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THE REACTIVITY OF LOW INDEX [(111) and (100)] AND
STEPPED PLATINUM SINGLE CRYSTAL SURFACES

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ABSTRACT

Several high Miller index crystal surfaces of platinum have been shown to consist of low index (111) or (100) terraces of constant width, linked by steps of monatomic height. The surface structures that form in the presence of diatomic molecules (H_2 , O_2 , CO , NO), aliphatic and aromatic hydrocarbons on the (111), (100) and on these standard stepped platinum surfaces were studied by low energy diffraction. Several catalytic reactions (H_2+D_2 ; H_2+O_2 ; dehydrocyclization of n-heptane) that take place on the various platinum crystal surfaces at low pressures were monitored by means of a mass spectrometer and the surface composition by Auger electron spectroscopy.

The chemisorption characteristics of diatomic molecules on stepped platinum surfaces are markedly different from those on low index [(111) and (100)] platinum surfaces. Organic molecules of different types form ordered surface structures on low index faces of platinum but decompose rapidly on stepped surfaces under identical experimental conditions.

Surface chemical reactions of diatomic molecules that were studied take place only on stepped surfaces at a detectable rate. The dehydrocyclization of n-heptane to toluene occurs slowly on the Pt(111) face. The rate of decomposition of n-heptane on stepped platinum surfaces is rapid and the carbon deposit that forms prevents dehydrocyclization. In the presence of hydrogen, however, dehydrocyclization occurs at a rapid rate on stepped surfaces with atomic terraces of (111) orientation while at a slower rate on stepped surfaces with atomic terraces of (100) orientation.

It appears that catalytic reactions can readily be studied using one face of a single crystal of small surface area. Dissociation of diatomic molecules and breaking of C-C and C-H bonds occur preferentially at atomic steps while the structure of the atomic terraces plays an important role in the more complex dehydrocyclization reaction.

INTRODUCTION

In recent years there have been important gains in our understanding of chemical phenomena at solid surfaces and at the solid-gas interface. These advances were partly due to the application of new techniques that permit the determination of the atomic structure and of the chemical composition of surfaces and of adsorbed layers. Low energy (5-200 eV) electron diffraction (LEED) (Somorjai and Farrell, 1971) permits studies of the atomic structure of solid surfaces and of adsorbed gases, while Auger electron spectroscopy (AES) (Chang, 1971; Somorjai and Szalkowski, 1971) or photoelectron spectroscopy (Siegbahn et al., 1967) determines the surface chemical composition and the valency of surface atoms. These techniques detect electrons that are backscattered from the surface as a function of electron energy, and an experiment can be carried out in such a way that the scattered electrons predominantly contain information about the atoms at the topmost layer of the surface. In other fields of science, for example in gas phase chemistry or in solid state physics, the development of chemical analytical techniques to determine composition, and the development of diffraction and spectroscopic techniques for structure determination preceded and served as the foundation for definitive studies of molecular dynamics of complex chemical reactions and of various transport phenomena. It is thus likely that in surface science the development of these techniques for the determination of surface structure and surface chemical composition will serve as the starting point for studies of complex surface reactions.

Perhaps one of the most puzzling materials that is the subject of surface studies using these new techniques is platinum. This precious, face-centered cubic metal is one of the best catalysts for a variety of surface chemical reactions (oxidation, hydrogenation, dehydrogenation, cyclization, isomerization, etc.). In the past seven years we have studied the atomic structure of the low Miller Index [(111) and (100)] (Morgan and Somorjai, 1968; 1969) and high Miller Index (stepped) surfaces of platinum (Lang, Joyner and Somorjai, 1972a,b). In order to uncover the reasons for this remarkable catalytic activity in so many diverse chemical reactions, we have been investigating the possible correlations between reactivity and surface structure, and between reactivity and chemical composition. Building on what we have learned from LEED and AES studies about platinum surfaces, we have recently studied in some detail the dehydrocyclization of n-heptane to toluene on various platinum single crystal surfaces, and have been able to correlate catalytic reactivity to surface structure and composition.

The path from the first LEED studies of platinum single crystal surface by Dr. H. B. Lyon (1967), to the detection of toluene signals from the various crystal surfaces by Dr. Richard Joyner from the University of Bradford, who spent a year in Berkeley on a postdoctoral fellowship, took many turns. It was uncovered that there are metal surfaces whose atomic structure is not necessarily the same as that expected from the x-ray unit cell. It was found that carbon is the major impurity in our single crystals, and we learned to eliminate it along with the tenacious carbon monoxide, that is present in the ambient

of ultrahigh vacuum systems. It was learned that oxygen and hydrogen, commonly known to adsorb readily on platinum, do not adsorb readily on the low index crystal faces of platinum. Studies of high Miller index surfaces yielded surface structures with ordered atomic steps that exhibit remarkable thermal stability. The nature of the interaction of stepped surfaces with gases was found to be markedly different from the interaction of low index platinum surfaces with gases, and it provided information necessary to decipher the complex surface chemistry of small platinum particles. Adsorption studies on low index and stepped platinum surfaces allowed us to reconcile many of the striking differences in chemical behavior reported in experiments using various platinum surfaces. Finally, it was found that with the techniques presently available one may study complex catalytic surface reactions of low reaction probability using one face of a single crystal of surface area less than 1 cm^2 .

EXPERIMENTAL

A conventional LEED four grid electron optics system was used to study the diffraction patterns emanating from the various platinum surfaces. The ultrahigh vacuum chamber ($\sim 10^{-9}$ torr) was fitted with a gate valve that allowed adsorption studies to be carried out either in a controlled flux of gas or in equilibrium between the surface and the gas. An auxiliary electron gun was attached to the chamber that was used in Auger electron spectroscopy studies. The energy spectrum of the back-scattered electrons was analyzed with the same grid system used

in the diffraction studies. A quadrupole mass spectrometer was attached to the reaction chamber with an ionizer 7 cm away from a single crystal surface of surface area $.8 - 1 \text{ cm}^2$. The scheme of the reaction vessel is shown in Figure 1.

[Figure 1 here (for legend see p. 23)]

A needle permitted direct incidence of the gas molecules onto the platinum surface so that their contact with the sample was assured before collision with the chamber walls. The walls of the reaction chamber were coated with a thin gold film for the catalytic reaction studies, to minimize the rate of certain chemical reactions on the wall surface that might compete with the reactions that take place on the sample surface of much smaller surface area. The maximum pressure in the reaction chamber that allowed reliable operation of the mass spectrometer was about 2×10^{-4} torr. The crystal samples were oriented by x-ray back reflection techniques, cut, polished and etched, using warm aqua regia and mounted on polycrystalline platinum holders before placing them into the diffraction chamber. Although ion bombardment cleaning could be carried out, it was rarely used in our studies to clean platinum surfaces. Since carbon was found to be the most tenacious impurity, heat treatments in oxygen were found to be the most effective way to clean the surface (Joyner, Gland and Somorjai, 1971). Heating the surface to 800°C for 5 minutes in 1.0×10^{-6} torr oxygen or for three hours at 400°C was sufficient to remove the carbon deposit. The adsorbed oxygen could be removed readily by subsequent heating in vacuum

to 800°C. The Auger spectrum was used to test the cleanliness of the platinum surfaces. The sensitivity of this technique to carbon and most other impurities was about 1% of a monolayer ($\approx 10^{13}$ atoms/cm²). Figure 2 shows the Auger spectra of a clean and of a carbon and carbon monoxide contaminated platinum surface.

[Figure 2 here (for legend see p. 23)]

THE STRUCTURE OF LOW INDEX AND STEPPED PLATINUM SURFACES

The (111) and (100) Crystal Faces of Platinum

Low energy electron diffraction patterns from the (111) face indicate (Figure 3a) that this surface is characterized by an atomic structure that is expected from the projection of the x-ray unit cell onto this surface. The surface structure (Fig. 3) is characterized by an interatomic distance of 2.77 Å and a six-fold rotational symmetry. When the diffraction pattern that is shown in Figure 3 was obtained, the Auger spectrum of that characteristic of clean platinum.

[Figure 3 here (for legend see p. 23)]

Low energy electron diffraction studies in Cambridge (Lambert, Weinberg, Comrie and Linnett, 1971) confirmed that the clean platinum (111) surface have a (1x1) surface structure.

Projection from the x-ray unit cell suggests that the (100) crystal face of platinum should have a square unit mesh (four-fold rotational

symmetry). However, LEED studies (Morgan and Somorjai, 1968; Lyon, 1967) indicated that this was not so and that the actual unit mesh was a rectangle of approximate size (5x1) with respect to that predicted. The diffraction pattern that is characteristic of the Pt(100) surface with the (5x1) surface structure is shown in Figure 4a. This surface structure for the (100) platinum face was confirmed by studies in other laboratories (Burggraf and Mosser, 1969; Berthier et al., 1971). Auger electron spectroscopy studies by Palmberg (1969) and in our laboratory demonstrated the cleanliness of the Pt(100)-(5x1) surface. Although the surface had to be cleaned (of carbon deposit) by heating in oxygen in order to obtain this pattern in most cases, oxygen could be removed readily from the surface in vacuum and no sign of an oxygen signal could be detected in the Auger spectrum. The (100) crystal faces of gold (Fedak and Gjostein, 1969) and iridium (Grant, 1969) also exhibit the (5x1) surface structure even under conditions of epitaxial deposition in thin film form on various substrates (Palmberg and Rhodin, 1967). This surface structure can best be interpreted as due to a hexagonal overlayer forming a (5x20) coincidence lattice with the underlying square (1x1) unit mesh. The platinum atoms in the topmost layer rearrange into a hexagonal structure by a slight out-of-plane buckling (Figure 4b). On adsorbing gases that are electron donors (Morgan and Somorjai, 1969) (olefins, carbon monoxide or in the presence of carbon), the (5x1) surface structure rearranges to the (1x1) surface structure (Figures 4c and 4d). In the presence of electron acceptors (O_2 , Cl_2)

[Figure 4 here (for legend see p. 23)]

the (5x1) surface structure is stable. The rearrangement of gold and platinum may be explained in terms of changed surface valency (Rhodin, Palmberg and Plummer, 1969). The rearrangement of the (100) surface of platinum and the effect of various adsorbates on the Pt(100) surface structure can be explained as due to a surface phase transformation from a face centered cubic to a hexagonal close packed structure. In the condensed phase, electron promotion changes the electron configuration of the platinum atom (d^9s) to d^7sp^2 according to the Hume-Rothery (1936) and the Engel-Brewer (1968) theories that explain its face-centered cubic crystal structure. The energy requirement for such an electron promotion is less than the bonding energy due to the additional electron-pair bonds with other platinum atoms. If the unpaired s and/or p electron concentration per atom is lowered at the surface, this can explain the transformation into a close-packed hexagonal surface structure (Brewer, 1968). Thus electron deficiency can stabilize the hexagonal distortion (that gives rise to the appearance of the (5x1) surface structure) in vacuum or in the presence of electron acceptors, while in the presence of electron donors the surface assumes its bulk-like square unit mesh.

The High Miller Index or Stepped Surfaces of Platinum

Platinum single crystals that were cut 6.0° to 9.5° from the (111) crystal face or from the (100) crystal plane, were studied (Lang, Joyner and Somorjai, 1972a). The diffraction patterns that characterize these high Miller Index surfaces are shown in Figure 5.

[Figure 5 here (for legend see p. 23)]

The patterns differ from those expected from crystals with low index faces only in that the diffraction spots are split into doublets at certain voltages. This splitting is due to ordered steps that are present on the surface (Ellis and Schwoebel, 1968; Perdereau and Rhead, 1971). The stepped surfaces with (111) orientation terraces have the usual (1x1) surface structure, while stepped surfaces with (100) terraces have the (5x1) surface structure with its period of five normal to the step direction. Schematic diagrams of the stepped surfaces corresponding to the patterns are also shown in Figure 5. The terrace width is calculated from the doublet separation while the electron energy dependence of the doublet intensity is a function of the step height. The diffraction features indicate that the clean high Miller Index platinum surfaces consist of terraces of low Miller Index linked by steps of monatomic height. The appearance of ordered steps has been observed on high index surfaces of many substances with different types of chemical bonding (Ellis and Schwoebel, 1968; Perdereau and Rhead, 1971; Hengler, 1970), and thus such a surface structure may be regarded as a general structural property of high index surfaces. It is necessary, therefore, to identify stepped surface structures by a simple nomenclature, since Miller indices do not represent the surface structure accurately. The ordered step array can be completely designated by the width and orientation of the terraces and the height and orientation of the steps. Thus the surface structure of the single crystal surface whose diffraction pattern is shown in Figure 5 can be designated as Pt(S)-[6(111)x(100)],

where the postscript (S) indicates a stepped platinum surface, 6(111) designates the terrace widths and orientation and 1(100) designates the step height and orientation. In the case of steps of monatomic height the prefix 1 may be omitted. Thus the two surfaces in Figure 5 may be designated Pt(S)-[6(111)x(100)] and Pt(S)-[5(100)x(111)]. A detailed discussion of the various properties of stepped surfaces and the nomenclature that may be used in the presence of gases is discussed elsewhere (Lang, Joyner and Somorjai, 1972a). In table 1 the angles of cut, the Miller index and the designation of the stepped surfaces using this nomenclature are listed.

[Table 1 here; see p. 19]

The ordered stepped platinum surfaces that were studied exhibited remarkable thermal stability. They were stable in vacuum up to 1500°K and readily reordered after ion bombardment by heating in vacuum. Although the adsorption of gases may disorder the steps in some cases or change the step periodicity (Lang, Joyner and Somorjai, 1972b), after desorption the surface returns to its original surface structure. The thermodynamic stability of these surfaces with respect to the lowest free energy low index surfaces has been examined. Detailed analysis and calculations (Schwoebel, 1969) indicate that even under conditions of appreciable surface diffusion the ordered step structure should be stable.

Chemisorption on Low Index and Stepped Surfaces of Platinum

It has been well established that the adsorption characteristics of various gases, such as sticking probability or surface structure, may vary from crystal face to crystal face. We have found that the difference between the chemisorption characteristics of low index and stepped crystal surfaces is even more pronounced. Molecular oxygen adsorbs only poorly on the (111) or (100) crystal faces of platinum (Morgan and Somorjai, 1968). Recent investigations (Weinberg, Lambert, Comrie and Linnett, 1972) indicate that the sticking probability of oxygen on Pt(111) is in the range of 10^{-6} and there is no indication of the formation of ordered surface structures. Molecular hydrogen also appears to chemisorb poorly on the low index surfaces of platinum (Lampton, 1971). The sticking probability on the Pt(111) face is in the range of 10^{-2} and it forms an ordered surface structure on the Pt(100) face only at relatively high temperature and gas pressure (Morgan and Somorjai, 1968). On the other hand, oxygen or hydrogen adsorb readily on stepped surfaces at low temperatures; they form ordered surface structure and there is indication of hydrogen diffusion into the crystal lattice and of oxide formation at elevated temperatures ($> 600^{\circ}\text{C}$) (Lang, Joyner and Somorjai, 1972b). Carbon monoxide appears to have at least two binding states on the (100) face of platinum and one binding state on Pt(111) (Morgan and Somorjai, 1969). It forms several ordered surface structures on these two low index surfaces as a function of surface concentration and temperature. On stepped surfaces, carbon monoxide is disordered and upon heating there was noticeable thermal decomposition of the molecule

that resulted in the formation of ordered surface structures that could be attributed to carbon (Lang, Joyner and Somorjai, 1972b). Ethylene and other olefins form ordered surface structures on the low index surfaces of platinum (Morgan and Somorjai, 1969). On stepped surfaces, however, the adsorbed layer is disordered and upon heating it transforms into ordered carbon surface structures of various types. The various surface structures that form on low index and stepped surfaces of platinum in the presence of selected adsorbates are listed in table 2. It can be seen that the surface structures that form and their chemisorption characteristics are very different on the two types (low index and stepped) of platinum surface.

[Table 2 here; see p. 20]

There is a great deal of conflicting evidence in the literature on the adsorption properties of various gases on platinum surfaces. Molecular oxygen or hydrogen have been known to adsorb readily on polycrystalline films (Brennan, Hayward and Trapnell, 1960; Sachtler and Dorgelo, 1960), on polydispersed supported platinum particles (Benson and Boudart, 1965), or on field emission tips (Lewis and Gomer, 1968, 1969), just as on stepped single crystal surfaces. On the other hand, studies using low index single crystal surfaces showed evidence for poor adsorption of these diatomic molecules (Morgan and Somorjai, 1968; Weinberg, Lambert, Comrie and Linnett, 1972; Lampton, 1971). These marked differences can be reconciled by taking into account the well-demonstrated ability of atomic steps to tightly hold or even dissociate large binding energy

diatomic molecules and efficiently dehydrogenate hydrocarbons. Although all crystal surfaces have a certain concentration of steps, the step density in well ordered single crystal surfaces appears to be sufficiently low as compared to stepped surfaces, that the chemisorption characteristics are markedly different.

Conversion of n-heptane to toluene on the (111) and stepped surfaces of Pt

N-heptane may undergo dehydrocyclization on a platinum catalyst surface to form toluene according to the net reaction $C_7H_{16} \xrightarrow{Pt} C_7H_8 + 4 H_2$. Although hydrogen is produced in this reaction the catalytic process is usually carried out in the presence of excess hydrogen in the temperature range 250-350°C. There are many other products (n-heptane isomers, dimethylcyclopentanes, etc.) that form on platinum surfaces during the surface reaction. We have carried out the dehydrocyclization of n-heptane on the Pt(111), Pt(S)-[6(111)x(100)] and Pt(S)-[5(100)x(111)] single crystal surfaces at a total pressure of 2×10^{-4} torr using n-heptane and n-heptane-hydrogen mixtures. The toluene formation can be monitored by a quadrupole mass spectrometer by the appearance of the (m/e) = 91, 92 peaks. The electron impact fragmentation pattern of the n-heptane and toluene are readily distinguishable (Figure 6). The minimum partial pressure of toluene detectable by the mass spectrometer is 2×10^{-8} torr in the presence of n-heptane and other hydrocarbons. The detection limit is an order of magnitude lower if only pure toluene is present.

[Figure 6 here (for legend see p.23)]

Toluene can be produced from n-heptane in the absence of hydrogen; however, the toluene yield was reduced for all crystal faces when compared to the yield detected in the presence of hydrogen, and the rate of toluene formation decreased rapidly as a function of time. Although it is difficult to assess the role of hydrogen in this hydrogen-producing reaction, it is likely that the presence of adsorbed hydrogen slows the rates of dehydrogenation of n-heptane or of other competing surface reactions so that dehydrocyclization can proceed more effectively. Thus most of the catalytic reaction studies were carried out using a 1:1 or 1:5 n-heptane:hydrogen mixture. The typical procedure followed in the course of the experiments is as follows. (1) The cleaning of the platinum surface by oxygen treatment at 3×10^{-7} torr O_2 , $850^\circ C$, 30 minutes. (2) Cooling of the crystal in ultrahigh vacuum ($\sim 10^{-9}$ torr) until its temperature is in the range of $120-140^\circ C$. (3) Introduction of the n-heptane-hydrogen mixture while closing the gate valve. The total pressure of 2×10^{-4} torr is established within 1 minute after the closure of the gate valve and the initial mass spectrum recorded. (4) Heating of the crystal to a temperature in the range $250-350^\circ C$, the maximum of the toluene peak is recorded. After a given reaction time the reaction chamber is evacuated while the crystal is kept at the reaction temperature, and then a second dose of the reaction mixture is admitted. (5) Evacuation and admission of the third dose, etc.

In comparing the toluene yields of three different crystal faces of platinum, we have found significant differences in both the amount of toluene produced and the rate of production as a function of time.

These are summarized in table 3. The stepped platinum surface with (111)

[Table 3; see p. 22]

terraces is nearly 20 times more reactive than the low index (111) surface, and at least 2 times more reactive than the stepped surface with (100) terraces. (The differences in reactivity increase with time.) Thus the reactivities are in the order of $\text{Pt(S)}-[6(111)\times(100)] > \text{Pt(S)}-[5(100)\times(111)] > \text{Pt}(111)$.

Although the differences in the amount of toluene produced are correlated with the surface structure of clean platinum, clearly the clean surface conditions do not persist during the catalytic reactions. The surfaces become covered by a carbonaceous layer as indicated by a strong carbon Auger peak. The most active $\text{Pt(S)}-[6(111)\times(100)]$ surface, maintained its activity as a function of time while the toluene forming ability of the other two crystal faces deteriorated (the formation of toluene is hardly detectable after 30 minutes). Low energy electron diffraction studies revealed the formation of an ordered $(\sqrt{3}\times\sqrt{3})R-30^\circ$ carbon-containing surface structure on the active platinum surface with (111) terraces that was stable in vacuum up to 600°C . At higher temperatures a new carbon-containing surface structure forms on this crystal face in vacuum which can be indexed (9x9). This structure can be interpreted as a coincidence lattice of a layer of graphite on top of a $(\sqrt{3}\times\sqrt{3})R-30^\circ$ structure, the unit cell vector of graphite being parallel to the clean platinum substrate. The stepped platinum (111) surface that exhibits the carbonaceous $(\sqrt{3}\times\sqrt{3})R-30^\circ$ or (9x9) surface structure

appears to have the same activity for toluene formation as that of the clean platinum substrate. On the other two platinum surfaces [Pt(111) and Pt(S)-[5(100)x(111)]] , however, continued exposure to n-heptane results in the deposition of a disordered carbonaceous layer as indicated by combined Auger and LEED studies. Once the surfaces become disordered there is no indication of the formation of new surface structures at the reaction temperature, as on the stepped platinum surface with (111) terraces.

The difference in reactivity between Pt(S)-[6(111)x(100)] and Pt(111) surfaces can be ascribed to the presence of high density ordered steps. Apart from the ability to dissociate diatomic molecules, steps appear to play an important role in nucleating the formation of ordered carbon-containing structures. The $(\sqrt{3}\times\sqrt{3})R-30^\circ$ structure which does not form on the Pt(111) face provides an example of ordering induced by the presence of steps.

The somewhat larger (by a factor of 2) initial reactivity of the stepped surface with (111) terraces as compared to the stepped platinum surface with (100) terraces may be due to the differences in terrace orientations. However, the rapid deterioration of the activity of the Pt(S)-[5(100)x(111)] surface as a function of time can be attributed to the formation of a disordered carbon-containing layer, while the reactivity of the Pt(S)-[6(111)x(100)] surface remains virtually unchanged as the ordered carbonaceous $(\sqrt{3}\times\sqrt{3})R-30^\circ$ structure forms on this crystal face.

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Table 1

Angle of cut, Miller Index, and designation of
three stepped surfaces of platinum.

<u>Angle of cut</u>	<u>Miller Index</u>	<u>Designation</u>
6.5° from (111)	(997)	Pt(S) - [9(111)x(111)]
9.5° from (111)	(775)	Pt(S) - [6(111)x(100)]
9° from (100)	(911)	Pt(S) - [5(100)x(111)]

Table 2

Structures and chemisorption characteristics of various adsorbates
on stepped and low index surfaces of platinum.

[Table 2 is on p.21]

Adsorbate	Substrate				
	Pt(S)-[6(111)×(100)]	Pt(S)-[9(111)×(111)]	Pt(111)-(1×1)	Pt(100)-(5×1)	
H ₂	25°C 600-1000°C	disordered 2(1d)-H	(2×2)-H (2×2)-H	disordered disordered	disordered (2×2)-H
O ₂	25°C 600-800°C	2(1d)-O disordered+PtO ₂	not adsorbed Pt(S)-[18(111)×2(111)]	not adsorbed not adsorbed	not adsorbed not adsorbed
CO	25°C	disordered	disordered	c(4×2)-CO, (2×2)-CO	(1×1)-CO, c(4×2)-CO
H ₂ +CO	25°C	structure not identified	($\sqrt{3}\times\sqrt{3}$)-R30°- (H ₂ ×CO)		c(2×2)- (H ₂ ×CO)
C ₂ H ₄	25°C 700°C	poorly ordered (2×2) pseudo-cubic (6×6)-R13°	disordered graphitic carbon	(2×2)-C ₂ H ₄ graphitic carbon	c(2×2)-C ₂ H ₄ graphitic carbon
C	700-900°C	(s×3)-C ($\sqrt{19}\times\sqrt{19}$)-R23.4°-C graphitic carbon facets (522), (511)	Pt(S)-[27(111)×3(111)] graphitic carbon facets (221), (331), (771)	graphitic carbon	graphitic carbon

0 3 0 0 5 8 0 1 0 4 3

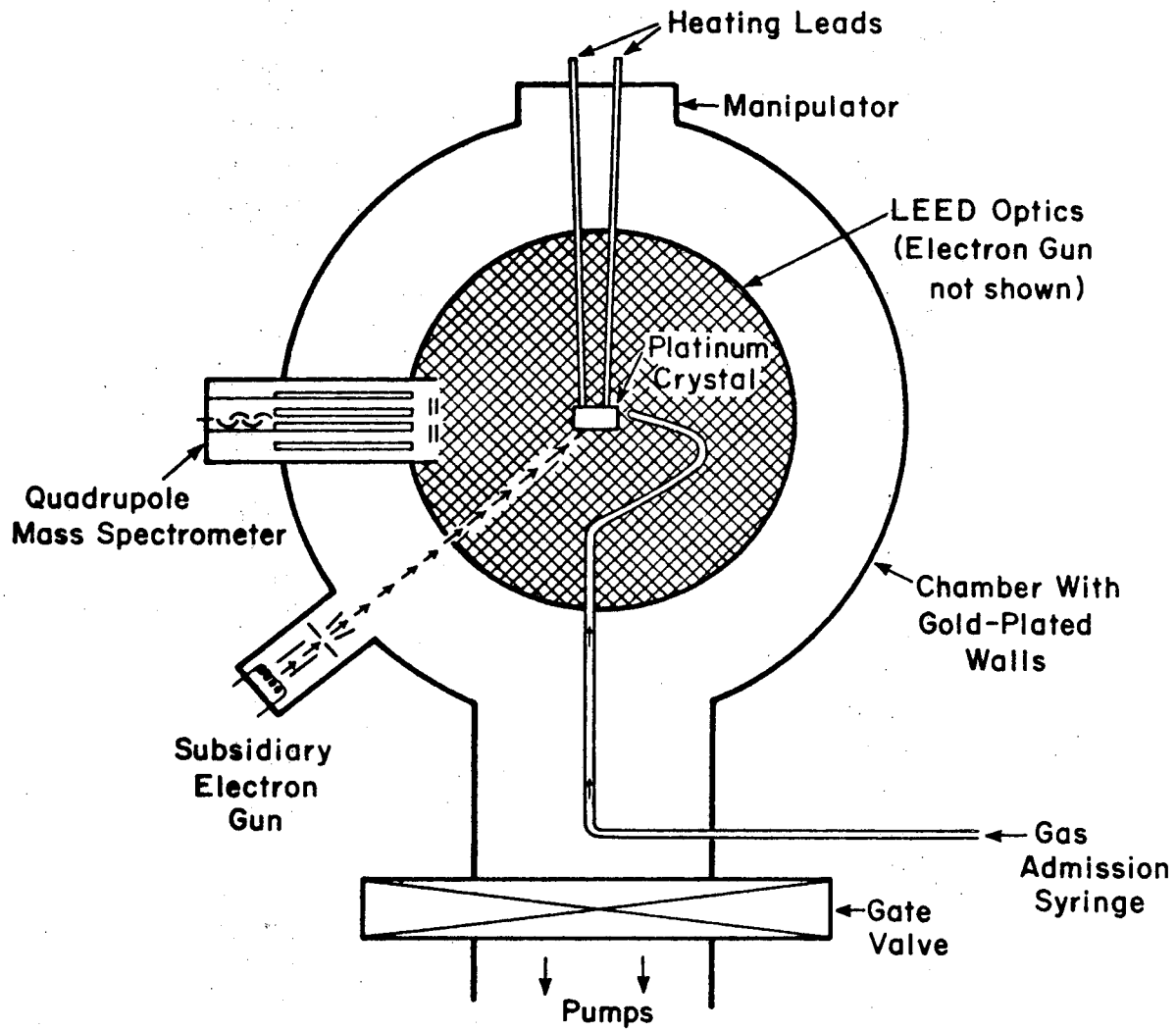
Table 3

The sample surface areas, the maximum toluene peak intensities and the times necessary to obtain the maximum intensities.

Sample Structure		Time to obtain maximum peak intensity (min)	Maximum toluene peak intensity (arbitrary units)		
			1st dose	2nd dose	3rd dose
Pt(S)-[6(111)x(100)]	0.85	4	2.2	2.0	1.5
Pt(S)-[5(100)x(111)]	0.5	8	1.3	0.7	0.4
Pt(111)	1.25	12	0.5	0.2	0
Pt polycrystal	1.2	8	0.3	0	0

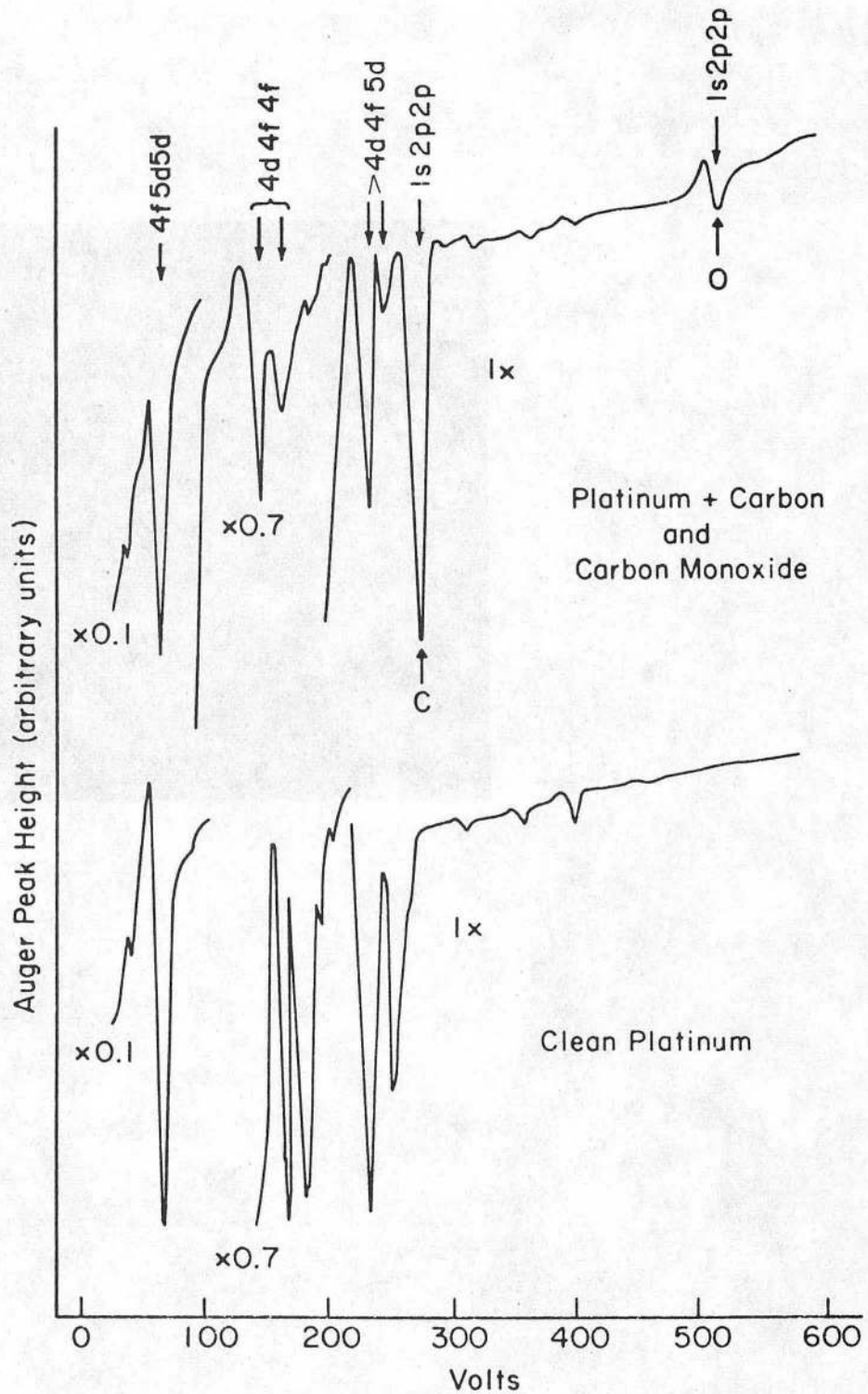
Figure Legends

- Figure 1. Schematic diagram of the diffraction chamber that was also used to carry out the low pressure ($\sim 10^{-4}$ torr) surface reaction studies.
- Figure 2. Auger spectra of platinum in the presence of carbon and carbon monoxide and in the clean state.
- Figure 3. Low energy electron diffraction pattern and schematic representation of the Pt(111) face.
- Figure 4. (a) Diffraction pattern from the Pt(100)-(5x1) structure;
(b) Schematic representation of the (100) surface with a hexagonal overlayer;
(c) Diffraction pattern from the Pt(100)-(1x1) structure;
(d) Schematic representation of the (100) surface.
- Figure 5. (a) Diffraction pattern from the Pt(S)-[6(111)x(100)] surface;
(b) Schematic representation of this surface;
(c) Diffraction pattern from the Pt(S)-[5(100)x(111)] surface;
(d) Schematic representation of this surface.
- Figure 6. Mass spectra of (a) n-heptane; (b) toluene.



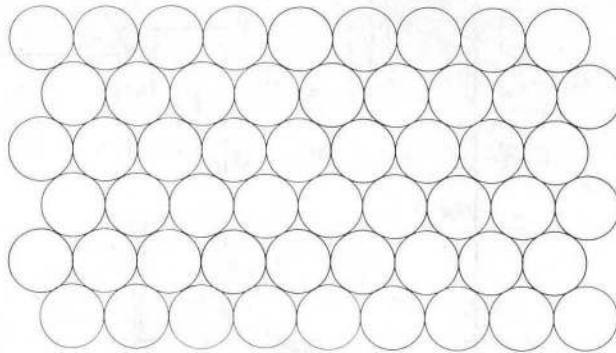
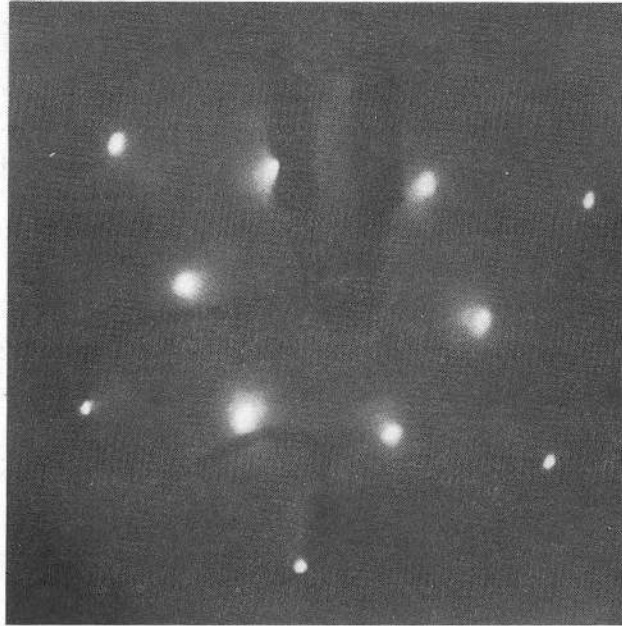
XBL 719-7296

Fig. 1



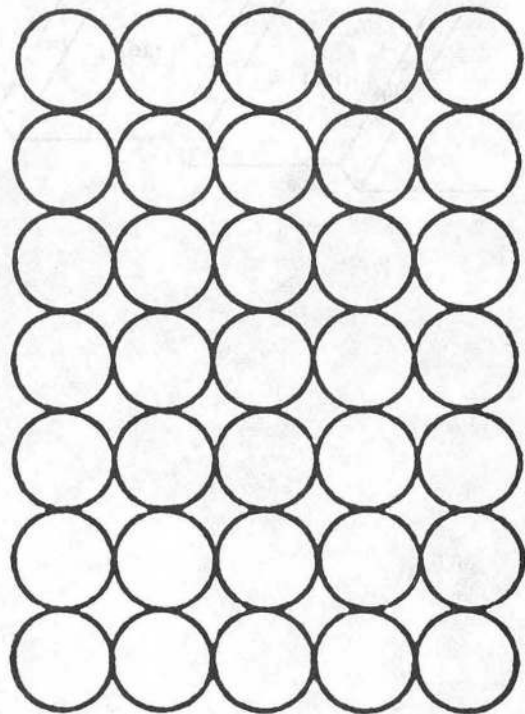
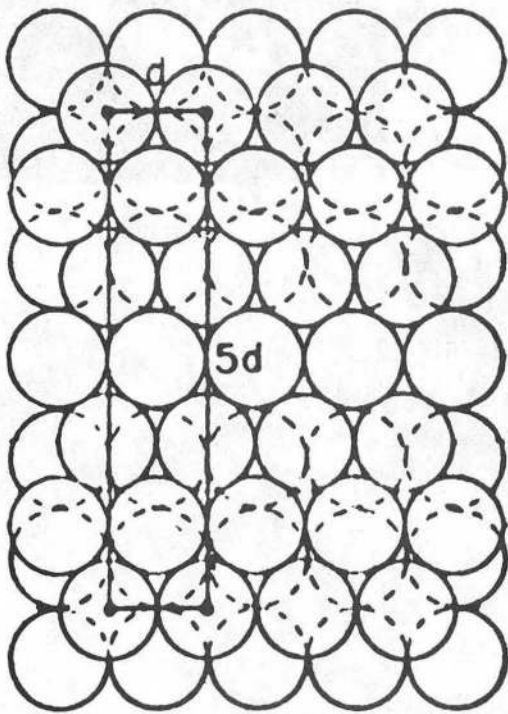
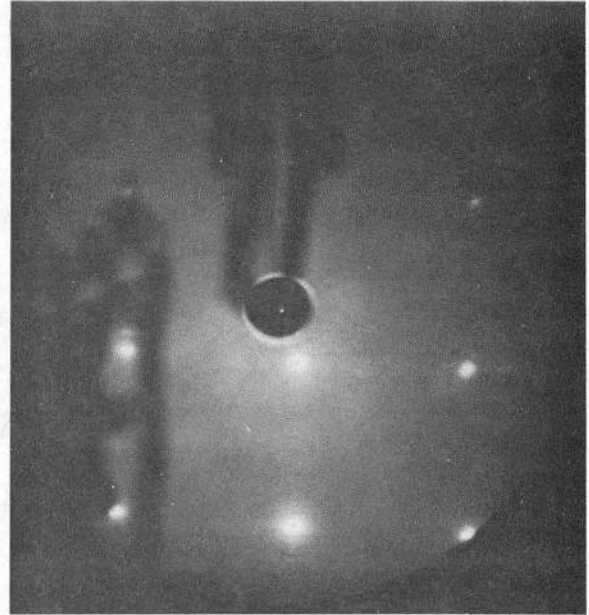
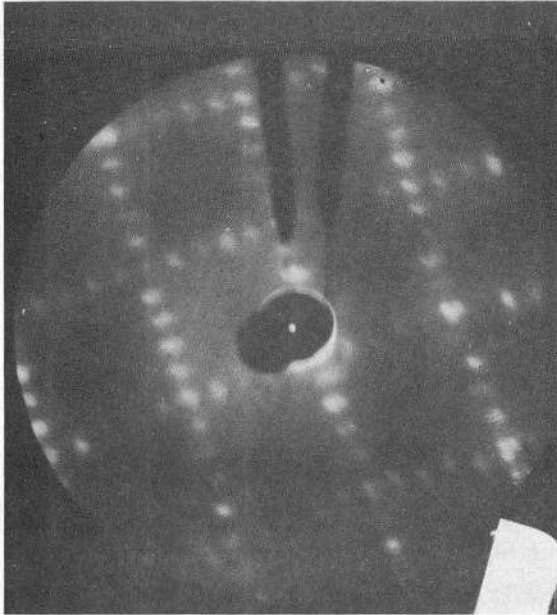
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Fig. 2



XBB 7110-5214

Fig. 3



XBB 7111-5356

Fig. 4

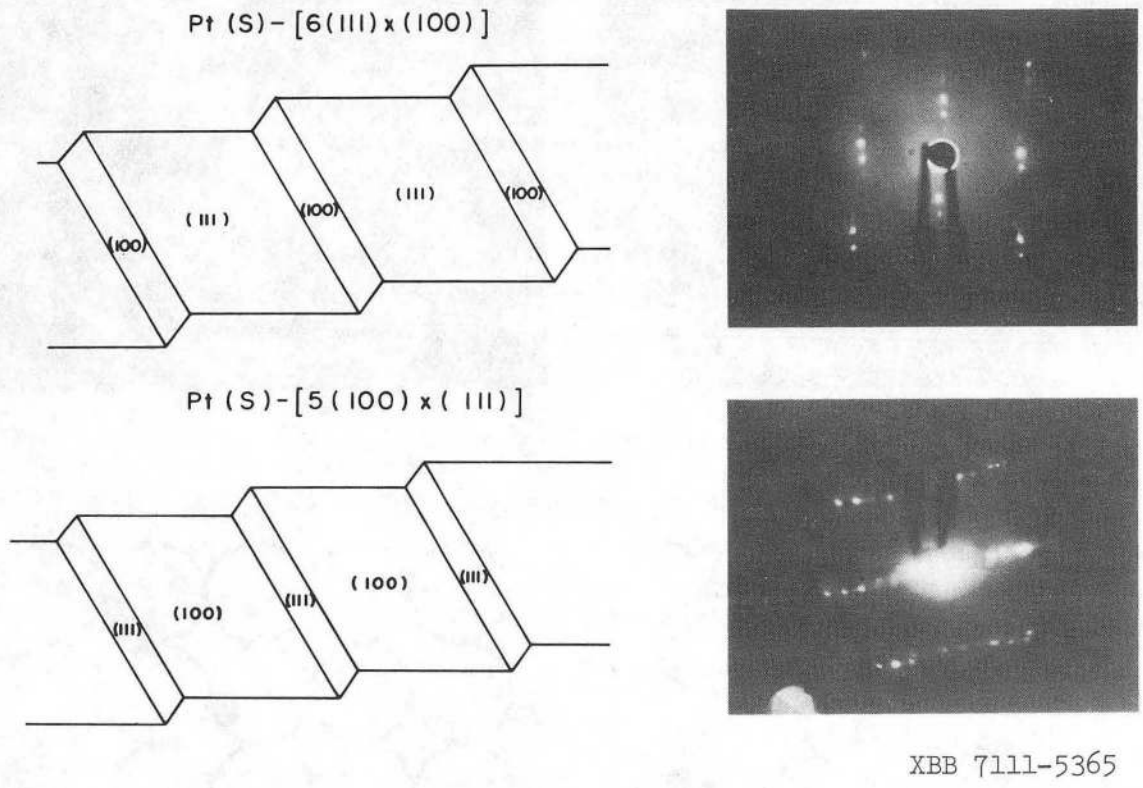
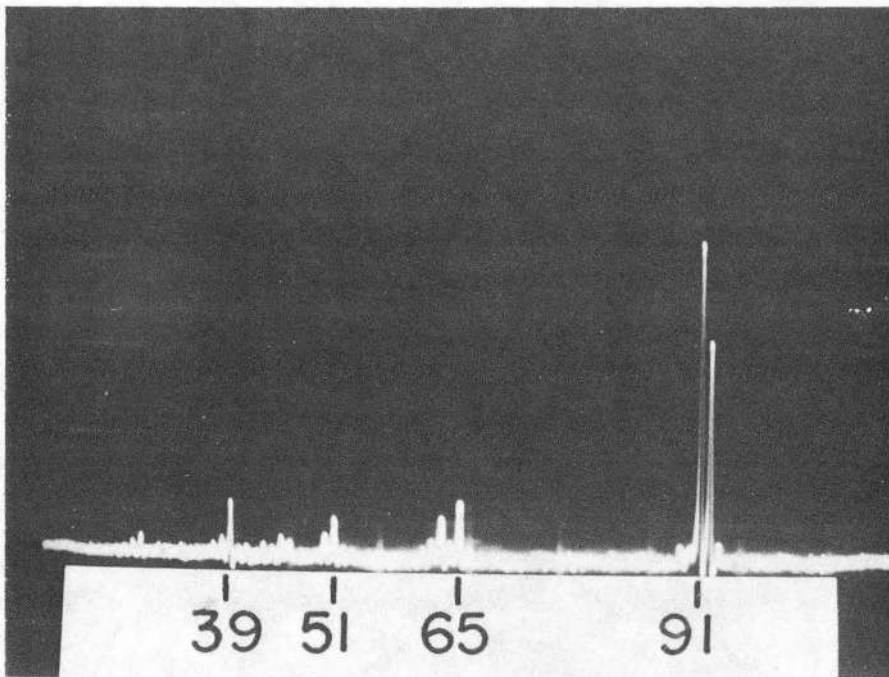
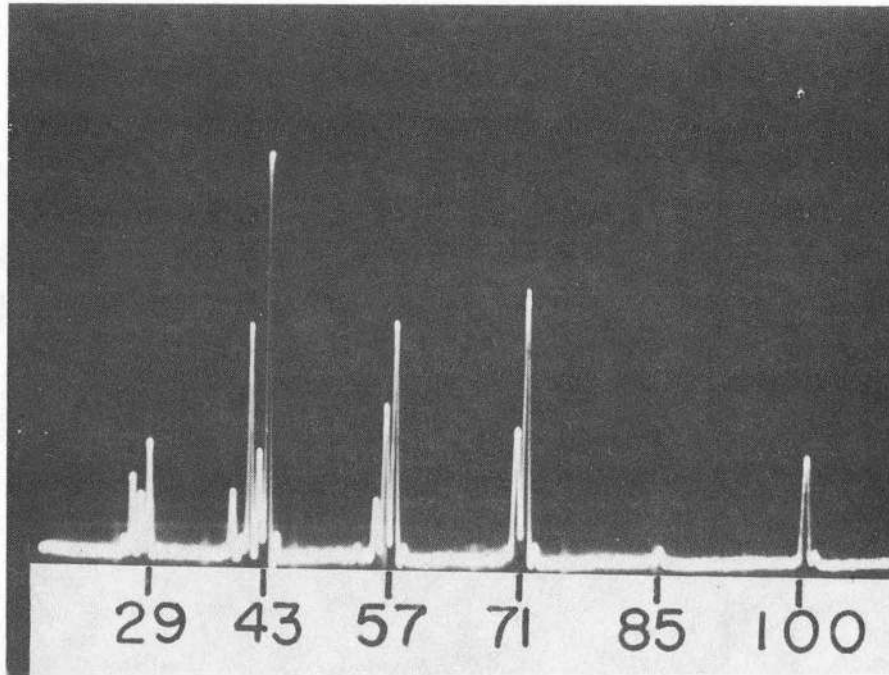


Fig. 5



XBB 7110-5215

Fig. 6

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