased with increasing temperature just as for tungsten surfaces. The hydrogen atoms underwent complete thermal accommodation on the surface. By varying the kinetic energy (beam temperature) of the incident beam, they have determined an activation energy of 1.4 kcal/mole for the atomization surface reaction. The atoms once formed cannot undergo recombination before desorption

from the hot surface. The rate limiting step in the reaction appears to be desorption of hydrogen atoms with an activation energy of about 75 kcal/mole. The surface diffusion of hydrogen atoms does not require activation energy.

The dissociation of N_2O on hot tungsten has been investigated by Muschlitz.¹⁸ The decomposition probability approaches unity at high surface temperature. The product N_2 was emitted with a cosine distribution while neither oxygen atoms or oxygen molecules could be detected in the scattered beams. It appears that oxygen reacts with the tungsten surface during the decomposition of N_2O . Both N_2 and NO were found in the scattered beam and the ratio of the two species, N_2/NO , was approximately 12:1 at 2500 K. During the dissociation of N_2O on platinum surfaces that was studied by West and Somorjai,¹⁹ again both NO and N_2 were found, the NO concentration being larger than that found on desorption from tungsten surfaces. The angular distribution of the product NO molecule that is formed by dissociation at the clean platinum surface was the cosine type, indicating complete accommodation of the NO molecules on the platinum (100) surface prior to re-emission. The angular distribution of NO product molecules is different however when they are emitted from carbon covered platinum surfaces at 1125 K. The angular distribution is certainly non-cosine, and it peaks at or near the specular angle. Such a peaked distribution reflects a lack of energy accommodation during the surface dissociation reaction of NO on the carbon covered platinum (100) surface and suggests a direct reactive scattering mechanism. N_2O may undergo a variety of chemical reactions on platinum and carbon covered platinum surfaces. Those chemical reactions that can take place between

the carbon on the platinum surface and N_2O are largely exothermic, yield CN, CO and CO_2 reaction products in addition to N_2 and NO. On the clean platinum surface, the incident N_2O molecule can only undergo endothermic chemical reactions. Direct scattering is commonly observed in studies of chemical reactions between cross-molecular beams that are exothermic and exoergic. The decomposition of formic acid was studied by Wachs et al.²⁰ from the Ni(100) crystal face. The product, CO_2 , whose formation is monitored could not be detected below 400 K, that is, decomposition does not appear to take place below that temperature. The amplitude of the reflected formic acid beam decreases slightly at 300 K and decreased abruptly at 355 K indicating the onset of decomposition of the incident beam. The rate constants below and above the decomposition temperature have been determined and are listed in Table 1. The experiments indicate low surface lifetime for the adsorbed $HCOOH$ molecule. Decomposition was also studied on nickel-copper alloys and the results were compared with those obtained on clean nickel surfaces. The decomposition probability of formic acid at 513°C is approximately 0.9.

In Table 1 we list all the pre-exponential factors, activation energies and reaction probabilities for the surface reactions that were studied by molecular beam scattering techniques and where such data were reported. All of the surface reactions that are reported here have low pre-exponential factors. Although it has long been known that surface reactions have rate constants with low pre-exponential factors, theoretical explanation of this observation has not been available. Theoretical investigations of surface reaction rate would certainly be desirable.

Reactions Between Gases and Solid Surfaces

The interaction between chlorine molecular beams and nickel surfaces have been studied by McKinley²¹ and Smith and Fite.²² The reaction probability is 0.8 at 1000 K and both NiCl and NiCl₂ are detectable among the reaction products. The formation of NiCl predominates at low temperatures, while NiCl₂ forms almost exclusively above 1400 K. The mechanism that is proposed involves an Ni₂Cl₂ surface intermediate. The formation of this dimer appears the rate limiting step in the overall reaction scheme while the desorption of NiCl and NiCl₂ are rapid reaction steps. The residence time of desorbing NiCl is 916 μsecs at 1150°C and 140 μsecs at 1300°C and the NiCl₂ residence times are even longer. The reaction probability of oxygen with molybdenum was determined to be approximately 0.3 by Ullman and Madix.²³ Surface diffusion of oxygen atoms to grain boundaries on the polycrystalline molybdenum surface appears to control the formation of volatile molybdenum oxides.

Olander et al.²⁴ has studied the oxidation of both the basal plane and the prism plane of graphite. The product of the oxidation reaction is CO although a small CO₂ signal was also detectable during oxidation of the prism plane. The reaction rate was monitored as a function of temperature. From the chopping frequency dependence of the reaction probability they have concluded that there must be at least two parallel reactions, one slow and one faster, taking place on the graphite surface. For the basal plane the fast reaction is attributed to the migration of atomic oxygen over the surface to reaction sites where oxidation occurs. The rate constant k for this step is given by $k = 2.5 \times 10^7 \exp[-30 \text{ kcal/RT}] \text{sec}^{-1}$. The slow reaction step is the desorption of CO and its rate constant K_d is

given by $k_d = 3 \times 10^{12} \exp[-50 \text{ kcal/RT}] \text{sec}^{-1}$, There are two types of reaction sites postulated with surface concentrations of 10^{11} cm^{-2} and 10^8 cm^{-2} respectively. Grain boundary and possible bulk diffusion of oxygen were found to be important steps in the oxidation of the prism face.

Surface diffusion is often suggested to be the slow step in surface reactions either between two adsorbates or between the adsorbate and the solid. It is possible that the low pre-exponential factor that is found for most surface reactions is due to the molecular processes that are associated with the diffusing atoms or molecules. The surface structure or electronic effects are likely to be responsible for the low reaction cross sections that are determined by the molecular beam surface scattering experiments.

The oxidations of germanium was studied by Anderson and Boudart²⁵ and Madix and Boudart.²⁶ The reaction probability was 0.04 and independent of temperature. However, the oxidation rate of the surface was dependent on the oxygen beam temperature which indicates 100 - 200 cal/mole activation energy for the adsorption. It appears that the dissociative adsorption of oxygen is the rate determining step in the reaction. The oxidation reaction using oxygen atoms instead of oxygen molecules was also investigated. The reaction probabilities in this case are in the range of 0.2 to 0.3, much higher than for oxygen molecules at surface temperatures in the range of 830 - 1110 K. The difference in the activities appears to be due to the requirements that both atoms in the oxygen molecule interact simultaneously with the surface atom, thus the interaction probability depends on the orientation of the incident oxygen molecule.

The residence times, T , of the reacting molecules on the surface that elapse between incidence of the reactants to desorption of the products appear to be in the range of 10^{-1} to 10^{-4} seconds for the few reactions where this data has 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 vibration times of surface atoms (10^{-12} seconds). As a result spectroscopic experiments of many types may be successfully performed to study the properties of reaction intermediates under steady state reactant flux conditions at low temperatures (less than 10^{-3} torr). Table 2 lists the reaction probabilities and the rate constants of gas-surface reactions for which these values have been reported.

STUDIES OF CATALYTIC REACTIONS

The purpose of these investigations is to understand the mechanism of catalyzed surface reactions on the atomic scale. Studies involve the steady state or time dependent measurements of the reaction rate and product distribution using catalyst surfaces with well-characterized atomic structure and chemical composition. Unlike in 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.²⁷ Using a single crystal surface, one can make good use of low-energy electron diffraction 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 the chemical technology. Usually small catalyst particles 20 - 150 Å in size that are dispersed on high surface area support (usually oxides or oxyhydrides of aluminum or silicon) are used at pressure ranges 1 - 100 atmospheres 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 atmospheres) and the pressure dependence of the reaction rate is determined over the nine orders of magnitude range. Then the rates and product distributions that were 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 molecules per surface atom per second. 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.²⁸

For the past five years new instruments have been developed in our laboratory to permit in situ studies of the reactivity of crystal surfaces at both low and high pressures. The scheme of one of these apparatus is shown in Figure 4. 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 low-

energy electron diffraction and Auger electron spectroscopy, respectively. Then a small cup (total volume approximately 10 cm^3) can be placed around the crystal sample that isolates it from the rest of the chamber that can be pressurized to over 100 atmospheres, 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 in this circumstance. The structure and composition can be determined in situ by LEED and Auger before and after the high pressure experiment once the cup is removed. The crystal sample may be heated during both low and high pressure experiments and a vacuum of 10^{-8} torr can be maintained outside the pressurized cup in the reaction chamber. The effect of adding an impurity or a second constituent (alloying) to the surface on the reactivity 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 the low pressure and high pressure studies of catalytic reactions that were reported were carried out using platinum surfaces. We shall review the results of some of these studies that add significantly to our knowledge of the atomic scale mechanism of catalytic reactions.

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 5. The low Miller Index Pt (111) surface has a very low density of surface imperfections (less than $10^{12}/\text{cm}^2$) as compared to the number of surface atoms (1.5×10^{15} atoms/ cm^2). The high Miller Index Pt(557) surface is characterized by a stable surface structure with 80% of the surface atoms in monatomic heights. The Pt(679) surface must have in addition to high step density, a high density of kinks in the step for atoms of lower coordination since the (679) plane does not lie between two close packed planes as does the (557) plane [(111) and (001)].

Thermal stability of high Miller Index 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.²⁹ The surface sites on the different Pt surfaces are distinguishable by a coordination number, i.e., the number of nearest neighbors ranging from kink atoms with only six nearest neighbors to atoms in (111) orientation terraces with nine nearest neighbors.

It was found that the dehydrogenation of cyclohexane and cyclohexene to benzene occurs only on stepped Pt surfaces in an appreciable rate.^{28,30} Figure 6 shows the step and kink density dependence of the reaction rate of cyclohexene dehydrogenation to benzene to demonstrate this effect. While the rate increases markedly with increasing step density, it remains relatively unaffected by changes of kink density.

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 4. Thus atomic steps appear to be preferred surface sites breaking H-H and C-H

bonds (H-H bond breaking has been studied by the H_2-D_2 exchange described above²⁷). 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 7, the rate of benzene production is independent of step and kink density while n-hexane production increases slowly with step density and rapidly with kink density. Rates of cyclohexane hydrogenolysis to produce n-hexane per kink site is determined by the slope of the line in Figure 7B representing hydrogenolysis and is 1×10^{20} moles of n-hexane/kink atom/sec. This is almost an order of magnitude higher than the slope in Figure 7A which is 1.2×10^{19} moles of n-hexane/step atom/sec. The observed low hydrogenolysis activity on the type of stepped surfaces represented by Figure 7A may be caused by some regenerated kink in the steps. n-Hexane formation and the formation of other hydrogenolysis products must be the result of C-C bond scissions. It appears that kinks are very effective in breaking C-C bonds in addition to C-H and H-H bonds. Thus we have been able to identify two active sites of lower coordination number of platinum surfaces: steps with C-H and H-H 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.^{28,31} The coverage was almost independent of the pressure in the range of 10^{-6} - 10^3 torr but varied 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 and pressures and double layers under certain conditions of the reactant adsorbed on the overlayer. 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 used in the reaction studies. Several reactions are very 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 surface has been studied by low-energy electron diffraction.³² These studies indicate that the organic molecules are stable on these low index surfaces; do not undergo dehydrogenation or chemical rearrangements readily in the temperature range of 300 - 600 K. Thus while low index surfaces are excellent substrates in studies of the surface structures of adsorbed molecules, they are very poor catalysts since they are not likely to break C-H and C-C bonds under catalytic reaction conditions on platinum surfaces. 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 structures

and 4) the rearrangement of the platinum substrate in some cases by facetting.³³ The effect of increased partial pressure of hydrogen over the surface is to slow down the rate of decomposition so that processes 1 and 3 may predominate on a stepped single crystal surface.

Catalytic Studies at High Pressures on Crystal Surfaces

The ring opening of cyclopropane to form propane, the dehydrogenation of cyclohexane to cyclohexene and benzene, the dehydrocyclization of n-heptane to toluene has all been studied at high pressures as well as at low pressures on crystal surfaces. Table 3 compares the rates of these reactions at high and low pressures at 300°C. The rates increase 3 to 5 orders of magnitude with increasing the pressure by 8 to 9 orders of magnitude. Studies of the pressure dependence of 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 the cyclopropane ring opening to form propane was compared with polydispersed supported platinum catalysts.³⁴ The rates obtained on stepped platinum single surfaces were identical to published values for this reaction on supported platinum particles. This is a significant result that 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. If the atomic surface structure would play a significant role in determining the reactivity, the platinum single crystal surface may not necessarily give the same result as a polydispersed particle system where particles have a variety of atomic structures available simultaneously

for the catalytic reaction.

Structure Sensitivity of Catalytic Reactions

There are catalytic reactions whose rates change by orders of magnitude by changing the catalyst particle size when they were studied over polydispersed supported systems. For other reactions the reaction rate was independent of the catalyst particle size. These two groups were called "structure sensitive" and "structure insensitive" reactions, respectively.³⁵ 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 group. This is shown in Table 4. It would be of great value to include in this classification several other hydrocarbon reactions (isomerization, hydrogenation and oxidation) as more experimental data becomes available.

Studies to correlate the reactivity and the surface structure and composition of platinum surfaces indicate that the active platinum 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 8. 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.

The discovery that kink sites with steps are effective in breaking C-C bonds in addition to 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 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

The inhibition of a large variety of surface reactions by very small amounts of impurities has been well documented. Estimates based on experimental data indicates that each impurity may render 5 to 10 metal atoms ineffective in catalytic surface reactions. Impurity atoms may inhibit the catalytic reactivity in two ways. They may block crucial active sites necessary to break a certain chemical bond.³⁶ (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 phenomena applicable to a wide range of catalyst materials. However, there is another mechanism for poisoning. Foreign atoms that adsorb on a crystal surface may

change the surface free energy and lowering of surface free energy would be expected in the presence of adsorbed impurities as compared to the surface free energy of the clean surface. If the adsorbed impurity changes the surface free energy of the various crystal planes by different amounts, it can induce the 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.³⁷ In general, surfaces that exhibit the highest atomic densities have the lowest surface free energies. These surfaces are the (111), (100) and (110) orientations of face centered cubic crystals and the (110), (211) and (111) faces of body centered cubic solids. The ratio of surface free energies of these high density surfaces has been found to be typically 0.9:0.95 when it was measured for typical metal surfaces. Schmidt and Luss³⁸ 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 have shown that the wire surface that was composed of predominantly (111) crystal planes, has restructured in the presence of H_2S to (100) crystal planes. 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 of the differences in chemical bonding of the sulfur 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^{39,40} in addition to 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 is the property of many important catalyst systems, better understanding of the mechanism of this phenomena on the molecular level would be of great importance.

Some of the Outstanding Experimental and Theoretical
Problems in Catalysis

Both molecular beam-surface scattering studies and studies of catalytic surface reactions are in their infancy. It is not too difficult to suggest a few experimental and theoretical problems of outstanding importance in these areas that would be of immediate interest to many working in the field of surface science and catalysis science. 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 a wide variety of substances, 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 $\text{CO} + \text{H}_2$ mixtures will become available as a result of coal gasification in large quantities as raw materials for many chemical technologies.

The oxidation of ethylene on silver, the selective catalytic oxidation reactions that take place on oxide surfaces using single crystal surfaces should be explored. The low pre-exponential 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 important problems to study.

Acknowledgement

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Figure Captions

- Figure 1. Scheme of the molecular beam-surface scattering experiment.
- Figure 2. Curve A) Angular distribution of highly specularly scattered beam. Arrow indicates angle of incidence. Curve B) Scattered beam with cosine angular distribution.
- Figure 3. a) Angular distribution of H_2 and D_2 scattered from Pt(111) single crystal (HD signal is undetectable). b) 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.
- Figure 4. 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).
- Figure 5. Scheme of three representative platinum crystal surfaces: a) the (111) surface containing less than 10^{12} defects/cm²; b) (557) surface containing 2.5×10^{14} step atoms/cm² with an average spacing between steps of 6 atoms; c) (679) surface containing 2.3×10^{14} step atoms/cm² and 7×10^{13} kink atoms/cm² with an average spacing between steps of 7 atoms and between kinks of 3 atoms.
- Figure 6. 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.

Figure 7. Initial steady state rates of cyclohexane dehydrogenation to benzene (-O-) and hydrogenolysis to n-hexane (--Δ--) 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/cm². 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} moles/cm²/sec with steps present but is less (0.3×10^{14} moles/cm²/sec) 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 1×10^{20} moles/kink atom/sec and 1.2×10^{19} moles/step atom/sec.

Figure 8. Model of the active platinum catalyst surface with a full carbonaceous overlayer showing exposed catalytic bond breaking sites.

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Table 1

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

Reaction	$A^*(\text{sec}^{-1})$	$E_a(\text{kcal/mole})$	Reaction Probability
$\text{H} + \text{D}_2 \xrightarrow{\text{Pt}} \text{HD} (<600 \text{ K})$	2×10^5	4.5	$\sim 10^{-1}$
$\text{H} + \text{D}_2 \xrightarrow{\text{Pt}} \text{HD} (>600 \text{ K})$	1×10^2	0.6	$\sim 10^{-1}$
$\text{D} + \text{O}_2 \xrightarrow{\text{Pt}} \text{D}_2\text{O} (700 \text{ K})$	0.22	12	-
$\text{CO} + \text{O} \xrightarrow{\text{Pt}} \text{CO}_2 (700 \text{ K})$	-	20	$\sim 10^{-3}$
$\text{C}_2\text{H}_4 + \text{O}_2 \xrightarrow{\text{Ag}} \text{CO}_2 (800 \text{ K})$	-	8	$< 10^{-2}$
$2\text{H} \xrightarrow{\text{graphite}} \text{H}_2 (800 - 1000 \text{ K})$	-	15.9	$10^{-3} - 10^{-2}$
$\text{H}_2 \xrightarrow{\text{Ta}} 2\text{H} (1100 - 2600 \text{ K})$	-	75	4×10^{-1}
$\text{HCOOH} \xrightarrow[\text{decomp}]{\text{Ni}} \text{CO}_2 (<455 \text{ K})$	10^{12}	20.7	-
$\text{HCOOH} \xrightarrow[\text{decomp}]{\text{Ni}} \text{CO}_2 (>455 \text{ K})$	5.8×10^3	2.5	~ 0.9

* For bimolecular surface reactions, the pre-exponential 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} monolayer ($10^{13} - 10^{15}$ molecules/cm²).

Table 2

Pre-exponential Factors, Activation Energies and Reaction Probabilities
for Several Solid-Gas Reactions Studied by Molecular Beam Scattering

Reaction	A*	E _a (kcal/mole)	Reaction Probability
$\text{C} + \text{O}_2 \xrightarrow{1000-2000\text{K}} \text{CO}$	$2.5 \times 10^7 (\text{sec}^{-1})$	30	$10^{-3} - 10^{-2}$
$\text{C} + \text{O}_2 \xrightarrow{1000-2000\text{K}} \text{CO}$	$3 \times 10^{12} (\text{sec}^{-1})$	50	$10^{-3} - 10^{-2}$
$\text{C} + 4\text{H} \xrightarrow{500-800\text{K}} \text{CH}_4$	$1.27 \times 10^{-18} (\text{cm}^4/\text{atoms-sec})$	3.3	$10^{-3} - 10^{-2}$
$2\text{C} + 2\text{H} \xrightarrow{>1000\text{K}} \text{C}_2\text{H}_2$	$1.59 (\text{cm}^2/\text{atoms-sec})$	32.5	$10^{-3} - 10^{-2}$
$\text{Ge} + \text{O}_2 \xrightarrow{750-1100\text{K}} \text{GeO}$	$10^{16} (\text{sec}^{-1})$	55	2×10^{-2}
$\text{Ge} + \text{O} \xrightarrow{750-1100\text{K}} \text{GeO}$	$10^{16} (\text{sec}^{-1})$	55	3×10^{-1}
$\text{Ge} + \text{O}_3 \xrightarrow{750-1100\text{K}} \text{GeO}$	$10^{16} (\text{sec}^{-1})$	55	5×10^{-1}
$\text{Ge} + \text{Cl}_2 \xrightarrow{750-1100\text{K}} \text{GeCl}_2$	$10^7 (\text{sec}^{-1})$	25	3×10^{-1}
$\text{Ge} + \text{Br}_2 \xrightarrow{750-1100\text{K}} \text{GeBr}_2$	$10^7 (\text{sec}^{-1})$	20	3×10^{-1}
$\text{Ge} + \text{Br}_2 \xrightarrow{750-1100\text{K}} \text{GeBr}_4$			
$\text{Si} + \text{Cl}_2 \xrightarrow{1100-1500\text{K}} \text{SiCl}_2$	$10^8 (\text{sec}^{-1})$	40	3×10^{-1}
$\text{Ni} + \text{Cl}_2 \xrightarrow{900-1400\text{K}} \text{NiCl}$	$10^7 (\text{sec}^{-1})$	30	8×10^{-1}

* For bimolecular reactions, the pre-exponential factor also includes the surface concentration of one of the reactants that is held constant during the experiments.

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Table 3

Initial Turnover Number (sec^{-1}) on Pt Crystal Surfaces
(300°C)

Reaction	High Pressure (Total pressure 215 torr reactant pressure 15 torr)	Low Pressure (Total pressure 8×10^{-7} torr reactant pressure 4×10^{-8} torr)
C_6H_{12} C_6H_6	3	6.3×10^{-5}
C_6H_{12} C_6H_{10}	2×10^{-2}	2.0×10^{-5}
C_6H_{10} C_6H_6	100	4×10^{-3}
n-heptane toluene	10^{-2}	10^{-5}
n-heptane methyl cyclohexane	10^{-1}	-
cyclopropane propane	150	10^{-3} (total pressure 7×10^{-5} torr)

Table 4

Classification of Reactions by Step Density and Carbonaceous Overlayer Dependence

Step Structure-Sensitive		Step Structure-Insensitive	
Overlayer structure sensitive	Overlayer structure insensitive	Overlayer structure sensitive	Overlayer structure insensitive
cyclohexene → benzene n-heptane → toluene	cyclohexane → n-hexane		cyclohexane → cyclohexene cyclopropane → propane

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XBL 708-1973

Figure 1

XBL 738-1710

Figure 2

0 0 0 0 4 4 0 1 1 7 3

Figure 3

Figure 4

XBL 756-3160

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

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

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

XBB 758-5903

Figure 5

XBL756-3164A

Figure 6

Figure 7

XBL 733-5908

Figure 8

0 0 0 0 4 4 0 1 1 7 6

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