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Low Energy Electron Diffraction Studies
of Chemisorbed Gases on Stepped Surfaces of Platinum

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ABSTRACT

The chemisorption of hydrogen, oxygen, carbon, carbon monoxide and ethylene was studied by low-energy electron diffraction on ordered stepped surfaces of platinum which were cut at angles less than 10° from the (111) face. The chemisorption characteristics of stepped platinum surfaces are markedly different from those of low index platinum surfaces and they are also different from each other. Hydrogen and oxygen which do not chemisorb easily on the (111) and (100) crystal faces chemisorb readily and at relatively low temperatures and pressures on the stepped platinum surfaces used in this study. In contrast to the ordered adsorption of carbon monoxide and ethylene on low index faces, the adsorption of CO was disordered on the stepped surfaces and there is evidence for dissociation

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of the molecule. Carbon formed several ordered surface structures and caused faceting on the stepped surface, which are not observed on low index platinum surfaces. There appears to be a much stronger interaction of chemisorbed gases with stepped surfaces than with low index planes that must be caused by the differing atomic structures at the steps. Evidence for the differing reactivities of the two stepped surfaces are also discussed.

1. INTRODUCTION

Most investigations of the surface structure of chemisorbed layers on single crystals using low energy electron diffraction, (LEED), have been carried out on low index planes. Among them the (111) and (100) crystal surfaces of platinum have been the subject of many detailed studies,¹ since platinum is one of the most versatile materials in chemical surface reactions. The surface structures of adsorbed diatomic molecules (O_2 , H_2 , CO), olefins and aromatic molecules have been studied using these surfaces as substrates.^{1,2}

The atomic structure of clean, high index surfaces of a few materials has been investigated only recently,³ and only one study of chemisorption on high index faces has been reported.⁴ The high index surfaces have a surface structure which is characterized by the presence of terraces of constant width linked by steps, usually of monatomic height. The ordered stepped structures exhibit remarkable structural stability to high temperatures even in the presence of surface contaminants and the possible causes of this thermal stability have been discussed elsewhere.⁵

Studies of the structure of chemisorbed gas layers on such surfaces are important for several reasons:

- 1) Chemisorbed layers may have structures on stepped surfaces that are different from those on low index planes. These structures could be intermediates in reactions at surfaces and should thus be identified;
- 2) Most catalytic surface reactions are performed on very small metal particles which are likely to possess stepped surface structures. These

studies may serve to bridge the gap between studies of surface reactions on low index, single crystals and on very small particles.

Several chemisorbed substances were found to have different surface structures from those observed^{1,2} on low index platinum surfaces (carbon and hydrogen). For other chemisorbed gases, such as carbon monoxide and ethylene, adsorption was more disordered on the stepped surfaces than on the low index planes. Oxygen adsorbed on the stepped surface, while it could not be detected on the (111) or (100) platinum surfaces. Thus there are striking differences in the chemisorption behavior of many gases on the stepped surfaces as compared to the low index platinum surfaces.

2. EXPERIMENTAL

Preparation of the stepped surfaces used in this study has been described in the previous paper.⁵ In the nomenclature given for stepped surfaces,⁵ the crystal faces were Pt(S)-[9(111)x(111)] cut at 6.5° from the (111) face in the $[\bar{1}10]$ zone, and Pt(S)-[6(111)x(100)] cut at 9.5° from the (111) in the $[01\bar{1}]$ zone. The single crystals, on polycrystalline platinum holders, were mounted in a Varian u.h.v. chamber in which the ambient pressure was about 10^{-9} torr. The LEED patterns were observed using Varian 4-grid optics and Auger Electron Spectroscopy (A.E.S.) was used to examine the platinum surface composition. The major contaminants at platinum surfaces are carbon monoxide from the ambient and carbon which diffuses from the bulk of the crystal at high temperatures ($> 700^{\circ}\text{C}$). The conditions necessary to generate a clean

platinum surface have been discussed in detail elsewhere,⁶ and normally involve heating the crystal in about 5×10^{-6} torr of oxygen for from 10 minutes to several hours, depending on the level of carbon concentration in the bulk of the sample.

3. RESULTS AND DISCUSSION

3.1

Figures 1a and 2a show the diffraction patterns for the two platinum crystals used in this study. The LEED patterns show the doublet features which are characteristic³⁻⁵ of ordered stepped surfaces. The intra-doublet separation is a function of terrace width and the intensity vs. voltage relation of the two components of the doublet is determined by the step height. Kinematic analysis of this relationship⁵ indicates that the steps on the clean platinum surfaces are of monatomic height, while the width of the terraces is dependent on the cutting angle of the crystal. Thus the average terrace width is six atomic rows for the crystal cut at 9.5° from the (111) face and nine atomic rows for the crystal cut at 6.5° from the (111) face. Although single crystal surfaces will possess disorder on the scale of 1μ ($10^4 \text{ \AA}$), the diffraction patterns suggest that domains of ordered terrace-step structures, which must be of the order of the size of the coherence length of the electron beam ($\approx 100 \text{ \AA}$), exist on the surface.

We consider now the surface structures which have been observed upon the adsorption of various gases on the two stepped platinum surfaces and

compare them to those detected on low index (111) and (100) surfaces of platinum. These surface structures are designated according to the nomenclature given in the previous paper.⁵

3.2 Hydrogen

Heating the Pt(S)-[6(111)x(100)] surface in 1×10^{-6} torr of hydrogen, at 650-800°C for five minutes, followed by cooling in the hydrogen atmosphere, resulted in the diffraction patterns shown in Fig. 1b-c. There are, at low voltages (< 100 V), continuous streaks in the direction normal to the steps (Fig. 1b). These streaks suggest a structure which is well-ordered along the steps, but rather disordered on the terraces. It is designated Pt(S)-[6(111)x(100)]-2(1d)-H. At higher voltages (Fig. 1c) the streaks resolve into a pattern indicative of a (2x2) unit cell. The extra features of the diffraction pattern could be removed by heating the crystal in vacuum in the range 800-950°C for 10 minutes; they reappeared, however, on heating the crystal at 650°C or above 1000°C in vacuum. The hydrogen structure was removed by exposure to 1 L of oxygen (2×10^{-8} torr for 1 minute), but again reappeared on heating to 650°C or above 950°C. Removal of the hydrogen structure by oxygen and regeneration by heat treatment in vacuum could be repeated several times.

Exposure of the Pt(S)-[9(111)x(111)] surface to 3×10^{-7} torr hydrogen at 25°C caused the appearance of the (2x2) diffraction pattern shown in Fig. 2b. The extra features disappeared after 5 minutes heating in vacuum at 300°C. Heating the clean crystal above 600°C and 1×10^{-4} torr hydrogen resulted in a (2x2) structure which formed on cooling in hydrogen and

showed extra spots streaked in the direction perpendicular to the steps. A sharp (2x2) pattern resulted from flashing the crystal to 800°C or by longer heating at lower temperatures. Although the extra features disappeared after prolonged heating at 300°C, they reformed on cooling of the crystal to room temperature. In the same way the (2x2) pattern reappeared at 25°C after heating in oxygen.

Reaction of the stepped platinum crystals with hydrogen appears to cause substantial dissolution of hydrogen in the bulk of the crystal. Reaction of the hydrogen covered surface with oxygen causes the removal of surface hydrogen, but the supply of hydrogen from the bulk is only removed after long periods of heat treatment in oxygen.

Low index platinum surfaces interact weakly, if at all, with hydrogen.^{1a} Heating a platinum (100) surface in 1×10^{-4} torr hydrogen above 1000°C causes the removal of the (5x1) pattern which is characteristic of a clean surface structure,⁶ and the formation of a (2x2) diffraction pattern. Although this structure is not generated at temperatures lower than 1000°C, it is very stable once formed. It is eliminated by heating in oxygen at 500°C. Reports indicate that high temperatures and hydrogen pressures are also necessary for ordered chemisorption on the (111) face of platinum.^{1b}

The stepped surfaces thus react with hydrogen in a manner which is dramatically different from that observed on low index platinum crystals. It seems likely that dissociation of the hydrogen molecules is the rate determining step in both the formation of surface structure and in the dissolution of hydrogen into the platinum lattice. It also appears that

the (111) steps are more active in the chemisorption of hydrogen than the (100) steps, since surface structures which were observed at 25°C on the Pt(S)-[9(111)x(111)] crystal required a temperature of 650°C for formation on the Pt(S)-[6(111)x(100)] crystal.

The extent to which the bulk of the crystal can function as a reservoir and supply hydrogen to the surface should be examined in the light of diffusion and solubility data for the platinum-hydrogen system. Such data are available from permeation experiments through Pt(100) crystal disks.⁷ The diffusion coefficient is

$$D = 6 \times 10^{-3} \exp(-5.9 \text{ kcal/RT}) \text{ cm}^2 \text{ sec}^{-1}$$

and the solubility at 1 atm pressure is

$$S = 1.2 \times 10^{-3} \exp(-11 \text{ kcal/RT}) \frac{g_{\text{atom H}}}{g_{\text{atom Pt}}}$$

Because the solubility decreases with decreasing temperature, dissolved hydrogen diffuses to the surface and can accumulate there once the temperature has fallen in a range where the desorption rate is slow. A random walk argument would predict a mean diffusion distance of 0.6 mm within 300 sec at 200°C. Since the crystal is ~1 mm thick, all the hydrogen contained in the bulk could reach the surface. The solubility at 1 atm is 1 H atom for every 10^{11} Pt atoms at 25°C, but 3 H atoms for every 10^6 Pt atoms at 650°C, which would supply several monolayers of hydrogen to the surface of our crystal. However, considering a pressure of hydrogen of 10^{-4} torr closer to that used in our experiments and assuming a square root dependence of the permeability on the pressure,

the solubility at 650°C drops to 1 H atom for every 10^9 Pt atoms, which would only provide a few per cent of a monolayer of hydrogen. Although the permeation method gives average values of solubility, it will not detect local variations, such as may exist close to the surface of the metal. The present study suggests that crystals exposing stepped surfaces have a higher solubility for hydrogen (at least near the surface) than that reported by Ebisuzaki et al.⁷ for a platinum crystal with a (100) surface plane.

Differences in hydrogen reactivity among platinum surfaces may have important effects on the metal's catalytic activity. A recent study has indicated these large differences in the rates of dehydrocyclization of n-heptane to toluene⁸ on the various crystal faces of platinum and this variation in reactivity is likely to be much more widespread over various catalytic reactions. Also, in view of the great reactivity at steps on the metal surface, previous studies of hydrogen reaction with nominally flat, low index surfaces may reflect only the degree of surface imperfection and the number of steps which existed on these surfaces.

It is known that hydrogen has a very low cross section for the back-scattering of low energy electrons.⁹ In the case of hydrogen adsorption on (100) tungsten Estrup and Anderson have suggested¹⁰ that hydrogen diffraction patterns may result from forward scattering of electrons by hydrogen, and the cross section for forward scattering is known to be much larger than for the back-scattering case.⁹ It is not clear in the present example whether the new diffraction patterns observed result from a mechanism of the forward scattering type or from

a genuine rearrangement of the platinum stepped surfaces. Formation of new diffraction patterns occurs simultaneously with dissolution of hydrogen in the metal lattice, so that a reconstruction may indeed occur. Indications of an ordered adsorption on the terrace planes suggest that it is more likely that diffraction is by forward scattering from hydrogen atoms, since adsorption is not expected to rearrange the terrace planes. A dual mechanism, in which adsorption rearranges the steps, while not moving platinum atoms in the terraces cannot, however, be ruled out. Recent advances in the interpretation of LEED intensities suggest that this problem may soon be capable of solution.

3.3 Carbon

Carbon is one of the major contaminants in the bulk of freshly prepared platinum single crystals and the problems associated with its removal have been extensively discussed.⁶ Several unusual structures, which have been shown by A.E.S. to be due to carbon, have been observed on freshly prepared surfaces used in this study, as well as on clean platinum surfaces which have become coated with carbon by heating to high temperatures in an atmosphere of hydrocarbons.

Heating the freshly prepared Pt(S)-[9(111)x(111)] crystal in vacuum at 750-900°C yielded the ring-like diffraction pattern shown in Fig. 3b. This structure is the same as that resulting from carbon on low index platinum surfaces; the ring is due to domains of graphite with a common c-axis normal to the (111) terraces, but otherwise random orientation with respect to the underlying platinum crystal. Broad reinforcements

are often seen along the ring, centered at 23.4° from the platinum spots. Longer heat treatments in this temperature range produce a transformation which appears in Fig. 3b as doublets of one-third the initial separation; the width of the terraces and the height of the steps are tripled with respect to the original stepped surface. The new structure is designated $\text{Pt(S)}-[27(111)\times 3(111)]\text{-C}$. The identification of this structure is performed using the kinematical analysis mentioned earlier.³ The crystal surface could be restored to its original structure by heating in vacuum to 950°C for 5 minutes.

Heating the freshly prepared $\text{Pt(S)}-[6(111)\times(100)]$ crystal at $750\text{--}900^\circ\text{C}$ resulted in the structure shown in Fig. 3a which may be designated $\text{Pt(S)}-[6(111)\times(100)]\text{-(sx3)-C}$. This nomenclature⁵ indicates that the periodicity of the new structure was equal to that of the clean surface in the direction normal to the step, while being three times that of the clean surface in the direction parallel to the step. This structure was removed from the surface by heating the crystal in vacuum to 950°C by diffusion of carbon into the bulk of the crystal. Heating the crystal to 800°C caused the carbon to return to the surface and the (sx3) structure reappeared. The removal and reappearance of this structure could be repeated by cycling the temperature of the crystal between 800°C and 950°C .

If the clean $\text{Pt(S)}-[6(111)\times(100)]$ crystal was heated at $600\text{--}800^\circ\text{C}$ in 1×10^{-8} torr of ethylene a new surface structure was observed (Fig. 3c). The new unit cell is $\text{Pt(S)}-[6(111)\times(100)]\text{-(}\sqrt{19}\times\sqrt{19}\text{)-R}23.4^\circ\text{-C}$, giving two domains by rotation of $\pm 23.4^\circ$. A layer of graphite (0001) can generate this unit cell by coincidence with the $\text{Pt}(111)$ terraces. Further exposure

of this surface to carbon resulted in the appearance of the ring-like diffraction pattern characteristic of graphitic carbon. In addition, carbon induces some faceting of the surface, two facet planes being observed. One facet, whose diffraction pattern possesses only a specular reflection and a carbon ring, was at an angle of 24° from the (111) pole in the $[01\bar{1}]$ zone, and was identified as having Miller Index (522). The other facet yielded a whole set of diffraction spots (Fig. 3d) converging toward a specular reflection which lay outside the fluorescent screen, the angle from the (111) pole in the $[01\bar{1}]$ zone being about 40° , corresponding probably to (511). This facet had a periodicity, in the direction of the step, which was twice that of the platinum substrate.

No simple carbon adsorption structures other than the carbon ring were observed on the $\text{Pt(S)}-[9(111)\times(111)]$ surface, although three types of facets were observed. Each facet showed a specular reflection and its own carbon ring; the angles from the (111) pole in the $[1\bar{1}0]$ zone were 15.5° , 22° , and 29.5° , the Miller Indices being respectively (221), (331) and (771). It may be noted that only facets which have a zone axis parallel to the step direction have been observed.

All of the new surface structures can be removed from the stepped platinum surface by heating the crystal in oxygen. For freshly prepared crystals a long heating may be required (full details are given in Ref. 6); once carbon has been removed from the crystal bulk, heating in 1×10^{-6} torr at 800°C for 10 minutes is usually adequate.

Low index (111) and (100) platinum surfaces show only graphitic rings after interaction with carbon and carbon containing compounds at

high temperatures. The stepped surfaces thus aid the formation of carbon structures and show a tendency to facet which is not unexpected. The ability of the stepped surfaces to reorder after adsorption is surprising, and again demonstrates the remarkable stability of these vicinal surfaces.

3.4 Carbon Monoxide

Adsorption of carbon monoxide at room temperature on both of the stepped surfaces resulted in increased intensity of the scattered background, but no ordered structures were found. This contrasts with observations of carbon monoxide chemisorption on the (111) face of platinum, where two ordered surface structures have been noted. One, with a $c(4 \times 2)$ unit cell, has been reported previously.² While this observation could not be repeated during this study, a structure with a (2×2) unit cell was noted. Carbon monoxide causes the disappearance of the $Pt(100)-(5 \times 1)$ clean surface diffraction pattern and its replacement by a (1×1) pattern.¹

The lack of ordering on the stepped surfaces may be due to partial dissociation of the carbon monoxide at the stepped surface. It has already been noted that the stepped surfaces appear to readily dissociate molecular hydrogen, which has a bond energy of 104 kcal/mole; the carbon oxygen bond energy, however, is 256 kcal/mole. There is evidence,⁶ that the electron beam is active in splitting the carbon-oxygen bond and this influence may also be important here. Flashing the stepped surfaces results in carbon monoxide desorption at about 200°C, the same temperature

at which desorption is observed on the (111) platinum face. After flashing, however, carbon remains on the surface as detected by Auger electron spectroscopy, suggesting carbon monoxide dissociation at the steps on the crystal surface.

The differences between the behavior of stepped and low index surfaces during the chemisorption of carbon monoxide are again striking. Here, in contrast to hydrogen, interaction with the stepped surface yields disordered adsorption, whereas the low index surfaces both yield ordered adsorption. Failure to observe ordered structure on the stepped surfaces may be due to the very low domain size, or alternatively may be due to the partial dissociation of CO on account of the strong interactions at the atomic steps. The diffraction patterns observed from carbon monoxide on flat surfaces are not highly ordered so that disordered adsorption on the rather narrow terraces of the stepped surfaces may be expected.

3.5 Coadsorption of Carbon Monoxide and Hydrogen

New surface structures were observed when carbon monoxide was allowed to interact with the previously hydrogenated surfaces, generated as described earlier. On the Pt(S)-[6(111)x(100)] surface, extra spots visible below 50 V were noted after an exposure of 1 L at room temperature (Fig. 4). The presence of this adsorbed carbon monoxide layer prevented the removal of the hydrogen structure by oxygen, which otherwise took place rather rapidly (see Sec. 3.2).

Exposure of the Pt(S)-[9(111)x(111)]-(2x2)-H surface to carbon monoxide at room temperature and 10^{-7} torr for 3 minutes resulted in

the $(\sqrt{3} \times \sqrt{3})\text{-R}30^\circ$ pattern shown in Fig. 5 and the same transition occurred by exposure to the ambient atmosphere of the vacuum chamber, well known to largely consist of carbon monoxide.

Coadsorption of CO and H₂ has also been noted on low index platinum surfaces.¹ The Pt(100)-(2x2)-H structure was converted to a c(2x2) structure after exposure to carbon monoxide. Coadsorption of hydrogen and carbon monoxide is thus seen to be a general feature of platinum surfaces; however, it always requires that hydrogen be adsorbed first.

3.6 Ethylene

Room temperature exposure of the Pt(S)-[6(111)x(100)] clean surface, at a pressure of 5×10^{-8} torr for 5 minutes, caused the appearance of a weak (2x2) diffraction pattern. The background of the diffraction pattern was high, indicating that much of the adsorbed ethylene was disordered, (adsorption of hydrocarbons on platinum leading to disordered adsorption in many cases²). Heating this surface to 800°C in vacuum resulted in the pattern shown in Fig. 6. The unit cell is pseudo-cubic with an angle of 94° rotated by 13° with respect to the platinum lattice and a size of about (6x6).

Adsorption of ethylene on the Pt(S)-[9(111)x(111)] clean surface was disordered as indicated by a high background intensity. Heating to 700°C rapidly formed the graphitic ring-like diffraction pattern, no intermediate structures being observed.

Chemisorption of ethylene on the platinum (111) clean surface yielded a (2x2) structure, while a c(2x2) unit mesh was observed on the

Pt(100) surface. Heating both of the low index planes to 700°C resulted in the formation of ring-like diffraction patterns. Heating either low index or stepped surfaces which had adsorbed ethylene resulted in partial desorption and partial decomposition of the hydrocarbon.

In the case of ethylene, as with carbon monoxide, adsorption on the stepped surfaces appears to be more disordered than on the low index planes. In the case of ethylene, however, it is clear that substantial dissociation takes place on both types of surfaces. The ability of stepped surfaces to form high temperature carbon structures has been noted above (Sec. 3-3) and it is interesting that the carbon structure, which was formed by adsorption at room temperature followed by heating to 700°C, was not observed when the clean surface was exposed to ethylene at that temperature. The reactions of platinum surfaces with carbon containing compounds are very important from the catalytic standpoint and present results suggest that the interaction is complex.

3.7 Oxygen

Exposure of the Pt(S)-[6(111)x(100)] surface to 3×10^{-8} torr of oxygen at room temperature resulted in the appearance of weak, continuous streaks normal to the direction of the steps after about thirty seconds. The oxygen structure, shown in Fig. 7a indicates that adsorption occurs at the steps, with a periodicity twice that of the platinum atoms in the step, and the structure is therefore designated Pt(S)-[6(111)x(100)]-2(1d)-O. The structure is of low stability, being removed by exposure to residual gases, mainly carbon monoxide, in about ten minutes.

Heating this clean platinum surface to 800°C for 15 minutes in 1×10^{-6} torr of oxygen, followed by cooling in oxygen caused disordering of the stepped surface. The doublet spots became diffuse, indicating surface disorder and the specular reflection from a facet was noted at 12-13° from the (111) pole in the [011] zone. Longer oxygen treatment at this temperature yielded a diffuse ring centered on the specular reflection of the facet with a radius corresponding to a spacing of 2.68 ± 0.15 Å (Fig. 7b). This could indicate the presence of domains of PtO₂(0001) with random orientation around the c-axis. Platinum dioxide has a hexagonal lattice¹⁵ with parameters: $a = 3.08$ Å, $c = 4.19$ Å, hence a spacing of 2.67 Å in the (0001) plane. Flashing the crystal above 900°C in vacuum removed the ring.

No new adsorption structures were observed on exposing the Pt(S)-[9(111)x(111)] clean surface to oxygen at room temperature. Heating the crystal in 2×10^{-4} torr at 600-800°C for ten minutes followed by cooling in oxygen caused the doublets to become very diffuse, eventually resolving into new doublets of half the initial separation (Fig. 7c). The new structure is designated as Pt(S)-[18(111)x2(111)]-O, the intensity vs. voltage relationship indicating that the steps are now two atomic layers high. This oxygen structure could be removed by heating in vacuum for 10 minutes above 500°C, the initial clean platinum surface structure being restored.

At low pressures, such as were used in this study, oxygen adsorption is not detected on the low index (111) and (100) planes of platinum. A Field Emission Microscope investigation, due to Melmed,¹¹ suggests oxygen

adsorption around the (100) area of the F.E.M. tip. It is suggested that his observation was of oxygen interaction with stepped areas of his specimen, and not with low index planes. LEED investigations of oxygen adsorption on low index platinum show no adsorption structures, and the presence of oxygen could not be detected by A.E.S.

Thus the stepped surfaces are more reactive to oxygen than are the low index faces; these differences again may be of catalytic significance, particularly in the ammonia oxidation reaction where platinum is an important industrial catalyst. The increased activity in chemisorption, as with hydrogen, suggests the increased activity of stepped surfaces in dissociation reactions. Although there is no general agreement as to the state of chemisorbed oxygen on metal surfaces, it seems probable that the chemisorbed state on platinum will be atomic rather than molecular. The observation of what may be a platinum oxide is also of interest as these oxides are known to be of rather low thermodynamic stability. Hitherto only stable oxides, such as those of nickel¹² and copper¹³ have been reported.

4. GENERAL DISCUSSION AND SUMMARY

Studies of the chemisorption of hydrogen, carbon, carbon monoxide, ethylene and oxygen on two stepped surfaces of platinum [cut at angles less than 10° from the (111) face] reveal that the chemisorption characteristics are markedly different compared to low index surfaces and also different from each other. The data are summarized in Table 1,

which gives the surface structures which have been observed and the appropriate experimental conditions. Hydrogen and oxygen which do not chemisorb easily on the (111) or (100) platinum crystal faces chemisorb readily and at relatively low temperatures and pressures on the stepped surfaces used in this study. Hydrogen formed ordered structures on both stepped surfaces and there is strong evidence for its dissociation at the surface and its subsequent dissolution in the crystal lattice. There is evidence that oxygen formed a platinum oxide layer on the crystal with (100) steps, while it caused steps of double height to appear on the surface with (111) steps.

In contrast with the ordered adsorption on low index faces, the adsorption of carbon monoxide on the stepped surfaces was disordered and this may be explicable in terms of dissociation of the molecule at the step on the surface. Ethylene, as was expected, dissociated on both surfaces on heating, forming no ordered structures at room temperature on the surface with (111) steps and a poorly ordered (2x2) structure on the surface with (100) steps. Heating the latter surface caused the appearance of an ordered structure which is attributable to carbon. Carbon which diffused to the surface from the bulk of the crystal or was deposited by heating to high temperatures in the presence of hydrocarbons also formed several ordered structures on the (100) stepped surface which are not observed on low index platinum-surfaces.

There is therefore evidence for a much stronger interaction of chemisorbed gases with the stepped platinum surfaces than with low index planes of platinum.

Oxygen and hydrogen are more strongly adsorbed at the steps, while carbon monoxide and ethylene are much more readily dissociated at the steps. The reason for the increased chemical activity of the stepped surfaces clearly lies in the differing atomic structures at the steps. A molecule adsorbed at the step has a greater number of nearest neighbor metal atoms compared to a molecule at a flat surface and therefore there is an increased availability of metal atom orbitals at the stepped surface for adsorption and reaction.

The marked difference between the chemistry of stepped and low index surfaces also explains the discrepancy in the results reported by different workers: different surface structures of adsorbed gases, existence or lack of adsorption, evidence or absence of dissociation. Low index surfaces with small concentrations of atomic steps, which may not even be ordered, would show such differences.

Comparing the two stepped surfaces used in this investigation, it appears that the surface with (111) steps dissociates hydrogen more easily (room temperature adsorption) than the surface with (100) steps. The interaction of oxygen with the surface containing (111) steps (above 600°C) is strong enough to produce a rearrangement to steps of double height, while there is evidence of platinum oxide formation only at steps of (100) orientation. Carbon generates several ordered structures at high temperatures on the surface containing (100) steps prior to the formation of a graphitic layer, while it yields directly the graphitic layer on the surface with (111) steps.

A distinctive feature of LEED studies of stepped surfaces is the additional information which can be gained by looking at the fine structure of the doublet diffraction spots. Following heat treatments in gases (such as H_2 , O_2 , and hydrocarbons), the appearance of diffuseness inside the initial doublet spots or the appearance of a doublet of smaller width indicates a disordering of the steps or a step reconstruction which yields a new step periodicity, respectively. It should be noted that steps of (111) orientation show a stronger tendency to a rearrangement into steps of multiple height than steps of (100) orientation do.

The atomic structure of small Pt particles dispersed on alumina or silica carriers is likely to be similar to the atomic structures of stepped surfaces. Thus, the chemistry of stepped surfaces should shed light on the chemistry of poly-dispersed metal systems which are catalysts for many surface chemical reactions.

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Table I

Structure and Chemisorption Characteristics of Various Adsorbates
on Stepped and Low Index Surfaces of Platinum

Adsorbate		Substrate			
		Pt(S)-[6(111)x(100)]	Pt(S)-[9(111)x(111)]	Pt(111)-(1x1)	Pt(100)-(5x1)
H ₂	25°C	not adsorbed	(2x2)-H	not adsorbed	not adsorbed
	600-1000°C	2(1d)-H	(2x2)-H	not adsorbed	(2x2)-H
O ₂	25°C	2(1d)-O	not adsorbed	not adsorbed	not adsorbed
	600-800°C	disordered + PtO ₂	Pt(S)-[18(111)x2(111)]	not adsorbed	not adsorbed
CO	25°C	disordered	disordered	c(4x2)-CO, (2x2)-CO	(1x1)-CO, c(4x2)-CO
H ₂ +CO	25°C	structure not identified	(√3x√3)-R30°-(H ₂ +CO)		c(2x2)-(H ₂ +CO)
C ₂ H ₄	25°C	poorly ordered (2x2)	disordered	(2x2)-C ₂ H ₄	c(2x2)-C ₂ H ₄
	700°C	pseudo-cubic (6x6)-R13°	graphitic carbon	graphitic carbon	graphitic carbon
C	700-900°C	(sx3)-C	Pt(S)-[27(111)x3(111)]	graphitic carbon	graphitic carbon
		(√19 x√19)-R23.4°-C	graphitic carbon		
		graphitic carbon facets (522),(511)	facets (221),(331),(771)		

Figure Captions

Figure 1 Diffraction patterns from Pt(S)-[6(111)x(100)]:

- a. clean surface, 75 V
- b. hydrogen adsorption: low-voltage streaks, 68 V
- c. hydrogen adsorption: high-voltage extra-spots, 213 V

Figure 2 Diffraction patterns from Pt(S)-[9(111)x(111)]:

- a. clean surface, 85 V
- b. hydrogen adsorption: (2x2)-H, 85 V

Figure 3 Diffraction patterns of carbon structures:

- a. (sx3)-C, on surface with (100) steps, 140 V
- b. Pt(S)-[27(111)x3(111)]-C and carbon ring, 140 V
- c. ($\sqrt{19} \times \sqrt{19}$)-R23.4°-C, on surface with (100) steps, 58 V
- d. extra-spots due to facets on surface with (100) steps, 121 V

Figure 4 Schematic diffraction pattern due to co-adsorption of H₂ and CO on surface with (100) steps.

Figure 5 Diffraction pattern after co-adsorption of H₂ and CO on surface with (111) steps: ($\sqrt{3} \times \sqrt{3}$)-R30°-(H₂+CO), 85 V

Figure 6 Diffraction pattern obtained at 100 V, upon heating the ethylene-covered surface with (100) steps.

Figure 7 Diffraction patterns after exposure to oxygen:

- a. streaks indicating one-dimensional order along (100) steps,
61 V
- b. Platinum oxide ring on surface with (100) steps, 123 V
- c. $\text{Pt(s)}-[18(111) \times 2(111)]-0$, 85 V

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Fig. 1

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Fig. 2

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Fig. 3

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Fig. 4

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Fig. 5

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Fig. 6

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Fig. 7

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