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LOW ENERGY ELECTRON DIFFRACTION STUDIES OF THE SURFACE STRUCTURES OF ADSORBED HYDROCARBONS (n-HEPTANE, TOLUENE, BENZENE, ETHYLENE, AND CYCLOHEXANE) ON STEPPED (HIGH MILLER INDEX) PLATINUM SURFACES

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by

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Abstract

The chemisorption of hydrocarbons (n-heptane, toluene, benzene, ethylene and cyclohexane) was studied by LEED on four different stepped crystal faces of platinum, the Pt(S)-[9(111)x(100)], Pt(S)-[6(111)x(100)], Pt(S)-[7(111)x(310)], and Pt(S)-[4(111)x(100)]. The first three surfaces exhibit thermal stability (25-1000°C) in vacuum and in the presence of hydrogen and hydrocarbons, while the last face is unstable and facets. The chemisorption of hydrocarbons produces carbonaceous deposits whose characteristics depend on the substrate structure, the of type of hydrocarbon chemisorbed, the rate of adsorption and the surface temperature. Hydrocarbons on the [9(111)x(100)] and [6(111)x(100)] crystal face, form mostly ordered structures, while disordered carbonaceous layers are formed on the [7(111)x(310)] surface, which has a high concentration of kinks in the steps.

The distinctly different chemisorption characteristics of these platinum surfaces can be explained by considering the interplay of four competing processes: (1) the nucleation and growth of ordered carbonaceous surface structures, (2) dehydrogenation, (3) decomposition of the organic molecules, and (4) rearrangement of the substrate (faceting). On the [9(111)x(100)] and [6(111)x(100)] crystal faces, processes (1) and (2) predominate. On the [7(111)x(310)] face, process (3) is predominant, while process (4) is the most important on the [4(111)x(100)] face.

The effect of varying partial pressure of hydrogen on the chemisorption and ordering characteristics of hydrocarbons are also discussed.

Introduction

Studies of several high Miller index clean crystal faces of platinum have revealed the existence of stepped surfaces which are characterized by the presence of terraces of well defined crystallographic orientation [for example, (111) or (100)] separated by ordered arrangements of monatomic steps. These stepped surfaces exhibit remarkable thermal stability, and the step periodicity gives rise to extra diffraction features that permit investigation by low energy electron diffraction. Studies[1,2] of the chemisorption of various diatomic molecules on these high index surfaces have shown chemisorption characterisitics that are entirely different from those on low Miller index (111) and (100) crystal faces.[2] Oxygen and hydrogen chemisorb readily on most stepped surfaces, while these gases have low sticking probabilities, and do not form surface structures[3] at low temperatures, on low index surfaces. Molecular beam scattering studies have shown that the hydrogen-deuterium exchange reaction takes place readily on stepped surfaces, while it is hardly detectable on the (111) crystal face.[4] Carbon monoxide that forms several ordered surface structures on the the (100) face of platinum, yields a disordered deposit on stepped surfaces, and upon heat treatment there is evidence of dissociation.[3,5] Carbon monoxide was found to decompose exclusively in the stepped regions of oriented thin films.[6] These investigations have shown that atomic steps play a key role in dissociating large binding energy diatomic molecules, H_2 (103 kcal), O_2 (118 kcal), CO (256 kcal), which could be a major reason for their markedly different structure forming and chemisorption characteristics.

There is another important property of stepped surfaces that was discovered during chemisorption of hydrocarbons. Upon chemisorption of various aliphatic and aromatic molecules, several ordered surface structures have formed that can be identified due to carbonaceous deposits by Auger electron spectroscopy. The surface structures that form depend on the structure of the clean platinum surface, the type of hydrocarbon molecule adsorbed, the hydrocarbon flux incident on the surface, and the exposure. The abundance of surface structures should be contrasted with the chemisorption behavior of these molecules on low Miller index surfaces. On the (111) and (100) crystal faces the ordered surface structures of organic molecules are very different,[3,7,8] if present, and heating to elevated temperatures give rise to the formation of a graphitic overlayer independent of the crystallographic orientation of the substrate. Thus, stepped surfaces have the ability to nucleate the formation of ordered carbonaceous deposits that would not form on low index crystal surfaces. Recent studies of catalytic reactions on stepped surfaces of platinum revealed the importance of these ordered carbonaceous surface structures in hydrocarbon catalysis.[9] Thus, it appears important to investigate, in detail, the nature of ordered carbonaceous surface structures and to undertake a systematic investigation of the dependence of the carbon deposit on both the structure of the platinum substrate and on the structure of the hydrocarbon adsorbed. In this paper we report on low energy electron diffraction studies of the chemisorption of n-heptane, toluene, benzene, ethylene, and cyclohexane on a

series of stepped platinum surfaces that are distinguishable by the width of their atomic terraces or by the orientation of their atomic steps. Since the structure of the carbonaceous layer may change as a function of temperature, the structure of adsorbed layer was studied in a wide temperature range of 20°C to 850°C.

Experimental

The apparatus has been described previously;[1] in brief, the high purity, electron beam zone refined, platinum single crystals (Materials Research Corporation) were X-ray oriented by back-reflection Laue technique, cut in the required orientation, polished, etched and then the orientation rechecked.

The single crystals, on polycrystalline platinum holders, were mounted in a Varian ultra-high vacuum,gold plated chamber in which the ambient pressure was typically 2×10^{-9} torr. The low energy electron diffraction patterns were observed using Varian 4-grid optics, a Vacuum Generators Auger electron spectrometer was used to monitor the platinum surface composition, and a quadrupole mass spectrometer (Electronic Associates Inc.) was used to analyze the gases in the chamber. Temperature was measured with a platinum/platinum-10% rhodium thermocouple spot welded to the top edge of the crystal, and also with an optical pyrometer.

The only detectable impurity on the platinum surface was carbon, removed by repeated heat treatment in oxygen (10^{-6} torr, 850°C). The clean platinum surface structure can be identified by both the low energy electron diffraction pattern and the Laue X-ray diffraction pattern. Table I lists the orientations of various crystal faces that are used in these studies with the notation that is described, in detail, elsewhere.[1] In brief, (S) indicates a stepped surface, [6(111)x(100)], for example, identifies a surface with atomic terraces of (111) orientation six atoms

wide, on the average, separated by steps of atomic height of (100) orientation(deduced from the direction of the cut). The first three samples that are listed in Table I are different only by the terrace width. The fourth surface structure was obtained by cutting the crystal 20° from the $[01\bar{1}]$ zone toward the $[1\bar{1}0]$ zone. The direction of the cut and the angle with respect to the (111) crystal face are shown in Figure 1. Figures 2a, 2b, 2c, and 2d show schematic diagrams and observed diffraction patterns of the various stepped surfaces. The step height is obtained from the variation of the intensity maxima of the doublet diffraction beam features with electron energy which has been discussed in detail elsewhere.[1] All of the surface structures, with the exception of the Pt(S)-[4(111)x(100)] crystal face, that are shown in Figure 2a-d exhibit remarkable thermal stability. These surfaces can be heated in vacuum to at least 1100°C without appreciable deterioration of the surface structure. After chemisorption of various hydrocarbons the surface structure characteristic of the clean substrate could be regenerated readily. This removal of the carbon deposit was carried out by oxygen heat treatment and by subsequent removal of the adsorbed oxygen by vacuum heat treatment. The Pt(S)-[4(111)x(100)] crystal face undergoes faceting when heated in vacuum to 1000°C, when new diffraction features appear. The faceting was even more marked and took place at 300° to 500°C in the presence of adsorbed hydrocarbons or hydrogen. The original surface structure could be restored after removal of the adsorbate by heat treatment in oxygen at up to 900°C. Above that temperature faceting occurred even in the presence of oxygen.

The organic vapors were introduced through a needle that permitted

direct incidence of the vapor molecules on the platinum surface. The rates of incidence can be calculated[10] and varied from about 10^{12} to 10^{17} molecules per second per cm^2 of crystal, and exposures from 10^{-1} to 10^5 Langmuirs. It was also possible to introduce hydrogen along with the hydrocarbons (in a variety of ratios) and examine the effect of surface structures obtained as a result of co-adsorption of these mixtures. In Table IIa, b, c, we list all the surface structures that have been found on the platinum stepped surfaces upon adsorption of hydrogen, n-heptane, toluene, benzene, ethylene, and cyclohexane, along with the experimental conditions required to generate these structures. It should be noted that the type of surface structure which formed depended on the temperature, the magnitude of the incident flux on the crystal surface and the exposure time. The effective pressure at the surface can be estimated,[10] assuming isotropic, hemispherical effusion from a point source, and this has been incorporated into the table.

The surface structures that have been found for the majority of species on the platinum stepped single crystals, and the transformation matrix, giving the coefficients of the unit cell vectors of the surface structure with respect to the original platinum surface unit cell vectors, is given where possible in Table II. When the admission of a gas had no effect on the LEED pattern, this has been recorded as "no change" in the table. When the background intensity of the LEED pattern was high relative to the pattern from a clean surface then the "disorder" on the surface has been noted in the table.

When streaks occurred on the LEED pattern, indicating disorder in one particular dimension, we have used the nomenclature n(1d)-X where 1/n represents the fractional position of the streaks with respect to the original distance between the diffraction spots from the terraces of the stepped platinum surface; (1d) indicates a one-dimensional diffraction feature; and X is the species assumed responsible for the streaking. Thus, for example, 2(1d)-H means streaks on the LEED pattern, due to hydrogen adsorption, halfway between the platinum diffraction spots. Some of the structures are not well ordered, for example, diffuse 1/2 order indicates poorly resolved details halfway between the platinum spots.

Other structures are difficult to interpret in terms of simple unit cells. Thus, the adsorption of ethylene and cyclohexane (at 850°) on Pt(S)-[9(111)x(100)] produces a complex structure with insufficient resolution to identify the unit cell of the surface structure. Likewise, cyclohexane at 850° on Pt(S)-[6(111)x(100)] gives another complex structure that could not be characterized.

Where no experimental data exists a dash has been shown in the tables.

The surface structures of the same hydrocarbon molecules that form on the low index Pt(111) crystal face are listed in Table IIc for comparison.

The Pt(S)-[6(111)x(100)] surface was reproduced on a second crystal cut separately from the original Pt(S)-[6(111)x(100)] crystal. The results of adsorption, including the formation of the ordered surface structures were identical on both crystals to within the experimental error.

Results

A. The Pt(S)-[9(111)x(100)] Surface

This surface, with the widest atomic terraces of all the stepped surfaces studied, was expected to behave similar to the (111) crystal face. Indeed, the ordered carbon deposits frequently were found to coexist with a rotationally disordered graphitic overlayer that is characterized by ring-like diffraction features, an example of which is shown in Figure 3. On low index platinum surfaces (111) and (100) only the ring-like diffraction patterns appear with heat treatment of any hydrocarbon adsorbates (750°C or greater). On the [9(111)x(100)] surface the ring-like diffraction features appear at as low as 300°C during the adsorption of most hydrocarbons that are listed in Table II. Depending on the conditions of exposure, more or less of the surface is covered by the ordered carbonaceous structure. High incident flux favor the formation of the graphitic overlayer while the ordered surface structures predominate during lower rates of adsorption. It was found that when hydrogen is simultaneously incident with the hydrocarbon on the surface the formation of the graphitic overlayer is retarded. At high partial pressures of hydrogen the ring-like diffraction features do not form at all. Many of the surface structures exhibit one-dimensional order indicating ordering only along the steps while the adsorbed layer is disordered in the terrace in directions away from the step direction. The adsorption of most hydrocarbons however gives rise to the formation of ordered two-dimensional surface structures that are characterized by unit cells of various sizes from ($\sqrt{3}$ x $\sqrt{3}$) rotated at 30° to the original platinum substrate unit cell to larger sizes.

Since the carbon Auger signal is of the same intensity in the presence of surface structures of both small or large unit cells it is concluded that the latter diffraction features are probably due to the presence of coincidence lattices in which close packing in the adsorbed layer is maintained. The apparent large unit cells are due to the small mismatch in the lattice parameters in the adsorbed layer with respect to that in the platinum substrate. The surface structure changes as a function of temperature are indicated in Table II. These temperature dependent changes are general properties of the carbonaceous structures on the stepped platinum surfaces.

B. The Pt(S)-[6(111)x(100)] Surface

The adsorption of hydrocarbons of various types produced many ordered surface structures on this crystal face. The type of structure that forms depends on the hydrocarbon molecule that is being adsorbed. It is apparent that the geometry of the adsorbed molecule and small differences in the bonding characteristics can markedly change the structure of the carbonaceous deposit. Heat treatment of an adsorbed layer on this crystal <u>does not</u> produce a rotationally disordered graphitic overlayer. The surface structures convert, as a function of temperature, to other structures that are characterized by different unit cells. However, the formation of the new type of surface structure depends on both the

exposure and the temperature. For example, when ethylene is first adsorbed at low (25°C) temperature, a surface structure with unit cell matrix, $\begin{vmatrix} 2 & 0 \\ 0 & 2 \end{vmatrix}$ or a (2x2), is obtained as noted in Table IIa. When the layer is heated to 800°C a $\begin{vmatrix} 6 & 1 \\ -1 & 7 \end{vmatrix}$ diffraction pattern appears as shown in Figure 4c. If the clean platinum surface is heated in vacuum to 800°C and then exposed to the same pressure of ethylene, a different surface structure, that is shown in Figure 4d, appears with a $\begin{vmatrix} 3 & 2 \\ -2 & 5 \end{vmatrix}$ unit cell. On this surface the formation of the various ordered surface structures was independent of the hydrogen partial pressure within the accuracy of the experiment.

C. The Pt(S)-[4(111)x(100)] Surface

This crystal surface was not stable when heated in vacuum above 1000°C, when faceting produced a new crystal plane whose (00) diffraction beam was readily detectable. From knowledge of the geometry of the system the angle between this newly formed plane and the (111) face was estimated to be 31°. The [4(111)x(100)] surface could be regenerated in oxygen by heating the surface to between 800°C and 900°C and subsequent heating in vacuum to 700°C to remove the oxygen. Faceting was faster and took place above 300°C in the presence of various hydrocarbons. Although no detailed study was made to analyze the diffraction features that form, faceting yields the same crystal planes in the presence of adsorbed hydrocarbons as in vacuum. At large hydrocarbon pressures faceting was very pronounced with the formation of graphitic carbon at high temperatures. The surface rearrangement could not be arrested by the presence of large partial pressures of hydrogen.

D. The Pt(S)-[7(111)x(310)] Surface

This crystal face exhibits a very large concentration of kinks in each step as shown in the schematic diagram in Figure 2d. Therefore, it was expected to exhibit unique chemisorption and structure forming properties. Indeed, this crystal face behaves very differently in the presence of hydrocarbons than the other stepped platinum surfaces that must have much lower kink concentrations. We have been unable to detect the formation of ordered surface structures of carbonaceous deposits on this crystal face. Initial exposure to hydrocarbons only increases the background intensity of the diffraction pattern and also causes the doublets (due to the step periodicity) to become diffuse, indicating disordered adsorption and disordering of the steps. Heating the surface had little effect on the diffraction pattern, except that during the adsorption of ethylene and toluene, graphitic carbon was produced.

Discussion

Of the four stepped crystal faces that we studied, three, the [9(111)x(100)], [6(111)x(100)], and [7(111)x(310)], showed remarkable thermal stability in vacuum and in the presence of adsorbed hydrocarbons. These surfaces could be heated above 1000°C without marked restructuring, thus they are likely to be important surface structures in various catalytic surface reactions. The [4(111)x(100)] surface, however, was unstable in vacuum at temperatures greater than 900°C and faceted even at 300°C in the presence of hydrocarbons. McLean and Mykura[11] found a similar affect when measuring surface energies of platinum crystal faces. Surfaces with a high angle (greater than 15°) between the surface normal and the (111) pole "roughened" at temperatures approaching 1000°C, while lower angle surfaces were stable to approximately 1500°C. At this temperature the surfaces were radically altered to form large (111) facets while maintaining the same angle between the macroscopic surface normal and the (111) pole. High and low angle faces of copper were found to be stable in vacuum to at least 600°C, but heat treatment in the presence of carbon caused faceting.[12] Niobium steps are stable to 1900°C, but deform at 2400°C probably from the presence of carbon on the surface.[13] These studies confirm the thermal stability of stepped surfaces of several metals to temperatures approaching the melting point of the solid.

Hydrocarbons form several ordered surface structures on the various stepped platinum surfaces. The structures that form depend on the width of the terrace, and the geometry and bonding of the hydrocarbon molecules

that are chemisorbed. In addition, the surface structures are dependent on the surface temperature and the hydrogen partial pressure as well. In short, most of the variables that were tested in this study influenced the formation of ordered carbonaceous deposits. Closer inspection of Table II reveals that ordering of the hydrocarbon deposits improves with increasing temperature. The exception to this trend is the behavior of hydrocarbons on the Pt(S)-[7(111)x(310)] surface. On this high kink density stepped surface, none of the molecules form ordered surface structures in the entire temperature range (20°-850°C) that was studied.

Both the thermal behavior and the Auger spectra indicate that the adsorbed layer contains carbon. However, the amount of hydrogen that is contained in the ordered deposits cannot be monitored directly. Table IIc also reveals that these same hydrocarbons form entirely different types of surface structures on the low index platinum (111) crystal face. Detailed work function measurements which accompanied the LEED studies indicated the absence of dehydrogenation of the hydrocarbons on the (111) surface at moderate temperatures (< 200°C).[8] Since stepped surfaces have been found to dissociate large binding energy diatomic molecules readily,[2,4] the steps are likely to facilitate the breaking of C-H bonds as well, causing rapid dehydrogenation of the adsorbed hydrocarbons even at low temperatures.

In Table III we list the energies of the various chemical bonds of carbon, hydrogen and platinum. The energies of the bonds involving only carbon and hydrogen have been obtained by experiments while those involving platinum have been estimated.[14] It is apparent that breaking of the C-H

bonds should be easier than breaking of the various C-C bonds and just as easy as breaking the H-H bonds.

Not surprisingly, the rate and the extent of dehydrogenation of the adsorbed hydrocarbons can be controlled to some extent by changing the partial pressure of hydrogen over the platinum surface. For example, the ratio of hydrogen to hydrocarbon and the rate of incident flux have a marked effect on the surface structure formed on the Pt(S)-[9(111)x(100)] crystal face. As the surface temperature is raised to above 300°C there is a competition between the formation of ordered surface structures and rotationally disordered graphitic structures. Figure 3 shows the diffraction pattern of the most common ordered structures, a composite of two structures, $\begin{vmatrix} 2 & 0 \\ 0 & 2 \end{vmatrix}$ or (2x2) and a $\begin{vmatrix} 1 & 1 \\ -1 & 2 \end{vmatrix}$ or $(\sqrt{3}x\sqrt{3})$-R30°, along with the disordered graphitic overlayer. The ordered structures form best under low incident hydrocarbon flux and/or high hydrogen flux. A low flux allows the adsorbed hydrocarbon flux and/or high hydrogen flux. A low flux allows the adsorbed hydrocarbon molecules time to diffuse unobstructed to a favorable position along the step before dehydrogenation and the formation of an immobile layer occurs. Hydrogen, incident on the surface, should slow the rate of dehydrogenation and give surface species more time to order. On low index crystal faces, ring-like diffraction features do not appear until 500°C[3,15] or higher indicating the importance of steps in initiating dehydrogenation.

In addition to being able to break strong chemical bonds (H-H, C-H) another striking property of the stepped surfaces is to serve as substrates for the nucleation and growth or ordered carbonaceous surface structures.

These are totally absent from the low index Pt(111) or Pt(100) surfaces. It is likely that dehydrogenation and the formation of ordered carbonaceous deposits are interrelated, as the behavior of the Pt(S)-[9(111)x(100)] surface discussed above, indicates. The rate of dehydrogenation can certainly effect the mobility of the adsorbed species so necessary for ordering to take place in the surface layer. Improvement in the ordering with increasing temperature may also be caused by increased mobility or enhanced dehydrogenation or both. Dehydrogenation and ordering of the hydrocarbon residues are the most significant characteristics of stepped surfaces which distinguish them from the hydrocarbon chemisorption characteristics of low Miller index platinum surfaces.

The behavior of the Pt(S)-[9(111)x(100)] crystal face represents a transition between the behavior of the Pt(111) and Pt(S)-[6(111)x(100)] surfaces. Its step density is high enough to cause dehydrogenation. Nevertheless, the rate of dehydrogenation can be controlled by varying the partial pressure of hydrogen. Similarly, there is a competition between the formation of a rotationally disordered graphitic layer that forms exclusively on the Pt(111) surface upon dehydrogenation of adsorbed hydrocarbons, and the formations of ordered carbonaceous surface structures that form on the Pt(S)-[6(111)x(100)] surface.

The Pt(S)-[6(111)x(100)] face has the most favorable surface atomic arrangement (of the four types of stepped surfaces studied) to induce the nucleation and growth of ordered carbonaceous deposits. Inspection of Table IIa indicates that ordered structures were obtained on this surface during chemisorption of all of the hydrocarbons that were studied. The surface

structure may change as a function of temperature for a specific adsorbed hydrocarbon species,and it also varies from one hydrocarbon to another. When the surface structure formed by the chemisorption of benzene or n-heptane is heated above 700°C the $\begin{vmatrix} 9 & 0 \\ 0 & 9 \end{vmatrix}$ structure forms, Figure 4a. This transformation is accompanied by a change in the step periodicity as evidenced by the absence of doublets with spacing one-sixth that of the platinum-platinum unit cell distance. The new step width is probably more than 50 atoms wide (that is, a step spacing that is too wide to resolve the doublet). Reversible changes in step periodicities have been reported previously on Pt,[2] Cu,[12] and UO_2.[18] The change of periodicity can be caused by the well ordered, specifically oriented, carbonaceous overlayer if it lowers the surface energy of the (111) orientation with respect to the stepped surface enough to cause growth of the (111) terraces. Surface carbon has been shown to preferentially decrease the surface energy of some metals in alloy solutions[19] and could stabilize certain crystal face orientations.

What is the likely structure of the ordered carbonaceous layer? One type of surface structure that may form is composed of a hexagonal overlayer, similar to the structure of the basal plane of graphite, deposited on the (111) orientation atomic terraces of platinum. Since the carbonaceous deposit may be at various stages of dehydrogenation we may assume that the C-C distance is either 1.42 Å or 1.39 Å corresponding to the C-C distance in graphite or in an aromatic molecule, respectively. In Table IV we tabulate some of the coincidence lattices that can be

generated by the rotation of the hexagonal carbonaceous structure with respect to the platinum unit cell. Since the Pt-Pt distance is 2.78 Å, the large number of coincidence lattices are generated due to the mismatch of the unit cell size of the carbon structure and the platinum substrate. The ratio of the magnitudes of the platinum unit cell vector (2.78 Å) to the graphite unit cell vector (2.46 Å) is nearly 9 to 10, and the platinum unit cell vector to aromatic unit cell vector (2.40 Å) is nearly $\sqrt{3}/2$ (0.866) to 1. Table IV shows that some of the carbonaceous surface structures that form (for example, ($\sqrt{3}$x$\sqrt{3}$)-R30°, (9x9), etc.) can be generated by this model while others [for example, (2x2)] cannot. The table also indicates that only a few of the many predictable coincidence structures have been detected.

The Pt(S)-[4(111)x(100)] crystal face is unstable in vacuum above 1000°C. Its faceting is accelerated in the presence of hydrocarbons or hydrogen so that restructuring occurs rapidly even at 300°C. It appears that faceting dominates the structural transitions, and that ordered chemisorption of hydrocarbons could not take place at all on this crystal surface.

The Pt(S)-[7(111)x(310)] face must contain a high concentration of kinks in the steps. This surface exhibits thermal stability similar to the Pt(S)-[9(111)x(100)] and Pt(S)-[6(111)x(100)] crystal faces. As a result of its unusual surface structure,however, adsorption of all of the hydrocarbons produced a disordered layer. Ordering could not be induced by changing the temperature of the partial pressure of hydrogen. It appears that this surface is so reactive that in addition to dehydrogenation (breaking of C-H bonds), the breaking of C-C bonds also takes place readily which causes rapid decomposition of the

hydrocarbons. As a result, an amorphous layer forms before ordering of the carbonaceous deposit can occur.

The studied four stepped platinum surfaces (Pt(S)-[9(111)x(100)], Pt(S)-[6(111)x(100)], Pt(S)-[4(111)x(100)] and Pt(S)-[7(111)x(310)] exhibit very different behavior during the chemisorption of various hydrocarbons (n-heptane, toluene, benzene, ethylene, and cyclohexane). Their behavior is different when compared with the chemisorption characteristics of the Pt(111) surface as well. It is possible, however, to rationalize these diverse characteristics if we consider the interplay of four competing processes that can take place during the chemisorption of hydrocarbons on these various platinum surfaces. These processes are: (1) the nucleation and growth of ordered carbonaceous surface structures; (2) the dehydrogenation of the organic molecules (breaking of C-H bonds); (3) the decomposition of the organic molecules (breaking of both C-H and C-C bonds; and (4) the rearrangement of the substrate (faceting).

On a low index, (111) or (100), crystal face of platinum, none of these four processes take place at less than 200°C at an appreciable rate. Thus, the chemisorbed molecules can be maintained on the surface for experimental times long enough to study their packing and ordering characteristics. At elevated temperatures (above 500°C), thermal cracking produces decomposition and, in the absence of high density surface steps that may act as nucleation sites, a rotationally disordered graphitic overlayer forms.

On the Pt(S)-[9(111)x(100)] surface the presence of atomic steps leads to increased rates of dehydrogenation, and nucleation of ordered carbonaceous structures becomes possible. At low hydrogen partial pressures, dehydrogenation

is more rapid and a disordered carbonaceous deposit forms on these wide terraces before the domains of ordered carbon structures, that nucleate at the steps, can grow large enough to cover the terraces. Heating the overlayer will aggregate the disordered carbon and yields the rotationally disordered graphitic carbon deposits on the terraces, far from the steps. By increasing the hydrogen partial pressure over the substrate during the chemisorption of hydrocarbons, the rate of dehydrogenation can be diminished and the mobility of adsorbed species increased to the point where the rate of nucleation and growth of ordered carbonaceous structures can compete with it successfully. Thus, in the presence of high partial pressures of hydrogen,the formation of ordered carbonaceous surface structures predominate.

On the Pt(S)-[6(111)x(100)] surface the rates of C-C bond breaking are slower than the rate of nucleation and growth of the ordered carbonaceous structure. It appears that increasing the step density by decreasing the terrace width produces a situation favorable for the growth of highly ordered, very stable, carbonaceous overlayers. This surface represents the most favorable substrate structure tested so far for the formation of ordered carbonaceous structures. If these structures are important in hydrocarbon catalysis, and there are indications that they are,[9] the stepped substrate surfaces with terraces between 4 and 9 atoms wide should show optimum reactivity.

The Pt(S)-[4(111)x(100)] crystal face is no longer stable in the presence of adsorbed hydrocarbons. The rate of structural rearrangement of the substrate to new crystal faces is promoted by the presence of both hydrogen

and carbon and therefore becomes faster with the dehydrogenation of the hydrocarbons at the steps. Faceting of this crystal face is thus faster than either dehydrogenation or the growth or ordered overlayers. The new crystal faces that appear are apparently stabilized by the presence of carbon.

Finally, on the Pt(S)-[7(111)x(100)] kinked surface the rate of hydrocarbon decomposition is very rapid compared to the other three processes. Therefore, ordered carbonaceous layers cannot be produced at all. These crystal faces are thermally stable, however, and should be present on catalyst surfaces. Although excess hydrogen does not appear to detectably reduce the ability of this surface to decompose organic molecules, more strongly adsorbed species (sulfur, for example) could block the active kink sites and slow down, perhaps markedly, the decomposition of hydrocarbons, so that the nucleation and growth of ordered layers can compete with it.

The experimental variables that control the rates of these four processes will be the subject of future research. The stepped platinum surfaces that have been studied here may be viewed as prototypes whose different surface structures permit one of the competing surface reactions, a different one on each surface, to predominate.

Inasmuch as high density atomic steps nucleate the formation of ordered surface structures, their presence are desirable when surface structure analysis is to be performed. They would facilitate the formation and growth of large ordered domains of adsorbates so important in obtaining reproducible high intensity diffraction patterns.

Why are these ordered carbon deposits formed and stabilized on the platinum surface in a wide range of temperatures and hydrogen or hydrocarbon pressures? The stability of these structures can be explained by the thermodynamic properties of the Pt-C and Pt-H systems. Carbon and hydrogen have relatively low solubilities in platinum, and there are no platinum-carbon or platinum-hydrogen compounds in the solid state that are thermodynamically stable at elevated temperatures. Thus, the deposited carbon or hydrogen cannot undergo chemical reactions subsequently that would transform the ordered structure to a different chemical entity. On the other hand, simple calculations indicate that the Pt-C and Pt-H bonds are strong, 62 kcal and 67 kcal, respectively.[14] Thus, the strong substrate-adsorbate interaction is responsible for the formation and stability of the ordered carbonaceous structures. Future studies should explore the ordering of carbonaceous layers on other metals that exhibit similar thermodynamic properties in the presence of carbon and hydrogen as that of platinum.

Adsorption and Co-adsorption of Hydrogen

Heating the various stepped platinum surfaces in hydrogen (10^{-7} - 10^{-5} torr) has induced marked changes in the diffraction patterns which are indicated in Table II The appearance of streaks perpendicular to the direction of the steps indicate the appearance of a one-dimensional structure that is ordered along the steps while disordered perpendicular to the steps. In the absence of surface structure analysis, using the diffraction beam intensities, it is difficult to decide whether hydrogen has caused reconstruction of the stepped platinum surface or that the new structure is due to the chemisorbed hydrogen. Nevertheless, the surface structural changes are marked and readily detectable.

When hydrogen was co-adsorbed with n-heptane, toluene, or benzene several surface structures formed that were different from the surface structures that form in the presence of either hydrogen or hydrocarbon. These surface structures are listed in Table IIb. Hydrogen may change the ordering characteristics by a) retarding dehydrogenation or by b) forming co-adsorbed structures with unit cells that contain both the hydrogen and the hydrocarbon molecule. There are several examples reported for the ordered co-adsorption of CO[2,20] and O_2[21] with H_2. Comparison of the co-adsorbed surface structures that form on the stepped surfaces with the surface structure of n-heptane and benzene on the Pt (111) crystal face allows one to distinguish between the processes a) and b). If the surface structures on the stepped and low index platinum

surfaces are identical, the presence of adsorbed hydrogen merely retards dehydrogenation. The data listed in Table IIb indicates that the hydrogen surface structures on the stepped and low index surfaces are different. Thus, hydrogen forms co-adsorbed surface structures with hydrocarbons. Further exploration of these surface structures should be carried out since the hydrogen partial pressure may change the nature of carbon deposits if dehydrogenation at elevated temperatures proceeds via the co-adsorbed structures instead of via the adsorbed hydrocarbon.

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Table I

Angles of Cut, Miller Indices, and Designation of the Stepped Platinum Surfaces

Angle of Cut	Miller Index	Designation
14.5° from (111)	(533)	Pt(S)-[9(111)x(100)]
9.5° from (111)	(755)	Pt(S)-[6(111)x(100)]
6.2° from (111)	(544)	Pt(S)-[4(111)x(100)]
9.5° from (111) rotated 20°	(976)	Pt(S)-[7(111)x(310)]

Table IIa

Gas	Exposure (sec)	Pressure $\times 10^7$ torr		Pt(S)-[9(111)x(100)]			Pt(S)-[6(111)x(100)]		
		Ambient	At the Surface	20°C	350°C	850°C	20°C	350°C	850°C
Hydrogen	60	100	220	No Change	(1d)-H	No Change	No Change	2(1d)-H	2(1d)-H
Ethylene	600	100	490	Complex	—	Complex	$\begin{vmatrix} 2 & 0 \\ 0 & 2 \end{vmatrix}$	—	$\begin{vmatrix} 3 & 2 \\ -2 & 5 \end{vmatrix}$ and $\begin{vmatrix} 6 & 1 \\ -1 & 7 \end{vmatrix}$
Cyclohexane	60	100	650	Disorder	Disorder	Complex	2(1d)-C	Disorder	Complex
n-Heptane	600	2	14	No Change	$\begin{vmatrix} 5 & 0 \\ 0 & 5 \end{vmatrix}$ + C Ring	$\begin{vmatrix} 2 & 0 \\ 0 & 2 \end{vmatrix}$ + $\begin{vmatrix} 1 & 1 \\ -1 & 2 \end{vmatrix}$	—	—	—
	100	10	70	$\begin{vmatrix} 2 & 0 \\ 0 & 2 \end{vmatrix}$ + $\begin{vmatrix} 1 & 1 \\ -1 & 2 \end{vmatrix}$	Disorder	Half Order Diffuse	$\begin{vmatrix} 2 & 0 \\ 0 & 2 \end{vmatrix}$	$\begin{vmatrix} 1 & 1 \\ -1 & 2 \end{vmatrix}$	$\begin{vmatrix} 9 & 0 \\ 0 & 9 \end{vmatrix}$
	60	100	700	Disorder	2(1d)-C	2(1d)-C	—	—	—
Benzene	900	4	27	Disorder	Disorder	$\begin{vmatrix} 1 & 1 \\ -1 & 2 \end{vmatrix}$ + C Ring	3(1d)-C	—	$\begin{vmatrix} 9 & 0 \\ 0 & 9 \end{vmatrix}$
Toluene	100	10	67	Diffuse 1/3 Order Band	(1d)-C	(1d)-C	Disorder	—	$\begin{vmatrix} 9 & 0 \\ 0 & 9 \end{vmatrix}$
	60	100	670	Disorder	Disorder	1/2 Order Diffuse + C Ring	—	—	—

0 0 0 0 3 9 0 0 1 7

Table IIb

Hydrocarbon	Ratio Hydrogen: Hydrocarbon	Exposure (sec)	Hydrocarbon Pressure $\times 10^{7}$ torr		Pt(S)-[9(111)x(100)]			Pt(S)-[6(000)x(100)]		
			Ambient	At the Surface	20°C	350°C	850°C	20°C	350°C	850°C
n-Heptane	30:1	60	100	14	No Change	$\begin{vmatrix} 2 & 0 \\ 0 & 2 \end{vmatrix}$	—	—	—	—
	5:1	300	10	3	—	$\begin{vmatrix} 2 & 0 \\ 0 & 2 \end{vmatrix} + \begin{vmatrix} 1 & 1 \\ -1 & 2 \end{vmatrix}$	—	—	—	—
	5:1	1000	10	3	—	$\begin{vmatrix} 2 & 0 \\ 0 & 2 \end{vmatrix} + \begin{vmatrix} 1 & 1 \\ -1 & 2 \end{vmatrix}$ + C Ring	—	Disorder	$\begin{vmatrix} 1 & -1 \\ -1 & 1 \end{vmatrix}$	$\begin{vmatrix} 9 & 0 \\ 0 & 9 \end{vmatrix}$
	1:10	300	10	4	—	$\begin{vmatrix} 1 & 1 \\ -1 & 2 \end{vmatrix}$ + C Ring	C Ring	—	—	—
Toluene	30:1	100	10	1	No Change	Unstable	—	—	—	—
	30:1	60	100	13	—	(1d)-C	—	—	—	—
	1:1	100	10	3	—	Unstable	—	—	—	—
	1:1	60	100	31	—	C Ring	—	—	—	—
	1:5	100	10	1	—	C Ring	C Ring	—	—	—
Benzene	1:1	100	10	3	—	—	—	Disorder	—	(1d)-C

Table IIc

Gas	Exposure (sec)	Pressure $\times 10^7$ torr		Pt(S)-[4(111)x(100)]			Pt(S)-[7(111)x(310)]			Pt(111)		
		Ambient	At the Surface	20°C	350°C	850°C	20°C	350°C	850°C	20°C	350°C	900°C
Hydrogen	60	100	220	Weak Facets	Weak Facets	Weak Facets	—	—	—	No Change	—	—
Ethylene	60	100	490	Disorder	Disorder	Facets + C Ring	Diffuse Doublets	Diffuse Doublets	C Ring	Disorder	Disorder	C Ring
Cyclohexane	100	10	65	Disorder	Diffuse + Faint 2(1d)-C	$\begin{vmatrix} 4 & 0 \\ 0 & 2 \end{vmatrix}$	—	—	—	$\begin{vmatrix} 2 & 0 \\ 0 & 2 \end{vmatrix}$	Disorder	C Ring
	60	100	650	Disorder	Diffuse + Faint 2(1d)-C	Disorder	—	—	—	—	—	C Ring
n-Heptane	100	10	70	$\begin{vmatrix} 4 & 0 \\ 0 & 2 \end{vmatrix}$	Disorder	$\begin{vmatrix} 4 & 0 \\ 0 & 2 \end{vmatrix}$	—	Diffuse Doublets	Diffuse Doublets	$\begin{vmatrix} 2 & 0 \\ 0 & 2 \end{vmatrix}$	Disorder	C Ring
	60	100	700		Disorder + Faint 2(1d)-C	(1d)-C	—	—	—	—	—	C Ring
Benzene	100	10	70	Disorder	Facets	Facets	—	—	—	$\begin{vmatrix} -2 & 2 \\ 5 & 5 \end{vmatrix}$	Disorder	C Ring
	60	100	640	Disorder	Disorder	Facets + C Ring	—	—	—	—	—	C Ring
Toluene	100	10	67	Disorder + Facets	Disorder + Facets	2(1d)-C	Diffuse Doublets	Diffuse Doublets	C Ring	3(1d)-C	Disorder	C Ring
	60	100	670	Disorder + Facets	Disorder + Facets	2(1d)-C	Diffuse Doublets	Diffuse Doublets	C Ring	—	—	C Ring

Table III

List of Bond Lengths and Bond Energies (for Platinum, Carbon, and Hydrogen)

Bond	Order	Length (Å)	Bond Energy (kcal/g mole)	Remarks
Pt-C	1	2.15	62.5	See Reference 14 for details of calculation.
Pt-H	1	1.685	67.1	
Pt-Pt	1	2.77	43.6	
C-C	1	1.54	88 80 66 - 97	CH_3-CH_3 (ethane) average spread
C-C	"$1\frac{1}{3}$"	1.42	116	graphite
C-C	"$1\frac{1}{2}$"	1.39	121	aromatic
C=C	2	1.33	167 145 140 - 170	H_2C=CH_2 (ethylene) average spread
C≡C	3	1.20	~170	HC≡CH
C-H	1	1.09	104 104 73 - 112	H_3C-H average spread
H-H	1	0.75	103	

Table IV

Close-packed-Coincidence Lattices on Platinum

Coincidence structures generated assuming close-packed hexagonal carbonaceous layers on platinum (111).

a) Structures generated with C-C bond distances of 1.39 (graphite).

$\begin{vmatrix} 9 & 0 \\ 0 & 9 \end{vmatrix}^*$, $\begin{vmatrix} 5 & 1 \\ -1 & 4 \end{vmatrix}$, $\begin{vmatrix} 4 & 1 \\ -1 & 3 \end{vmatrix}$, and $\begin{vmatrix} 7 & 2 \\ -2 & 5 \end{vmatrix}$, $\begin{vmatrix} 3 & 1 \\ -1 & 2 \end{vmatrix}$, $\begin{vmatrix} 8 & 3 \\ -3 & 5 \end{vmatrix}$, $\begin{vmatrix} 5 & 2 \\ -2 & 3 \end{vmatrix}^*$ or

$(\sqrt{19}x\sqrt{19})$-R23.4°, $\begin{vmatrix} 7 & 3 \\ -3 & 4 \end{vmatrix}$, and $\begin{vmatrix} 1 & 1 \\ -1 & 2 \end{vmatrix}^*$ or $(\sqrt{3}x\sqrt{3})$-R30°

b) Structures generated with C-C bond distances of 1.42 (benzene).

$\begin{vmatrix} 7 & 0 \\ 0 & 7 \end{vmatrix}$, $\begin{vmatrix} 6 & 0 \\ 0 & 6 \end{vmatrix}$, $\begin{vmatrix} 9 & 1 \\ -1 & 8 \end{vmatrix}$, and $\begin{vmatrix} 9 & 4 \\ 4 & 5 \end{vmatrix}$, $\begin{vmatrix} 3 & 1 \\ -1 & 2 \end{vmatrix}$, $\begin{vmatrix} 8 & 3 \\ -3 & 5 \end{vmatrix}$, $\begin{vmatrix} 5 & 2 \\ -2 & 3 \end{vmatrix}^*$ or

$(\sqrt{19}x\sqrt{19})$-R23.4°, $\begin{vmatrix} 7 & 3 \\ -3 & 4 \end{vmatrix}$, and $\begin{vmatrix} 1 & 1 \\ -1 & 2 \end{vmatrix}^*$ or $(\sqrt{3}x\sqrt{3})$-R30°

Notes

An asterisk denotes a surface structure observed in these studies. The unit cells of the surface structures with respect to the platinum unit cell are given in matrix notation. For simpler structures the magnitude of the surface unit cell and its rotation with respect to the platinum unit cell is also indicated.

Figure Captions

Figure 1 Angles of cut, Miller indices, and designation of the stepped platinum surfaces.

Figure 2 Diffraction patterns and schematic representations of the platinum stepped surfaces used in these studies.

(a) Pt(S)-[9(111)x(100)] at 84V.

(b) Pt(S)-[6(111)x(100)] at 75V.

(c) Pt(S)-[4(111)x(100)] at 34V.

(d) Pt(S)-[7(111)x(310)] at 49V.

Figure 3 Diffraction pattern obtained from the Pt(S)-[9(111)x(100)] in the presence of carbonaceous deposits of $(\sqrt{3}x\sqrt{3})$-R30° and (2x2) unit cell dimensions, and domains of graphitic, as a result of coadsorption of hydrogen and n-heptane at 350°.

Figure 4 Diffraction patterns obtained from the Pt(S)-[6(111)x(100)] surface.

0 0 0 0 3 9 0 6 0 1 9

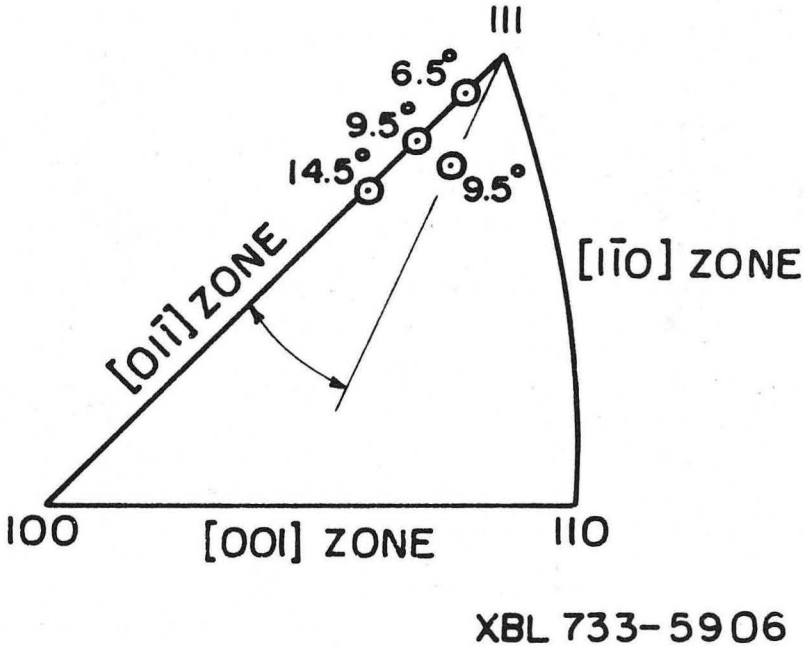
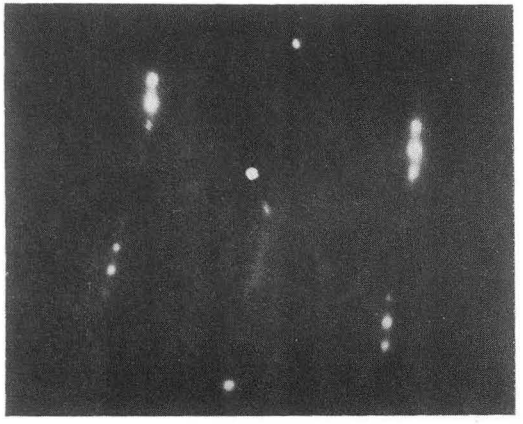
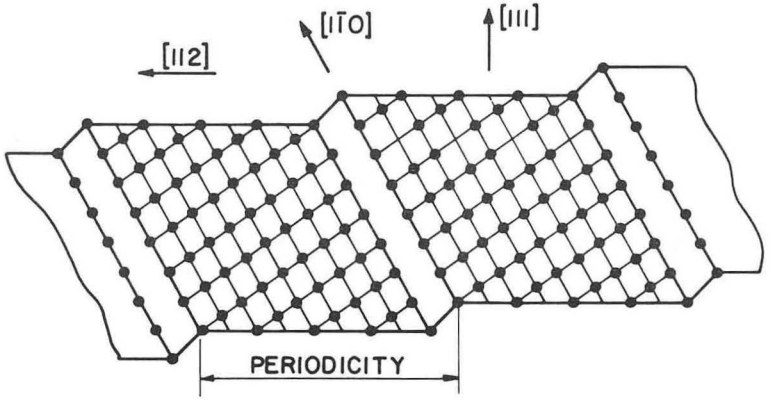
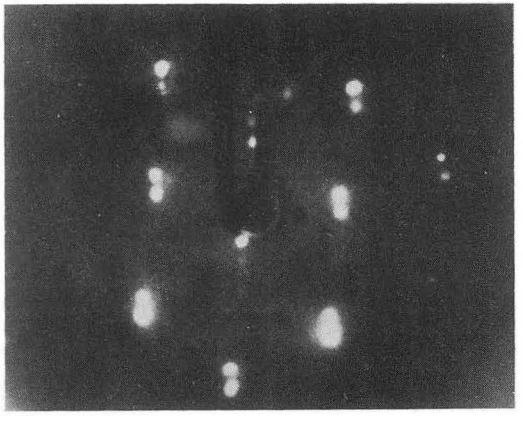


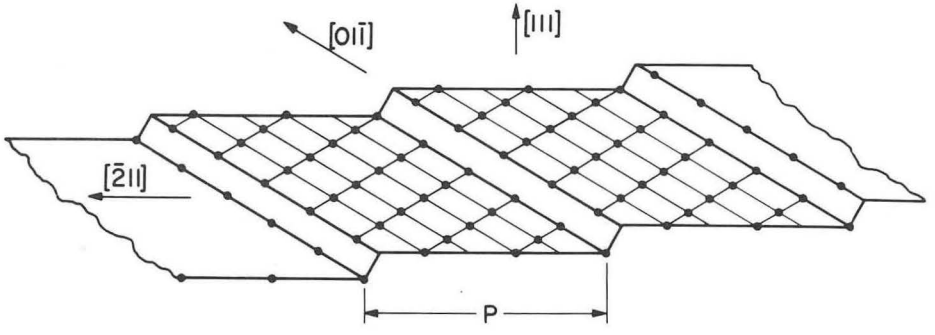
Fig. 1





A. $P_T(S)$-[9(111)x(100)]

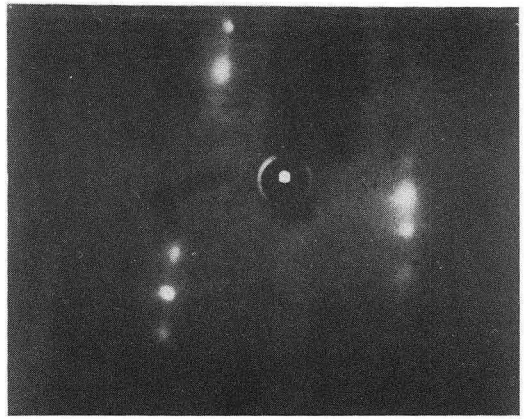


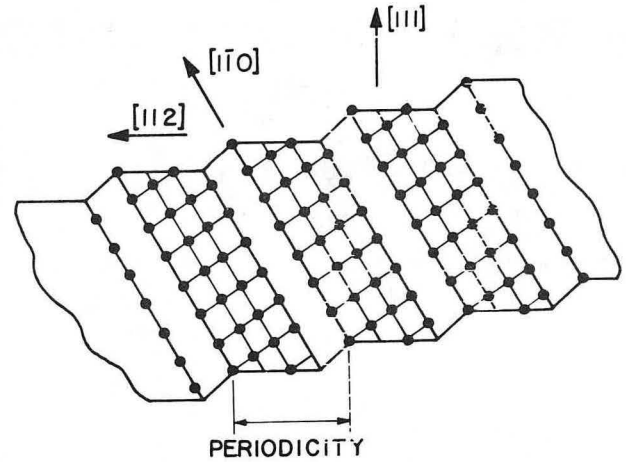


B. $P_T(S)$-[6(111)x(100)]

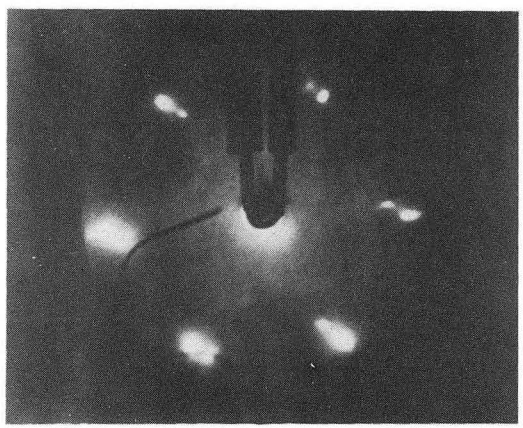
XBB 735-2961

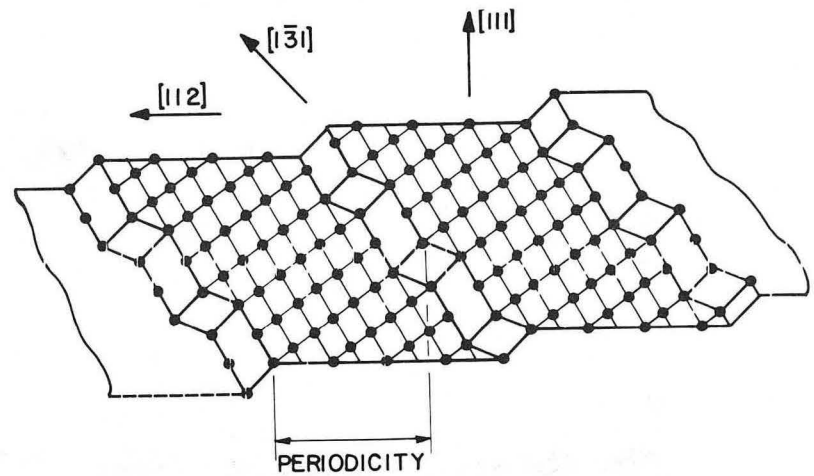
Fig. 2





C. $P_T(S)$-[4(111)x(100)]



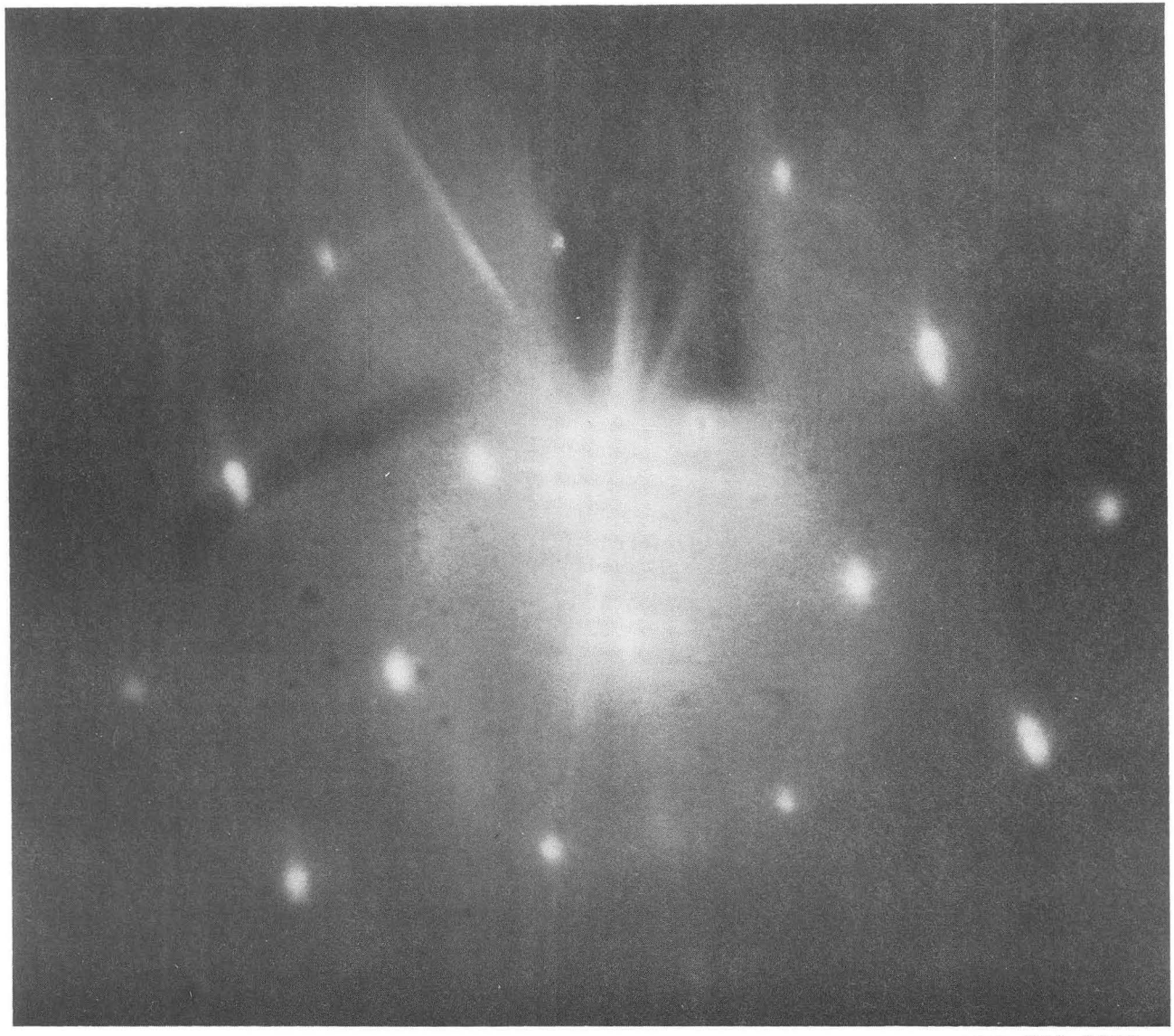


D. $P_T(S)$-[7(111)x(310)]

XBB 735-2960

Fig. 2 cont.

0 0 0 0 3 6 9 0 0 0 2 0

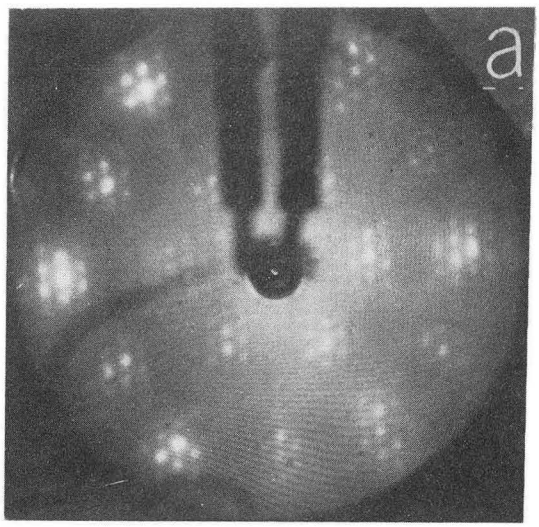


XBB 733-1869

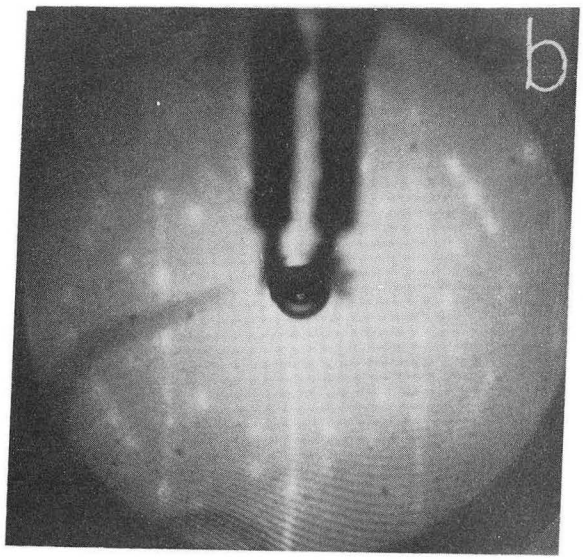
Fig. 3

0 0 0 0 3 9 0 6 0 2 1

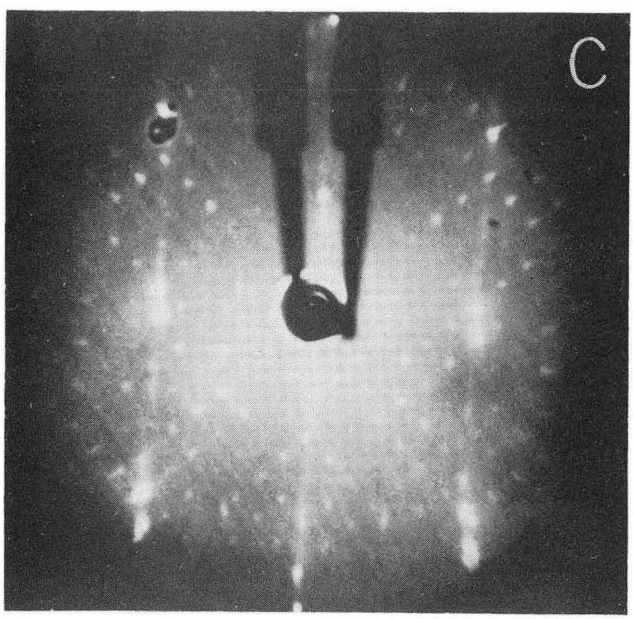
ORDERED CARBON STRUCTURES ON Pt(S)-[6(111)X(100)]



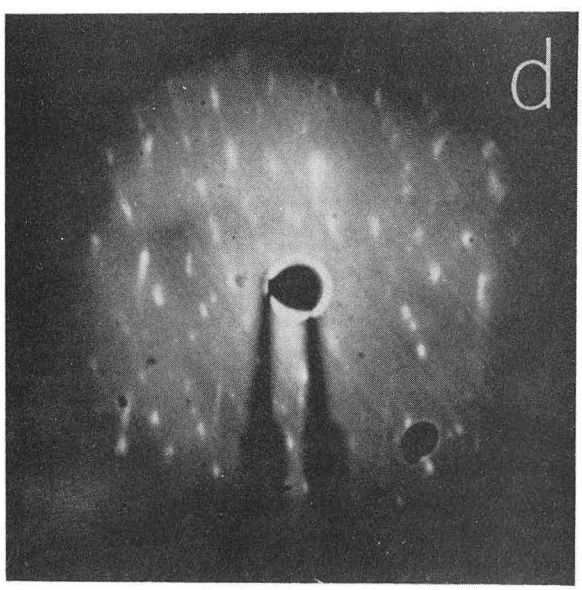
N-HEPTANE, BENZENE, TOLUENE



CYCLOHEXANE



ETHYLENE #1



ETHYLENE #2

Fig. 4

XBB 734-2807

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