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THE MECHANISM OF HYDROCARBON CATALYSIS ON PLATINUM CRYSTAL SURFACES

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THE MECHANISM OF HYDROCARBON CATALYSIS ON PLATINUM CRYSTAL SURFACES

by

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Abstract

In the past several years we have studied the atomic structure of platinum crystal surfaces and the structure of adsorbed hydrocarbons by low-energy electron diffraction and the surface composition by Auger electron spectroscopy. Catalytic reactions of low reaction probability (dehydrocyclization, dehydrogenation) have been studied on one face of a single crystal of area less than 1 cm^2 by mass spectrometry at low pressures ($\approx 10^{-4}$ torr) and by gas chromatography at high pressures ($\approx 10^{-3}$ torr).

The atomic structure of high Miller Index platinum surfaces is characterized by atomic height steps arranged periodically and separated by atomic terraces of low Miller Index orientation [(111)or(100)]. Experiments that compare the reactivity of crystal surfaces and supported platinum particles indicate that the atomic structure of polydispersed catalyst particles can be reproduced on these stepped crystal surfaces. The structure of adsorbed hydrocarbons have been studied on both low and high Miller Index platinum surfaces. Atomic steps play a controlling role in dehydrogenating the hydrocarbon molecules and in dissociating hydrogen and other diatomic molecules of large binding energy. n-Heptane may undergo isomerization, hydrogenolysis and dehydrocyclization on the various platinum surfaces. The atomic structure of the stepped crystal surfaces appear to control the product distribution for these competing reactions.

Introduction

Platinum is one of the most versatile elements utilized for heterogeneous catalysis. It is employed to catalyze a large variety of hydrocarbon reactions in reducing atmospheres, (for example in hydrogen), and oxidation reactions ranging from mild oxidation of alcohols to ketones to one of the most exothermic reactions, the ammonia oxidation. Moreover, it has been possible to prepare platinum catalysts (thin films or dispersed particle forces) in such a way that it selectively catalyzes one out of many competing hydrocarbon reactions. If the catalyst is prepared differently, it catalyzes another hydrocarbon reaction selectively and yields an entirely different product distribution from the same mixture of reactants.[1,2,3] We have, for years, been studying platinum crystal surfaces by a variety of techniques and I would like to suggest that the key to the platinum activity and selectivity that is built in by appropriate surface preparation is the atomic surface structure that forms. The microstructure in which platinum atoms have different atomic environments and different numbers and arrangements of nearest neighbors determines which way the complex hydrocarbon reaction proceeds. Thus, in order to understand and control hydrocarbon catalysis of platinum, we have to uncover the correlation between the atomic surface structure and the reactivity. This paper reports on the status of our research in this field in which we utilize a variety of techniques described below.

In order to solve such a complex problem as the understanding of the mechanism of platinum catalysis of hydrocarbons, we have divided our research and thus, this presentation into smaller segments. These parts are:

(a) The kinetics and mechanism of hydrogen dissociation via studies of H_2-D_2 exchange reaction, (b) The adsorption of hydrocarbons on various platinum surfaces, (c) Comparison of reaction rates of platinum crystals at high pressures with rates on platinum particles dispersed on porous alumina supports, and (d) Correlation of reactivity (turnover number) for a given hydrocarbon reaction with the atomic structure of platinum and correlation of product distribution with atomic structure. We shall discuss briefly and separately these various research studies and summarize only those observations that are important to the understanding of the mechanism of platinum catalysis that we have arrived at up to the present. It is hoped that clear statements of the key observations at the end of each of these sections will facilitate theoretical formulations of outstanding problems of metal catalysts.

The study of catalysis on the atomic scale was made possible by the availability of sensitive mass spectrometer and gas chromatograph detectors that can monitor the products of surface reactions coming from crystal surfaces of an area less than 1 cm^2. In this way, single crystals of well-defined orientation can be used as catalysts.[4] The surface structure is monitored by low-energy electron diffraction, the surface composition by Auger electron spectroscopy, and the kinetics of the surface reactions are monitored in a steady-state flux of reactants at high (1 atmosphere), or at low (10^{-4} torr) pressures, or in a well-defined molecular beam. With the combination of these powerful techniques at hand, the reactivity can readily be followed as a function of surface structure and surface composition.

The Platinum Crystal Surfaces and the Various Techniques used to Investigate Their Surface Characteristics

Platinum is a face-centered cubic metal with a melting point of 1769°. The highest density lowest free energy surface in vacuum is designated by the Miller Index (111) followed by the (100) crystal face. In the presence of surface impurities or adsorbates, the relative surface free energy of the various crystal faces may change. This can result in rearrangement of the atomic surface sturcture.[5] The low-energy electron diffraction pattern characteristic of the clean platinum (111) and (100) surfaces are shown in Figure 1a and 1b, along with the schematic representation of their real lattice structure. In the (111) crystal surface, each atom has six nearest neighbors and the structure is similar to that expected from the projection of the X-ray unit cell to the (111) surface. The clean (100) crystal face along with the clean (110) crystal face are reconstructed, i.e. the surface structures are different from the one expected from the X-ray unit cell. This surface reconstruction has been studied in several laboratories and it appears to be due to a hexagonal distortion of the surface layer in the (100) crystal face. The accurate location of the atoms in the reconstructed surface awaits the surface structure analysis from the low-energy electron diffraction beam intensities which is in progress in this laboratory and in others.

When the crystal is cut at an angle with respect to the low Miller Index surface along a high Miller Index plane, a stepped surface results. Figure 2 shows the low-energy electron diffraction pattern of the (775) surface that is cut at 9.5° to the (111) face in the direction of the (100) face along with the schematic diagram of the real space lattice that can

be deduced from the diffraction pattern. Detailed analysis of stepped surfaces of metals and semi-conductors have been made and the methods of analysis are described elsewhere.[6,7] The atomic surface structure of the (775) face is composed of (111) orientation terraces separated by steps of one atom height whose orientation is (100), as determined by the angle of cut. The step periodicity gives rise to the doubling of the diffraction beams at certain electron energies as indicated by Figure 2a. Experience in this laboratory indicates that these stepped or vicinal surfaces have a high degree of thermal stability if the terraces are five atoms wide on the average, or wider. The stepped surfaces can readily be regenerated after partial disordering by heat treatment near the melting point or ion bombardment. Stepped surfaces with three or four atom wide terraces appear to undergo faceting on heat treatment or during adsorption. In our notation the (775) surface is designated as Pt(S)-[6(111)x(100)] where S indicates a stepped surface, 6(111) indicates the widths and orientation of the terrace and (100) indicates the orientation of the steps that are of one atom in height (the 1 to indicate the step height is deleted for brevity). This notation describes the atomic surface structure more realistically than the Miller Index notation. Figure 3 shows the diffraction pattern and the schematic diagram of the real lattice structure of the surface cut at 9.5° from the (111) crystal face and rotated 20° in the direction of the (310) face. Since the step orientation is one of high Miller Index, the steps should have a fairly high concentration of kinks in addition to those that are thermally regenerated in the step. Indeed, the chemical behaviour of this Pt(S)-[7(111)x(310)] surface is different from that of the other stepped surfaces with (100) step orientation.[8]

These low index and stepped surfaces are representative of the variety of surface structures that are used in our catalytic studies of platinum. One may vary the angle of cut, thereby changing the terrace widths and step orientation of the platinum surface. We have prepared surfaces with 5 to 18 atom wide terraces of (111) or (100) orientation. As long as the stable stepped platinum surfaces are clean, the step height is monatomic. On adsorption of hydrocarbons, the step heights and terrace widths may change.

The surface structure of platinum and of adsorbed gases have been studied by low-energy electron diffraction and the surface composition monitored by Auger electron spectroscopy. The transport studies to determine the reactivity of the platinum surfaces were carried out in three ways. By the steady state transport method, the flux of reactants incident on the platinum surface and the reaction products that form were monitored by a mass spectrometer in a manner shown schematically in Figure 4.[9] Because of the mass spectrometer detector, the highest pressure that can be employed is of the order of 10^{-4} torr. The schematic diagram of the apparatus that is used at reactant pressures as high as two atmospheres is shown in Figure 5. Using the gas chromatograph detector, this "stirred batch reactor" can readily monitor the ring opening of cyclopropane on one face of a single crystal of area less than 1 cm^2.[10] Reactions at both low and high pressures can be investigated using the apparatus shown in Figure 5. The detailed description and working principles of these instruments are described in recent publications.[10,11]

Another method to study the kinetics of surface reactions is that of molecular beam scattering. Figure 6 shows the scheme of the molecular

beam scattering apparatus used in studies of the H_2-D_2 exchange reaction on the various platinum surfaces.[12] A well-collimated molecular beam of the reactant gas or gas mixture is scattered from the crystal surface and the products desorbed at a given solid angle are detected by mass spectrometer. In this fashion, the angular distribution of the scattered products can be determined. Moreover, since the incident molecular beam is chopped at a well-defined frequency, usually between 100-5000 Hz, the flight time of the scattered molecules can be measured. Thus, from the flight time the residence time of the reacting molecules on the surface, i.e. the minimum residence time necessary to detect reaction products, can be determined in the range of 10^{-6} to 10^{-2} seconds.[13] This is in contrast with the steady state transport method of reaction product analysis which gives time averaged reaction product concentration.

a. The kinetics of H_2-D_2 exchange on platinum crystal surfaces

Using molecular beams, the HD product concentration and angular distribtuion was monitored from the Pt(111), the Pt-[9(111)x(111)] and the Pt[5(111)x(111)] surfaces.[13] The chopping frequency of the incident beam was varied in such a way that product molecules that formed in a period of 10^{-2} seconds or less were detectable, while those formed in times longer than 10^{-2} seconds were not. Under these conditions, in the temperature range of 300-700°K, no HD molecules could be detected from the (111) platinum surface while quite large HD concentrations were observed from the two stepped surfaces. These observations indicate reaction probabilities of the order of 10^{-3} on the stepped surfaces and less than 10^{-6} on the (111) face. The reaction rate was first-order in hydrogen or deuterium pressure and from the temperature dependence of the HD signal amplitude,

an activation energy of 4.5 kcal has been deduced for this reaction. The HD product had cosine angular distribution indicating complete thermal accomodation with the platinum surface prior to desorption.

Atomic steps on the platinum surfaces are essential in dissociating hydrogen and deuterium. (Without the presence of a large concentration atomic steps the probability for the exchange reaction to occur is very low). In the presence of atomic steps the hydrogen molecules dissociate with low activation energy and the surface is able to store a large concentration of atoms. This way, the surface converts the bimolecular reaction between H_2 and D_2 which is improbable due to the large energy of dissociation of the molecules (~103 kcal) to an atom molecule reaction ($H + D_2$) at low activation energy. The atoms react with the incident molecules by a two branch mechanism. At low temperatures (<700°K) the the rate limiting step appears to be the diffusion of the molecule on the surface to a site where the hydrogen deuteride can be formed. At high temperatures the reaction between an adsorbed atom and a molecule incident at an atomic step competes with the diffusion controlled low temperature branch.[13] These reactions take place on the stepped surfaces in residence times of less than 10^{-2} seconds which appears to be too short for the reaction to occur on the low Miller Index (111) crystal face.

<u>Summary</u>: Atomic steps play controlling role in dissociating hydrogen molecules on platinum surfaces.

b. The adsorption of hydrocarbons on the low Miller Index and stepped platinum surfaces

The adsorption of hydrocarbons on the (111) and (100) and stepped platinum surfaces has been studied by low-energy electron diffraction and work function change measurements in the surface temperature range of

20-300°C.[14,15] Over forty organic molecules were investigated using the low Miller Index surfaces at low pressures in the range of 10^{-9} to 10^{-7} torr. The observed work function change is always negative indicating that the organic molecules that adsorb are net electron donors to the metal. Table I lists the work function changes and the surface structures that were obtained on adsorption of the various hydrocarbons. Both the work function change and the low-energy electron diffraction patterns indicate that on these low Miller Index platinum surfaces, the organic molecules are stable, do not undergo dehydrogenation or chemical rearrangements readily in the temperature range of 20-300°C. Following adsorption, re-orientation of the molecules in the adsorbed layer is necessary to form ordered structures. Molecules that have higher rotational symmetry or have only small size substituents on the benzene rings exhibit better ordering. The adsorbed layers are more ordered on the (111) crystal face than on the (100) face of platinum. Both the diffracton and the work function change data indicate that substituted benzenes chemisorb with their benzene ring parallel to the surface and interact with the metal via the π electrons in the benzene ring. Benzene itself undergoes re-orientation on the platinum surface with increasing exposure that indicates a change from predominantly π-bonding to σ-bonding as the surface coverage increases. The large work function change on adsorption of pyridine (-2.5 v) and the adsorption characteristics of substituted pyridines indicate that the nitrogen participates in the adsorbate-substrate bond.

The chemisorption of hydrocarbons has entirely different characteristics on stepped platinum surfaces.[8] While the hydrocarbon molecules remain largely intact on the low Miller Index surface in the temperature range

of 20-300°, they undergo chemical reactions readily, dehydrogenation and/or decomposition even at 20°. Products of the chemisorption are partially dehydrogenated carbonaceous deposits whose characteristics depend on the surface structure of the stepped platinum surfaces, the type of hydrocarbon chemisorbed, the rate of adsorption, and the surface temperature. The distinctly different chemisorption characteristics of the various stepped platinum surfaces, that are described in detail elsewhere, have been explained by considering the interplay of four competing processes;[8] (1) dehydrogenation, (2) decomposition of the organic molecules, (3) the nucleation and the growth of ordered carbonaceous surface structures, and (4) the rearrangement of the platinum substrate by faceting. 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 stable stepped crystal surface

Summary: Atomic steps and other microstructures due to platinum atoms in various states of coordination present in steps control the rates of breaking C-H and C-C bonds. In the absence of large concentrations of steps, the adsorbed hydrocarbon molecules remain intact below 300°C so that their surface crystallography can readily be studied.

c. Comparison of reaction rates for the cyclopropane ring opening on platinum crystals and supported platinum catalysts

There is a gap between chemisorption and surface reaction studies performed in ultra-high vacuum on single crystal surfaces and those carried out at one atmosphere or at higher pressures on highly dispersed supported catalysts. The purpose of this line of research is to breach

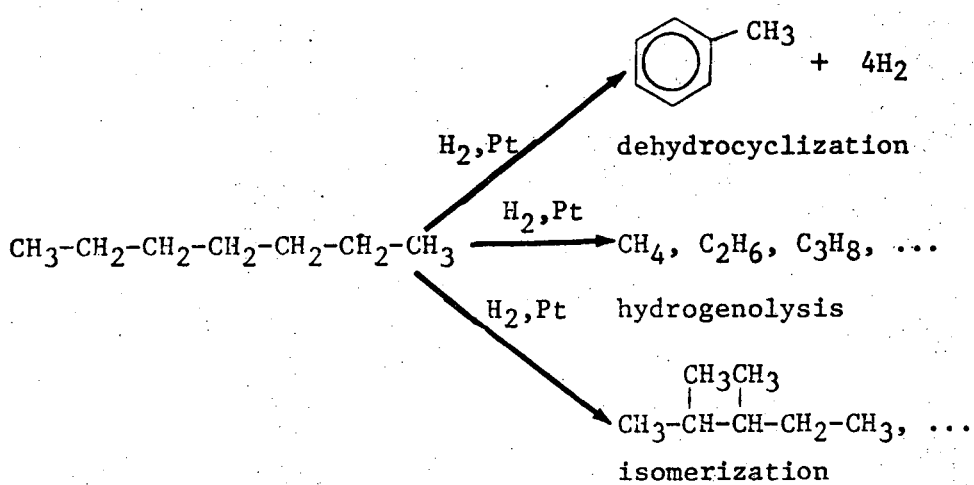
the gap between these two fundamental areas of catalytic research.[10] The objective was to measure reaction rates on well-defined single crystal surfaces both at high pressures (1 atmosphere) and at low pressures after preparation in ultra-high vacuum in the range of 10^{-4} to 10^{-8} torr within the same apparatus. The hydrogenolysis of cyclopropane was studied at 1 atmosphere total pressure on a stepped single crystal surface of platinum. The hydrogenolysis of cyclopropane was chosen as the test reaction because of the considerable amount of data and experience which has been collected in various laboratories. The rate is relatively high at room temperature on supported platinum catalysts and only one product, propane, is formed on platinum catalysts below 150° thereby simplifying the analysis of the results. Table II summarizes the results that were obtained and compares our results on stepped single crystal surfaces at atmospheric pressures with those of others obtained using supported platinum catalysts.[11] It appears that at one atmosphere pressure, the platinum stepped single crystal behaves very much like a highly dispersed supported platinum catalyst for the cyclopropane hydrogenolysis. This observation supports the contention that well-defined crystal surfaces are excellent models for polycrystalline supported metal catalysts. It also tends to verify Boudart's hypothesis that the cyclopropane hydrogenolysis is an example of a structure insensitive reaction. The initial specific reaction rates that were reproducable within 10% were within a factor of 2 identical to published values for this reaction on highly dispersed platinum catalysts. The activation energies that were observed for this reaction, in addition to the turn-over number (number of molecules

formed per platinum atom per width), are close enough on the various platinum surfaces, that we may call the agreement excellent.

Summary: Single crystal platinum surfaces with well-defined structures are realistic models for dispersed supported metal catalyst particles. Thus, the information obtained on crystal surfaces can be utilized to explain the reactivity of supported metal catalysts.

(d) The reactions of n-heptane on platinum surfaces of varying atomic structure.

n-Heptane may undergo a variety of chemical reactions on platinum surfaces that include hydrogenolysis, dehydrocyclization, and isomerization,



(16)

It has been well-documented in the patent literature[1,2,3] that, depending on the catalyst preparation, the ratio of products that form in these competing reactions can be varied widely. The turn-over numbers (number of product molecules per platinum atom per minute) have been measured and were in the range of 10^{-3} for hydrogenolysis and isomerization and 10^{-4} for dehydrocyclization. We have studied these various reactions in our steady state flux low-pressure system[17] using a mass spectrometer detector and hydrogen to n-heptane ratio of 5:1. In one study we used stepped surfaces with (111) terrace to (100) stepped orientation which differed only by the width of their terraces from 4-10 atoms wide. The rates of hydrogenolysis and isomerization reactions

appear to increase somewhat with increasing step density without exhibiting marked structural sensitivity. As long as atomic steps are present in fairly large concentrations, these reactions occur readily on single crystal surfaces at low pressures with turn-over numbers comparable to those reported on platinum powders at high pressures.[18] Low-energy electron diffraction and Auger electron spectroscopy studies have revealed that the platinum surface is covered with a layer of disordered carbonaceous deposit while these reactions take place at low pressures. The presence of this deposit does not hinder the catalyzed surface reactions in any way. While the over-all rate of the hydrogenolysis reaction shows minimal surface structure sensitivity, when the turn-over numbers are compared for the various stepped platinum surfaces, the product distribution is markedly dependent on the atomic structure of platinum. Using polycrystalline platinum foils that were cleaned by high temperature oxidation (approximately 1400°C, 10^{-7} torr oxygen), methane is the predominant hydrogenolysis product of n-heptane at 350°. Using the Pt(S)-[6(111)x(100)] surface, the ratio of methane to ethane to propane of 5:3:2 was observed at 350°. Thus, the nature of C-C bond breaking depends very much on surface structure. These results indicate a similar mechanism for the hydrogenolysis and isomerization reactions to that suggested by Touroude and Gault.[19] The presence of carbonaceous residues on the metal surface was also observed by Merta and Porec[20] during cyclopropane hydrogenolysis and by Sinfelt[21] for the hydrogenolysis of ethane.

The dehydrocyclization reaction to form toluene exhibited a behaviour very different from the other two competing reactions. Toluene formation is detectable only if the stepped platinum surface is covered with an ordered layer of carbonaceous deposit. It appears that this complex reaction will take place only in the presence of such a template that is

a partially dehydrogenated ordered carbonaceous deposit. The ordered deposit, in turn, forms only on stepped platinum surfaces with the appropriate atomic structure, terrace width and orientation and step orientation. These chemical reactions do not take place on the (111) crystal face of platinum. Within minutes, (using the same reaction conditions as that for stepped surfaces), the low Miller Index surface is covered with a layer of graphitic carbon that poisons the catalytic activity. If this ordered layer fails to form on account of the presence of surface impurities or high temperature oxidation of platinum or some other reasons of surface preparation, the dehydrocyclization reaction does not occur.

Summary: The catalytic activity of platinum in hydrocarbon reactions is controlled by platinum atoms surrounded by less neighbors than the atoms in the close-packed low Miller Index crystal planes.

The dehydrocyclization of n-heptane to toluene is only detectable at low pressures (10^{-4} torr) if the surface is covered with a layer of ordered carbonaceous deposits. While the competing hydrogenolysis and isomerization reactions do not require the presence of such ordered structures, the product distributions of these two reactions, just as in dehydrocyclization, are markedly dependent on the surface structure of platinum.

Discussion

The various studies using platinum surfaces that were reviewed all indicate that the key to the reactivity of platinum is the atomic step structure. Since the steps occur with well-defined periodicity, the atomic structure of these active sites can readily be studied by diffraction.

Platinum atoms in steps can exist in several different atomic environments which are distinguishable by the number of nearest neighbors, by the various nearest neighbor bond lengths and bond angles. Changing such a microstructure by suitable surface preparation can drastically alter the relative rates of competing hydrocarbon reactions and the product distribution. Thus, platinum catalysts can be tailored to yield desired products by manipulation of the surface structure. The marked differences in the reactivity of the various surface sites indicate differences in the strengths of the chemical bonds (Pt-C, Pt-H) from site to site. It is likely that such differences in chemical bonding are due to density variations for platinum atom in various surfaces sites. The largest difference in charge density is perhaps between platinum atoms in a step and in a terrace.

Since platinum atoms may be placed in several different atomic environments on a given surface each catalyst particle can be multi-functional and can catalyze several simple reactions simultaneously. It is our hope that using stepped crystal surfaces of well-defined atomic structure will allow the various catalytic functions of the surface microstructures to be identified and isolated.

There is a significant body of data available that indicates the presence of partially dehydrogenated carbonaceous residues (ordered or disordered) on the metal surface during hydrocarbon reactions at low or high pressures and in the presence of excess hydrogen. More detailed scrutiny of the mechanism of metal catalysis of hydrocarbons must include studies of the electronic structure of the adsorbed carbonaceous layer.

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TABLE I

Work Function Changes and Structural Information for Adsorption of Organic Compounds on the Pt(111) and Pt(100)-(5×1) Surfaces

		Pt(111)			Pt(100)-(5×1)			
Adsorbate	Temp °C	Work Function Change: Press (Torr)	Work Function Change: WFC (Volts)	Adsorbate Diffraction Features or Surface Structure	Work Function Change: Press (Torr)	Work Function Change: WFC (Volts)	Substrate Structure after Adsorption	Adsorbate Diffraction Features or Surface Structures
Acetylene	20°	1×10^{-8}	- 1.5	(2×2)	4×10^{-7}	- 1.65	(1×1)	$(\sqrt{2}\times\sqrt{2})R45°$
	20°	1×10^{-8} (10 min)	- 1.65	disordered				
	150°	4×10^{-7}	- 1.8	disordered	4×10^{-7}	- 1.7	(1×1)	$(\sqrt{2}\times\sqrt{2})R45°$
Aniline	20°	1×10^{-8}	- 1.8	Streaks at 1/3 order diffuse (1/2 0) features	1×10^{-8}	- 1.75	(1×1)	disordered
Benzene	20°	4×10^{-7}	- 1.8	poorly ordered	3×10^{-7}	- 1.6	(1×1)	diffuse ring-like 1/2 order streak
	20°	4×10^{-7} (5 min)	- 1.4	$\begin{vmatrix} -2 & 2 \\ 4 & 4 \end{vmatrix}$				
	20°	4×10^{-7} (40 min)	- .7	$\begin{vmatrix} -2 & 2 \\ 5 & 5 \end{vmatrix}$	3×10^{-7} (2 hrs)	- 1.3	(1×1)	diffuse 1/2 order streak
Biphenyl	20°	2×10^{-9}	- 1.85	very poorly ordered	2×10^{-9}	- 1.8	(1×1)	disordered
n-Butylbenzene	20°	8×10^{-9}	- 1.5	disordered	8×10^{-9}	- 1.5	(1×1)	disordered
t-Butylbenzene	20°	5×10^{-8}	- 1.7	disordered	5×10^{-8}	- 1.75	(1×1)	disordered
Cyanobenzene	20°	1×10^{-8}	- 1.6	diffuse (1/3 0) features	1×10^{-8}	- 1.5	faint (5×1)	disordered
1,3-Cyclohexadiene	20°	2×10^{-8}	- 1.75	poorly ordered	2×10^{-8}	- 1.7	(1×1)	diffuse 1/2 order streak
	20°C	2×10^{-8} (1 hr)	- 1.3	$\begin{vmatrix} -2 & 2 \\ 4 & 4 \end{vmatrix}$	2×10^{-8} (1 hr)	- 1.6	(1×1)	diffuse 1/2 order streak
	20°C	3×10^{-7} (5 hrs)	- .8	$\begin{vmatrix} -2 & 2 \\ 5 & 5 \end{vmatrix}$	2×10^{-8} (5 hrs)	- 1.4	(1×1)	diffuse 1/2 order streak
Cyclohexane	20°	6×10^{-9}	- 1.2	(1×1) low background	6×10^{-9}	- .75	(5×1)	low background
	20°	4×10^{-7}	- .7	very poorly ordered	4×10^{-7}	- .4	(1×1)	diffuse streaked (2×1) pattern
	150°	4×10^{-7}	- 1.1	apparent (2×2)	4×10^{-7}	- 1.2	(1×1)	streaked (2×1) pattern
	300°	4×10^{-7}	- 1.4	disordered	4×10^{-7}	- 1.5	(1×1)	disordered
Cyclohexene	20°	6×10^{-7}	- 1.7	$\begin{vmatrix} 2 & 2 \\ 4 & -2 \end{vmatrix}$	6×10^{-7}	- 1.6	(1×1)	diffuse (1/2 0) features
	150°	6×10^{-7}	- 1.6	apparent (2×2)	6×10^{-7}	- 1.5	(1×1)	streaked (2×1) pattern
Cyclopentane	20°	7×10^{-9}	- .95	(1×1) low background	7×10^{-9}	- .4	(5×1)	low background
	20°	4×10^{-7}	- .7	disordered	4×10^{-7}	- .3	(1×1)	diffuse features at 1/2 order
Cyclopentene	20°	-	-	----	2×10^{-7}	- 1.4	(1×1)	diffuse streaked (1/2 0) features
2,6-Dimethyl-pyridine	20°	4×10^{-8}	- 1.6	diffuse 1/3.2, 2/3.2 order streaks	4×10^{-8}	- 1.5	faint (5×1)	disordered
3,5-Dimethyl-pyridine	20°	6×10^{-8}	- 2.3	diffuse 1/2 order streak	6×10^{-8}	- 2.2	(1×1)	disordered

TABLE I, con't.

Work Function Changes and Structural Information for Adsorption of Organic Compounds on the Pt(111) and Pt(100)-(5×1) Surfaces

		Pt(111)			Pt(100)-(5×1)			
Adsorbate	Temp °C	Work Function Change		Adsorbate Diffraction Features or Surface Structure	Work Function Change		Substrate Structure after Adsorption	Adsorbate Diffraction Features or Surface Structures
		Press (Torr)	WFC (Volts)		Press (Torr)	WFC (Volts)		
Ethylene	20°	1×10^{-8}	- 1.5	diffuse (1/2 0) features	1×10^{-8}	- 1.2	(1×1)	$(\sqrt{2} \times \sqrt{2})R45°$
	250°	1×10^{-8}	- 1.7	disordered	1×10^{-8}	- 1.5	(1×1)	disordered
Graphitic Overlayer	950°		- 1.1	ringlike diffraction features		- 1.0	(1×1)	ringlike diffraction features
n-Hexane	20°	5×10^{-8}	- 1.1	disordered	5×10^{-8}	- .8	(1×1)	disordered
	20°	5×10^{-8} (5 hrs)	- .9	disordered	5×10^{-8} (5 hrs)	- .6	(1×1)	disordered
	250°	5×10^{-8}	- 1.5	disordered	5×10^{-8}	- 1.2	(1×1)	disordered
Isoquinoline	20°	6×10^{-8}	- 1.9	diffuse (1/3 0) and (2/3 0) features	6×10^{-8}	- 2.1	(1×1)	disordered
Mesitylene	20°	4×10^{-8}	- 1.7	Streaks at 1/3.4 order diffuse (2/3.4 0) features	4×10^{-8}	- 1.7	(5×1)	1/3 order streaks
	20°	4×10^{-7}	- 1.35	disordered	4×10^{-7}	- 1.2	(1×1)	disordered
2-Methyl-naphthalene	20°	6×10^{-8}	- 2.0	very poorly ordered	4×10^{-9}	- 1.6	faint (5×1)	disordered
Naphthalene	20°	9×10^{-9}	- 1.95	apparent (3×1)	9×10^{-9}	- 1.7	(1×1)	disordered
	150°	9×10^{-9}	- 2.0	(6×6)	9×10^{-9}	- 1.65	(1×1)	disordered
Nitrobenzene	20°	9×10^{-9}	- 1.5	diffuse (1/3 0) features (pattern electron beam sensitive)	9×10^{-9}	- 1.4	(1×1)	disordered
Piperidine	20°	8×10^{-8}	- 2.1	disordered	8×10^{-8}	- 2.05	faint (5×1)	disordered
Propylene	20°	2×10^{-8}	- 1.3	(2×2) (pattern electron beam sensitive)	2×10^{-8}	- 1.2	(1×1)	1/2 order streaks (pattern electron beam sensitive)
Pyridine	20°	1×10^{-8}	- 2.7	diffuse (1/2 0) features	1×10^{-8}	- 2.4	(1×1)	disordered
	250°	1×10^{-8}	- 1.7	well defined streaks at 1/3, 2/3, 3/3 order	1×10^{-8}	-	(1×1)	$(\sqrt{2} \times \sqrt{2})R45°$
Pyrrole	20°	6×10^{-8}	- 1.45	diffuse (1/2 0) features (pattern electron beam sensitive)	6×10^{-8}	- 1.6	(1×1)	diffuse (1/2 0) features
Quinoline	20°	3×10^{-8}	- 1.45	diffuse 1/3 order streaks	3×10^{-8} (6 min)	-	(5×1)	diffuse 1/3 order streaks
					3×10^{-8} (14 min)	- 1.7	(1×1)	disordered
Styrene	20°	6×10^{-8}	- 1.7	streaks at 1/3 order	6×10^{-8}	- 1.65	(1×1)	very poorly ordered
Toluene	20°	1×10^{-9}	- 1.7	streaks at 1/3 order	1×10^{-9}	- 1.55	(5×1)	streaks at 1/3 order
	150°	1×10^{-9}	- 1.65	(4×2)	1×10^{-9}	- 1.5	(1×1)	disordered
m-Xylene	20°	1×10^{-8}	- 1.8	streaks at 1/2.6 order	1×10^{-8}	- 1.65	(5×1)	streaks at 1/3 order

TABLE II

Comparison of Initial Specific Rate Data for the Cyclopropane Hydrogenolysis on Platinum Catalysts

Data source	Type of Catalyst	Calculated specific reaction rate @ P°_{CP} = 135 torr and T = 75°C $\left(\frac{\text{moles } C_3H_8}{\text{min} \cdot \text{cm}^2\text{Pt}}\right)$	$\left(\frac{\text{molecules } C_3H_8}{\text{min} \cdot \text{Pt site}}\right)$
Present study	Run 10A	2.1×10^{-6}	
	Run 12A	1.8×10^{-6}	
	Run 15	1.8×10^{-6}	
	Run 16	2.1×10^{-6}	
	Average	1.95×10^{-6}	312
Hegedus[30,49]	0.04 Wt%Pt on $\eta - Al_2O_3$	7.7×10^{-7} based on 100% Pt dispersion	410
Boudart *et al.*[17] and Dougharty[28]	0.3% and 2.0% Pt on $\eta - Al_2O_3$;	8.9×10^{-7}	480
	0.3% and 0.6% Pt on $\gamma - Al_2O_3$	2.5×10^{-6}	1340

Figure Captions

(1) [a] Low-energy electron diffraction pattern and schematic representation of the Pt(111) face.

[b] Diffraction pattern of the Pt(100) surface and schematic representation of the (100) surface with a hexagonal overlayer.

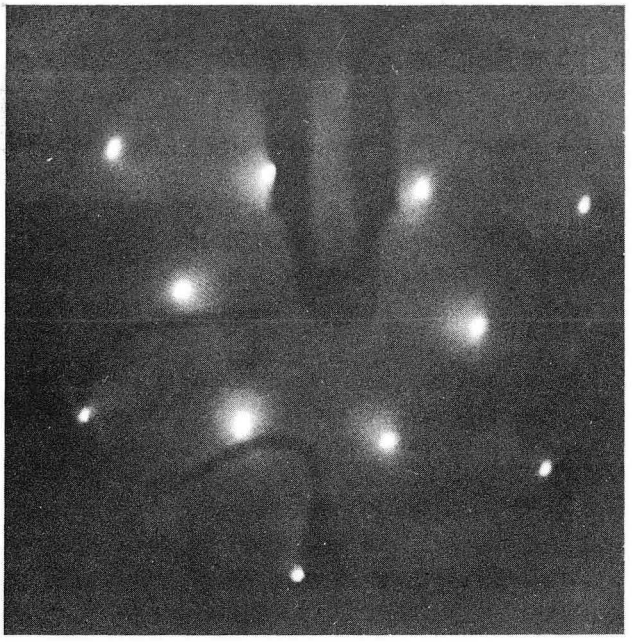
(2) Diffraction pattern from the Pt(5)-[6(111)x(100)] surface and its schematic representation.

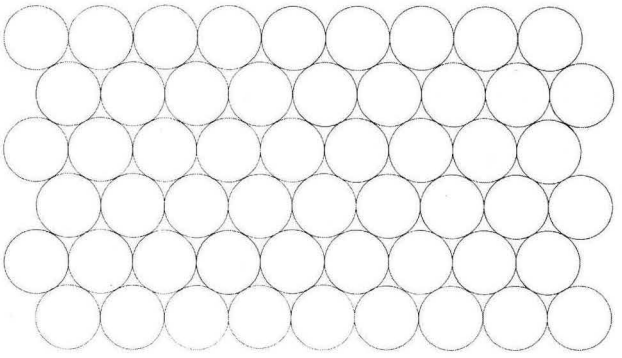
(3) Diffraction pattern and schematic representation of the Pt(S)-[7(111)x(310)] surface.

(4) Schematic diagram of the diffraction chamber that was also used to carry out the low pressure (~10^{-4} torr) surface reaction studies.

(5) Schematic of the UHV assembly for high pressure catalysis on single crystal platinum surfaces.

(6) Molecular Beam Surface Scattering Apparatus.

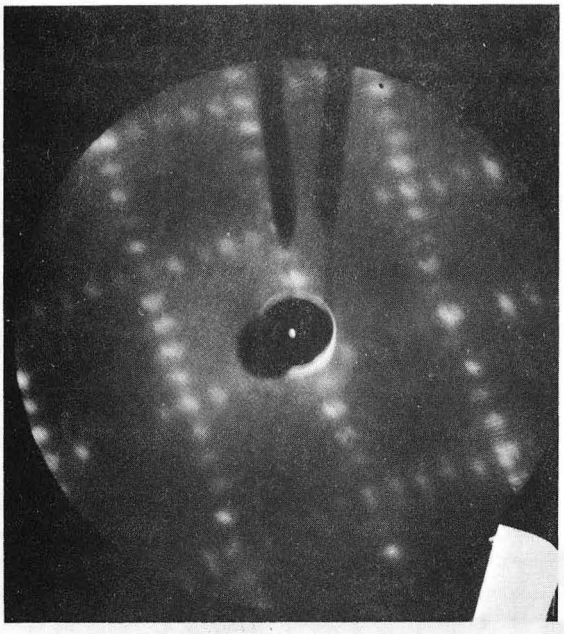


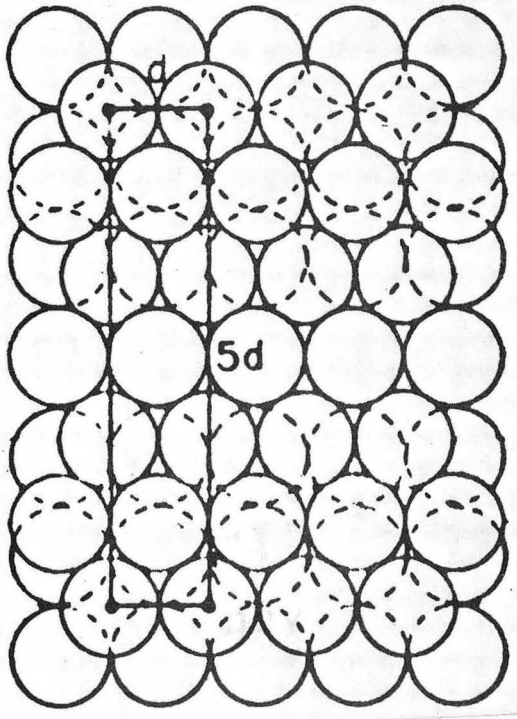


XBB 7110-5214

Figure 1a

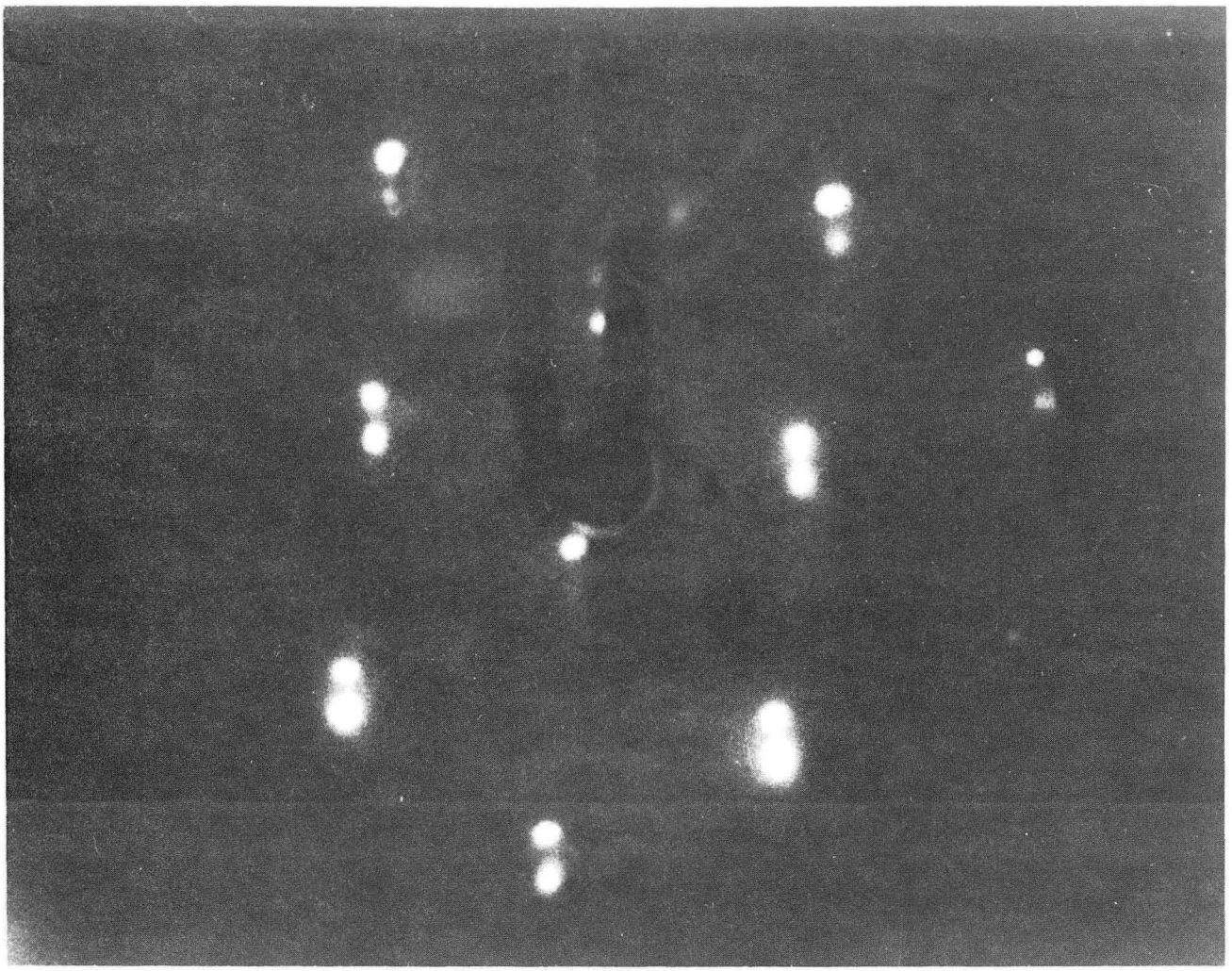
0 0 0 0 4 2 0 0 2 1 7

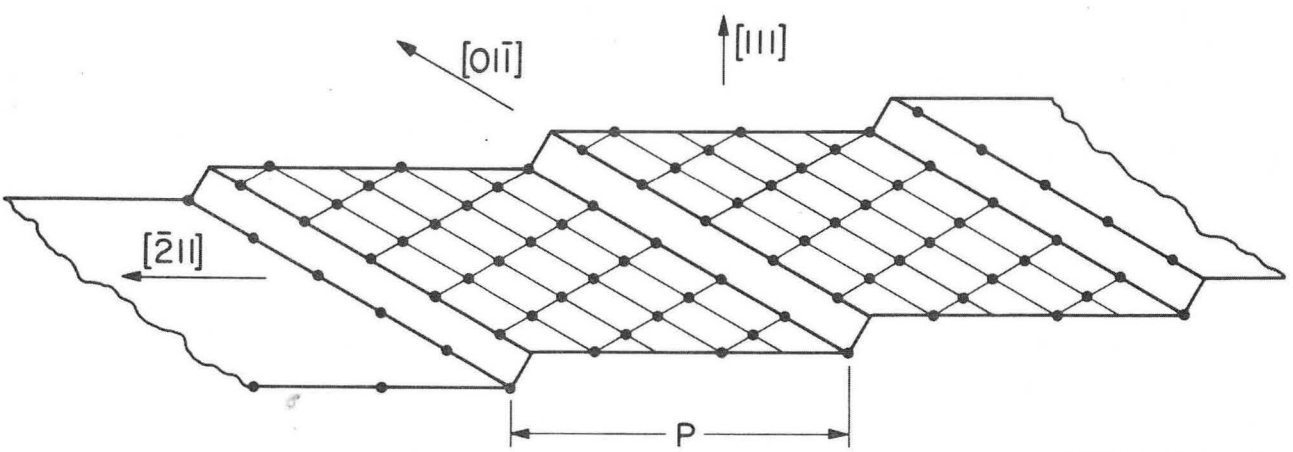




XBB 7110-5356

Figure 1b

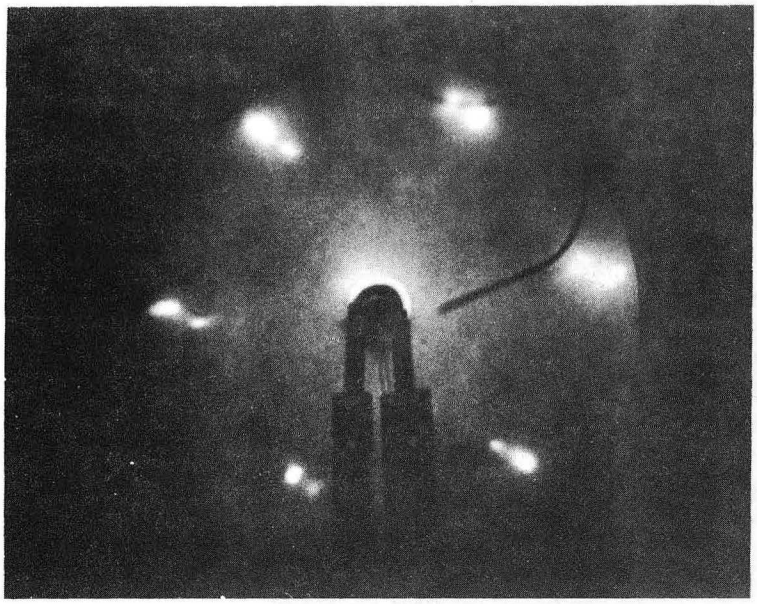


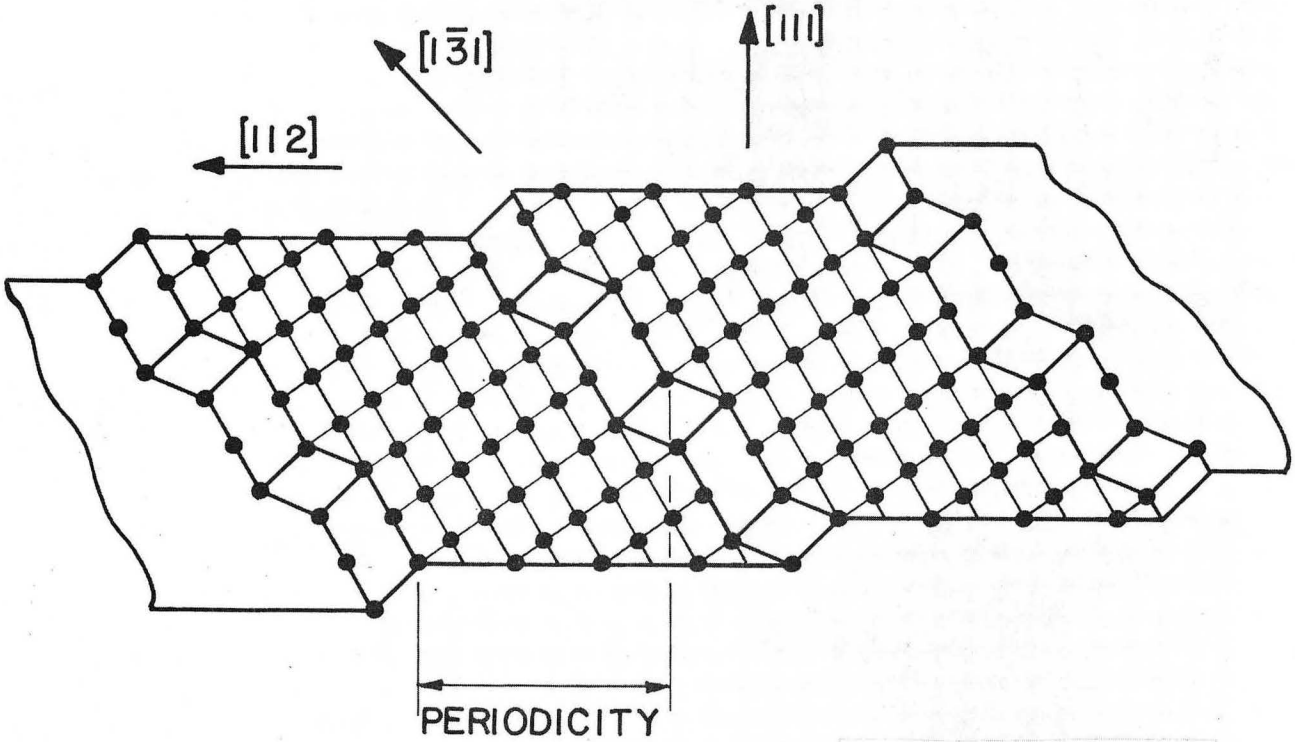


XBB 733-2083

Figure 2

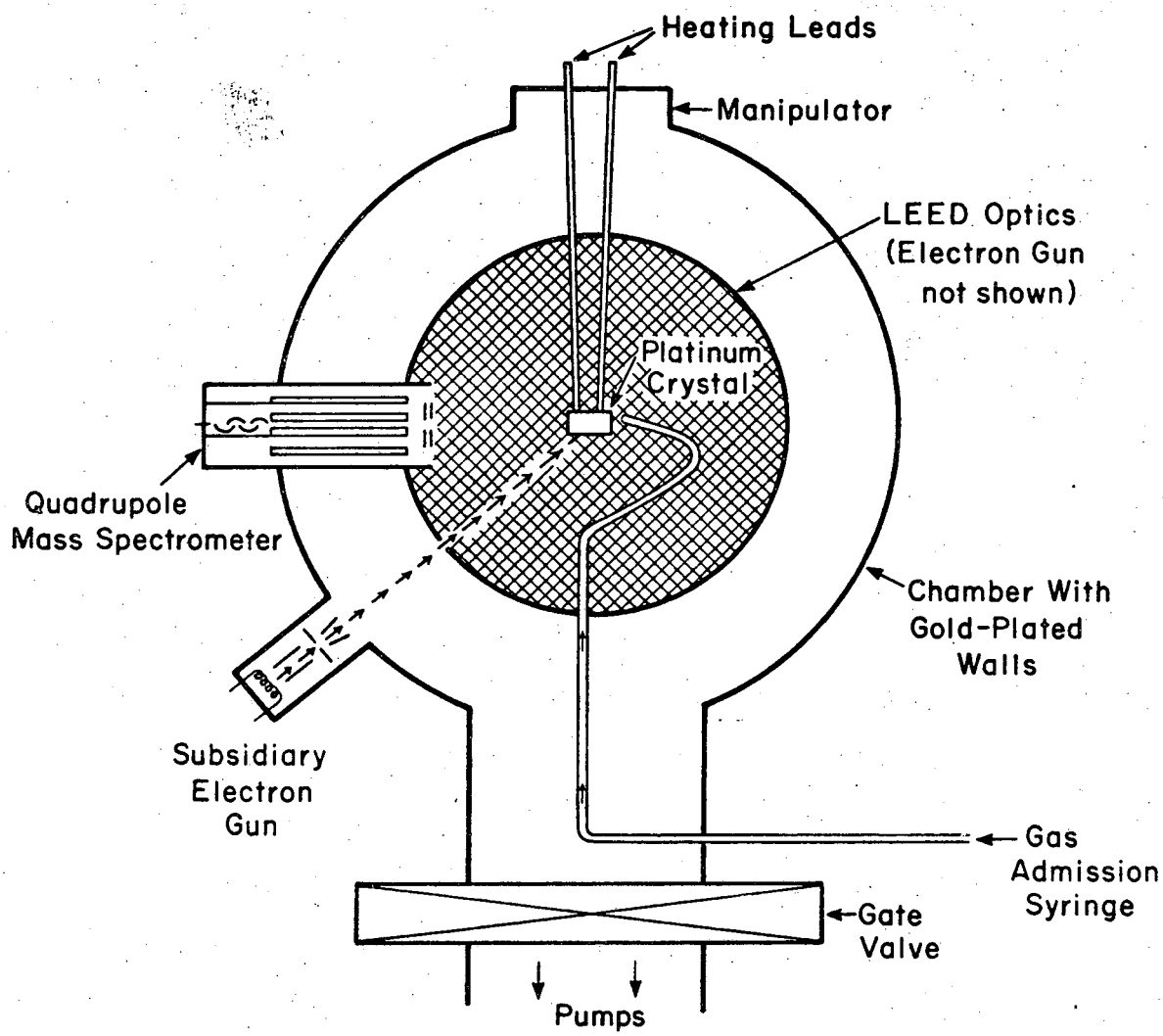
P+(S)-[7(111)X(310)]





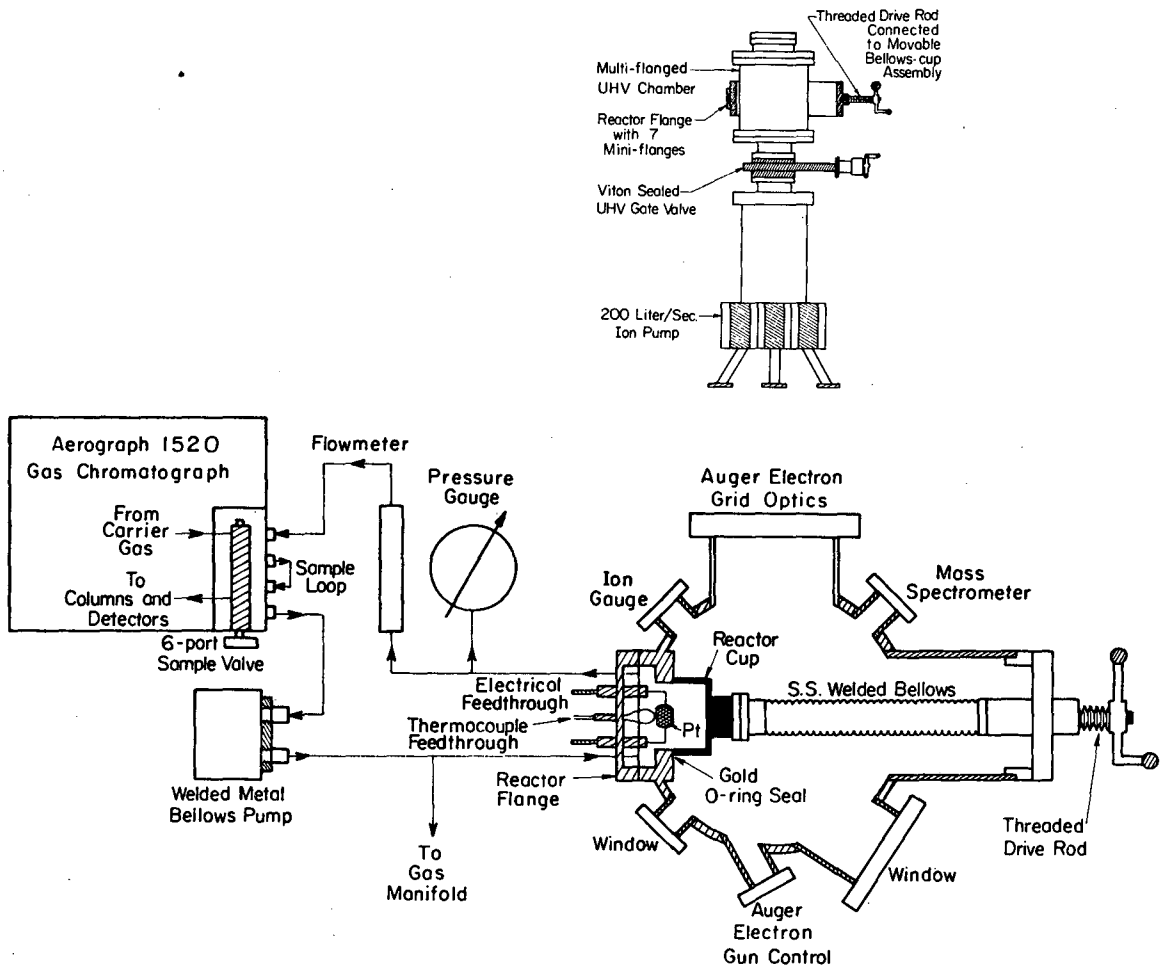
XBB 733-2189

Figure 3



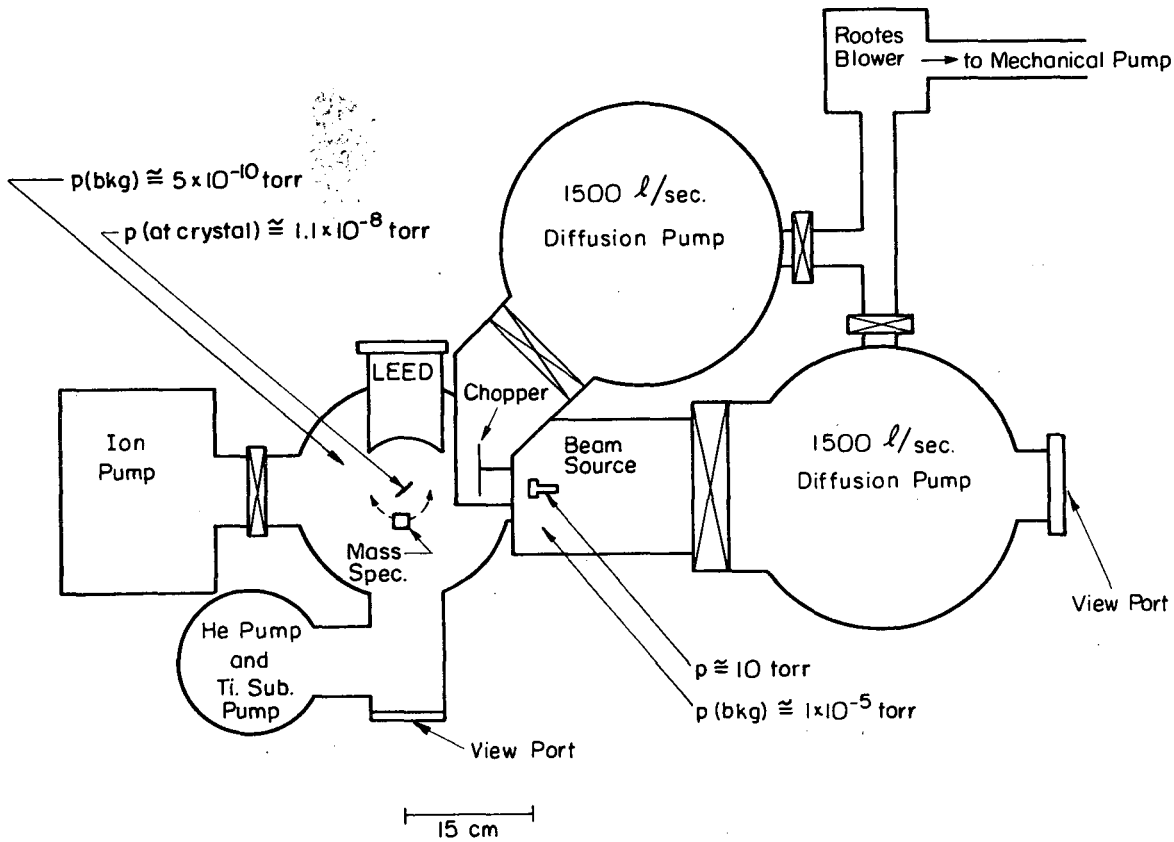
XBL 719-7296

Figure 4



XBL 734-5969A

Figure 5



MOLECULAR BEAM SURFACE SCATTERING APPARATUS

XBL 732-5744

Figure 6

0 0 3 0 4 2 0 0 2 1 9

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