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Publication Date
1971-11-01
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November 1971

AEC Contract No. W-7405-eng-48

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THE PREPARATION OF ATOMICALLY CLEAN PLATINUM SURFACES

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ABSTRACT

Selected structural and chemical properties of low index and stepped platinum surfaces are reviewed, and the properties of various contaminants in platinum, especially carbon and hydrogen, are discussed. Methods of cleaning of the different platinum surfaces have been developed, and their effectiveness monitored using Auger electron spectroscopy and low energy electron diffraction. The cleaning techniques developed for the different types of platinum crystal surfaces should also be applicable to the cleaning of polycrystalline samples.

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Introduction

Platinum is known as an effective catalyst in a variety of reactions and is considered to be one of the most versatile elements for studies in surface chemistry. Catalysis by platinum is useful in many types of reactions including hydrogenation (for example, ethylene\(^1\) and benzene\(^2\)), dehydrogenation, (cyclohexane to benzene\(^3\)), dehydrocyclization, (n-heptane to toluene,\(^4\) n-butylbenzene to naphthalene\(^5\)), hydrogenolysis\(^6\) and oxidation, (ammonia to nitric oxide\(^7\) is industrially one of the most important cases). The differing nature of these reactions suggests that the platinum surface may play a variety of roles and in order to study the reaction mechanisms it becomes necessary to characterize the metal surface in a number of ways. First, the structure of the platinum surface should be known on the atomic scale, since the nature of the active site may depend on the catalyst geometry. Secondly, the impurity concentration at the crystal surface should be known since the surface reactivity may change with the degree of contamination. This is especially important since many reactions deposit layers which may catalyze or inhibit surface reactions. Thus for definitive studies of catalytic activity and catalytic mechanisms, knowledge of the atomic structure and impurity concentration of platinum surfaces is important.

We have examined the conditions necessary to generate atomically clean platinum surfaces of differing structures in some detail. This paper summarizes information which has been accumulated in this and other laboratories over several years. Since it is now clear that different crystal faces of the same metal may possess substantially different adsorption and catalytic properties we begin with a discussion of the main
types of platinum surfaces, including low-index low free energy surfaces, high-index ordered stepped surfaces and polycrystalline planes. There follows a review of possible contaminants and their known chemisorption properties on platinum. Techniques of surface cleaning and their application to platinum are discussed briefly, and methods which may be applied to the generation of atomically clean surfaces of the different types are presented. It is our hope that the application of the suggested cleaning procedures for platinum surfaces will assist efforts to obtain reproducible and reliable data, even in the absence of the Low Energy Electron Diffraction (LEED) and Auger Electron Spectroscopy (AES) probes which were used in this study.

Platinum Surfaces

Platinum adopts the face-centered cubic crystal structure, with an inter-atomic distance of 2.77Å. Its melting point is 1773°C. Its vapor pressure reaches $1 \times 10^{-6}$ torr at 1400°C., so that the metal may be heated quite close to its melting point without substantial vaporization (the heat of sublimation being 135 kcal/gram atom). The three most closely packed, lowest free energy planes in the f.c.c. structure are, in order of decreasing density, (111), (100) and (110). We present a detailed examination of the Pt(111) and Pt(100) surfaces and discuss some recent structural data for the Pt(110) plane. Recent LEED studies of high index platinum surfaces have shown the existence of platinum surface structures composed of terraces of constant width, linked by steps of constant height and possessing high thermal stability. We discuss the preparation of these new and important types of surfaces, and we consider polycrystalline platinum surfaces.
The Platinum (111) Surface

LEED studies have shown that this face has the surface structure expected from the bulk unit cell. The surface unit cell is a rhombus, of side 2.77Å. The platinum (111) surface is the highest atomic density, lowest free energy of the platinum surface LEED studies as well as twin boundary measurements of McLean and Mykura 12 indicate that it is stable close to the platinum melting point. Figure 1 shows a diffraction pattern obtained from this surface and a schematic representation of its surface structure.

The Platinum (100) Surface

Projection from the bulk unit cell suggests that this face should have a square unit cell, of side 3090Å. However, early studies by Lyon and Somorjai 11 suggested that this was not so, and that the actual unit cell was a rectangle, of approximate size (5 x 1) with respect to that predicted. Similar anomalous structures were also reported for the (100) surfaces of gold 13 and iridium, 14 these metals also possessing face centered cubic bulk structure. Since these studies predated the wide application of the Auger Electron Spectroscopy (AES technique for analyzing the surface composition), it was inevitable that the cleanliness of the anomalous structures be called into question. 15 Palmberg and Rhodin 16 examined the epitaxial growth of gold on a (100) silver crystal. After deposition of three monolayers of gold the LEED pattern assumed the (5 x 1) structure. Palmberg subsequently 10 used AES to demonstrate the cleanliness of the Pt(100)-(5 x 1) surface. Similar evidence has been obtained in this laboratory and is presented below.
Grant and Haas\(^{15}\) have suggested that the \((5 \times 1)\) surface structure is stabilized by oxygen, and that the Pt\((100)-(1 \times 1)\) structure is representative of the clean surface. These arguments are not in agreement with the AES observation which indicates that the \((1 \times 1)\) diffraction pattern is associated with the presence of carbon, while the Auger spectrum from the \((5 \times 1)\) surface structure does not indicate the presence of any impurities. Typical Auger spectra from the \((5 \times 1)\) and \((1 \times 1)\) surface structures of the \((100)\) face of platinum are shown in Fig. 2.

The adsorption of carbon monoxide or hydrocarbons causes rapid disappearance of the \((5 \times 1)\) structure, changing the diffraction pattern to Pt\((100)-(1 \times 1)\). The \((5 \times 1)\) structure may be regenerated by desorption of the gases if no carbon is deposited during the desorption process. It is clear that the Pt\((100)-(5 \times 1)\) surface structure is atomically clean.

The interpretation of this surface structure is a more complex question. Fedak and Gjostein\(^{13}\) analyzed the diffraction pattern as being due to a hexagonal overlayer, forming a \((5 \times 20)\) coincidence lattice with the underlying square unit \((1 \times 1)\) mesh. Palmberg\(^{17}\) indicates that the coincidence unit cell is not rectangular, but a parallelogram, with dimensions close to those suggested by Fedak and Gjostein. It is possible to devise a hexagonal overlayer within the coincidence cell outlined by Palmberg, so that the analysis of Fedak and Gjostein does not have to be changed. Rhodin, Palmberg and Plummer\(^{18}\) have argued convincingly that rearrangements of gold and platinum may be explained in terms of enhanced surface valency. Lyon\(^{19}\) suggested that the \((5 \times 1)\) unit surface cell may be due to ordered vacancies at the platinum interface. However, the hexagonal overlayer is now considered more probable. Figure 3 shows
the diffraction pattern associated with the (5 × 1) surface structure and the schematic diagram of the (100) surface with the hexagonal overlayer. Burton and Jura\textsuperscript{20} using an analogy with the surface energy of argon, proposed that a range of anomalous structures may arise from the movement of rows of surface atoms. This argument can be applied to a simple (5 × 1) unit cell, but is considered unlikely to explain the complex net actually existing on the platinum surface.

A phase transformation of the platinum (100) surface is therefore considered to occur, in which the surface atoms adopt a hexagonal unit mesh resulting in small out of plane displacements (buckling) of the atoms in the outermost layer. The reason for this rearrangement is likely to be a modified free electron density at the surface and a reduction in surface free energy by an increase in close packing.

The Platinum (110) Surface

A recent study by Bonzel\textsuperscript{9} indicates that this crystal face is thermodynamically stable. It exhibits a (1 × 2) surface structure that has chemical properties similar to the Pt(100)-(5 × 1) surface. Bonzel has been unable to rule out the (110) surfaces that may have effected the stability of the (1 × 2) surface structure from the analysis of the Auger spectra. However, the rearranged platinum surface was reproducible in all conditions of the experiment and has been used to carry out studies of the catalytic oxidation of carbon monoxide. The same surface structure was found by Fedak and Gjostein on the (110) face of gold (Au(110)-(1 × 2)).\textsuperscript{13} In the absence of the auger technique, this gold surface structure was considered stabilized by impurities although the impurity
has not been identified. The remarkable stability of the (110)-(1 x 2) surface structure indicates that it is likely to be characteristic of the clean Pt(110) surface.

**Stepped Platinum Surfaces**

LEED studies of high index platinum surfaces have indicated the existence of surfaces consisting of terraces of constant width and steps of constant height. A recent study shows that ordered platinum stepped surfaces may be generated by cutting single crystals at small angles to low index planes. Figure 4 shows a diagram of one such surface together with the associated diffraction pattern. These structures are remarkably stable towards heat treatment in vacuo, surfaces with (111) terraces remaining unchanged close to the melting point.

Adsorption of hydrocarbons, oxygen or hydrogen may disorder the step arrangement although removal of the impurity completely restores the order. Hydrogen and oxygen will also adsorb at the steps in a manner not encountered for flat, low-index planes. It is therefore valuable to treat the cleaning techniques for stepped surfaces separately.

**Polycrystalline Platinum Surfaces**

Studies on single platinum crystals have involved the use of polycrystalline supports which have been monitored by both LEED and AES. It is believed, as a result of these examinations, that the procedures outlined below will generate clean polycrystalline platinum surfaces.
Contaminants at Platinum Surfaces

A metal surface in an ultra-high vacuum (u.h.v.) environment has three possible sources of contamination. The metal will possess a layer of impurity resulting from pretreatment before exposure to u.h.v. This layer, always carbonaceous in the case of platinum single crystals, is easy to remove. The two other sources, contamination from the ambient atmosphere of the vacuum chamber and diffusion of impurities from the bulk platinum to the surface, are more troublesome. A fourth possible source of surface impurity, which may be avoided by proper experimental design, is diffusion of impurity to the crystal from its supports. In this discussion impurities resulting from crystal pre-treatment are considered together with surface contamination resulting from bulk diffusion.

a. Intrinsic impurities (metals, O, Si, Cl, C). Let us consider, first those impurities which are initially present within the crystal. Table 1 shows a spectroscopic analysis obtained with a typical platinum crystal prepared by electron beam zone refining.

Although the metallic impurity content appears to be high, its effect on the surface seems to be imperceptible. The concentration of metal impurities is far below their solubility limit thus there is no energetic impetus to cause diffusion of the metallic impurities to the surface. The uniform distribution of these impurities is therefore maintained even under high temperature heat treatments. Another source of a metallic impurity, is the Pt/Rh thermocouple commonly attached to the sample.

Significant non-metallic impurities are oxygen, silicon, chlorine and carbon. Oxygen does not easily adsorb at low index platinum surfaces.
but readily chemisorbs on stepped surfaces. The platinum oxides are thermodynamically unstable at high temperatures and oxygen diffusing to the surface is likely to undergo instantaneous desorption. Palmberg has reported reversible segregation of silicon at platinum surfaces. An Auger peak was detected at 91 eV on heating the platinum sample to 1500°C and disappeared on cooling the sample to 1000°C. Reversible segregation of sulphur at the surfaces of copper and vanadium has been reported and more examples of this phenomenon may be expected. Palmberg reports that the silicon may be removed irreversibly by heating the sample in oxygen. Auger electrons from silicon have not been observed in this laboratory from any of the platinum crystals which had been treated in oxygen.

Little is known about the chlorine impurity in platinum. The chlorine Auger peak has not been observed at platinum surfaces. It may be that, as in the case of oxygen, chlorine volatilizes as it reaches the surface. Although the chlorine impurity content is only 1 ppm, it should be noted that this would correspond to a coverage of 5 monolayers if total segregation at the surface occurred.

The remaining intrinsic impurity is carbon. Since carbon is difficult to remove from platinum it will occupy the greater part of our attention. The solubility of carbon in platinum has been studied by Siller, Oates and McLellan and also by Selman, Ellison and Darling. Siller, et al. reported solubilities up to 0.13 st % carbon at 1245°C, equivalent to 2.0 atomic %. The latter group of workers claim that the carbon solubility is much lower than this, and also note very rapid rates of diffusion of carbon in platinum.
Palmberg\textsuperscript{17} and Lyon and Somorjai\textsuperscript{11} have noted that carbon diffuses to the platinum surface readily at 1000°C, where it can easily be detected by its Auger peak at 276 volts.

Recent studies in this laboratory reveal that after exposure to carbon-containing compounds, previously clean low index platinum crystal surfaces may be cleaned by heating \textit{in vacuo} at 700°C for 5 minutes. The decrease of the carbon Auger signal (276 v) has been monitored in several experiments. Apparently the carbon diffuses into the relatively carbon-free bulk. Platinum crystals which have not been previously cleaned by heat treatments in oxygen cannot be cleaned this way. The bulk carbon concentration is large enough to minimize the driving force for the in-diffusion of surface carbon. Amorphous carbon at the surface may aggregate into graphite, with the basal plane parallel to the surface. Graphitic carbon is easily detected by the characteristic ring diffraction pattern, which is shown in Fig. 5.

b. Impurities from the ambient (CO, O\textsubscript{2}, H\textsubscript{2}). Turning now to impurities which may adsorb at the surface from the ambient we consider three major species, carbon monoxide, oxygen and hydrogen. Carbon monoxide is well known as a primary constituent of the ambient atmosphere in most u.h.v. systems and is known to adsorb on platinum surfaces. Morgan and Somorjai\textsuperscript{24} have shown that adsorption of carbon at the Pt(100)-(5 \times 1) surface results immediately in the disappearance of the (5 \times 1) unit mesh, which is replaced by Pt(100)-(1 \times 1)-Co, and then by Pt(100)-c(4 \times 2)-CO. Adsorption of carbon monoxide at the platinum (111) surface is also reported to give a (2 \times 2) and a c(4 \times 2) diffraction pattern. Morgan and Somorjai suggest only one binding state for CO on platinum.
(111), with a desorption temperature, $T_d$, of 170°C and on Pt(100) report three binding states, with $T_d = 130°C$, $T_d = 170°C$, and $T_d = 600°C$. They note that CO adsorption increases the work function of both the (111) and (100) faces of platinum, (100) = 0.18 eV and (111) = 0.17 eV, and also note interaction of the adsorbed layer with the electron beam. No accurate measure of the carbon monoxide sticking probability on platinum surfaces is available, but an order of magnitude estimate is 0.1 to 1.0.

Recent work in this laboratory indicates that carbon monoxide does not form ordered structures on stepped platinum surfaces with (111) terraces. The main desorption state on these surfaces is at about 200°C, although there is evidence that CO adsorbed at these steps dissociates into carbon and oxygen, the carbon not being desorbed.

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. 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 structure at the steps. If a Pt(S)-[6(111)-(100)] surface is heated for 5 minutes to 1000°C in vacuo after adsorption of CO, the Auger carbon peak disappears, while the 525 volt oxygen peak remains. This is indicative of carbon monoxide dissociation, with the oxygen remaining adsorbed at the steps. This observation is in agreement with the field emission microscope observation of Melmed, who notes oxygen contamination around the (100) region of platinum tips. It is believed that atomic oxygen, whether bound covalently or as an ion, may reside at atomic steps on a platinum surface. The fate
of carbon generated by dissociation is not certain: it may diffuse into the bulk, as suggested by Melmed, or it may react with the small partial pressure of oxygen present in the ambient and desorb as CO or CO₂. Evidence will be presented that the reaction of surface carbon with gas phase oxygen is very efficient.

Heating the stepped platinum crystal at 800°C in 1 × 10⁻⁷ torr of oxygen, followed by cooling in oxygen, yielded the diffraction pattern shown elsewhere, which may be indexed assuming the formation of a platinum (IV) oxide, the platinum-oxygen distance in the surface plane being 1.8Å. Oxygen adsorption at room temperature was observed on Pt(S)-[6(111)-(100)] crystal.

The interaction of platinum with hydrogen is possibly the most important and certainly the least understood aspect of the metal's catalytic properties. Recent experiments make it clear that the hydrogen environment may control the route of catalytic surface reactions as in the cyclization of n-heptane.

The solubility and diffusion of hydrogen in (100) platinum disks has been examined by Ebisuzaki, Kass and O'Keefe. Their hydrogen permeability value of (7.6 ± 3.0) × 10⁻⁷ exp (-16.9 ± 0.5 kcal/RT) g-atom/cm⁻¹ sec⁻¹ is in good agreement with an earlier value due to Ham. The diffusion coefficient is given by D = (6.0 ± 3.5) × 10⁻³ exp (-5.9 ± 1.0 kcal/RT) cm² sec⁻¹ and the solubility at 1 atmosphere pressure is S = 1.2 × 10⁻³ exp (-11.0 kcal/RT) g-atom hydrogen/g-atom platinum. To calculate the effect of lower pressures of interest in u.h.v. experiments on the hydrogen solubility it is necessary to take into account the effect of pressure on permeability.
Adsorption of hydrogen on the platinum (100) surfaces has been examined by Morgan and Somorjai. At temperatures up to 1000°C and hydrogen pressures up to $10^{-7}$ torr no change of the (5 × 1) diffraction pattern was observed. Increasing the hydrogen pressure to $2 \times 10^{-5}$ torr resulted in the removal of the (5 × 1) pattern and the appearance of a 2 × 2) unit cell on the (100) square unit mesh. This structure was removed in vacuum only by heating to 1200°C. Convincing evidence is presented to show that this structure was due to the presence of hydrogen at the platinum surface and not to impurities. The (2 × 2) diffraction pattern could be removed by heating the crystal in $2 \times 10^{-8}$ torr oxygen at 500°C.

The hydrogen induced diffraction patterns may be interpreted in various ways, just as in the case of hydrogen on the (100) plane of tungsten, which has been discussed by Estrup and Anderson. Newly available scattering cross-sections indicate that back-scattering of low-energy electrons from hydrogen atoms is about two orders of magnitude weaker than that to be expected from metal atoms, so that the possibility that hydrogen gives rise to the high-intensity new diffraction beams may be eliminated. It is, however, not possible to make a clear distinction between forward-scattering of the emergent beams by hydrogen and a possible rearrangement of the metal atoms in the surface in the presence of hydrogen.

Results of hydrogen interaction with platinum stepped surfaces have recently become available. At 300°K hydrogen adsorption may occur along the monatomic steps, giving structures which are stable to heat.
treatment in vacuum, and to mild oxygen treatment. Diffraction patterns for these hydrogen induced surface structures are shown elsewhere.\textsuperscript{22} The rate determining step in the formation of a hydrogen structure and in the dissolution of hydrogen in the lattice appears to be the atomization of the hydrogen molecules. Dissociation may take place readily at the atomic step and subsequent diffusion into the bulk is likely to be rapid at most temperatures of interest. Step sites are thus likely to be important in catalytic reactions as they may serve to dissociate hydrogen molecules. Further investigation of this important phenomenon is in progress.

\textbf{c. Other Contaminants at the Platinum Surface (N\textsubscript{2}, N\textsubscript{2}O, S, H\textsubscript{2}O, CO\textsubscript{2}).} The remaining contaminants at platinum surfaces, which we will deal with briefly, are nitrogen and nitrogen containing compounds, sulfur, water and carbon dioxide.

Nitrogen does not adsorb either at low-index or at stepped platinum surfaces under the usual conditions of pressure used in LEED studies (10\textsuperscript{-10} - 10\textsuperscript{-3} torr) and up to high temperatures (1200°C). New evidence from Auger spectroscopy indicates some adsorption of nitrogen on surfaces which were partially covered with carbon. Indications of this type of co-adsorption are available from studies of reactive scattering of molecular beams of nitrous oxide from carbon-contaminated platinum surfaces.\textsuperscript{35} The carbon-nitrogen triple bond energy from gas-phase spectroscopic studies\textsuperscript{36} is 195 kcal/mole, and the formation of two CN bonds may be the driving force for the adsorption. Surface nitrogen is removed by heating the crystal to 400°C, which suggests a heat of desorption of less than 40 kcal/mole. Carbon overlayers should be considered to play...
a role in the reported activity of platinum in ammonia synthesis.\textsuperscript{37}

Nitrous oxide does not change the clean surface diffraction pattern on Pt(100) at least up to 700°C. Molecular beam studies suggest that at 1000°C a nitrous oxide beam will remove carbon contamination from the platinum surface.\textsuperscript{35}

Sulphur is known as an effective platinum catalyst poison although its presence has not been reported in any Auger study of the metal. Sulphur is likely to be removed by oxygen treatment, probably as sulphur dioxide. It is hoped that a detailed investigation of the important platinum sulphur interaction will be carried out in the near future.

In a study of hydrocarbon adsorption on platinum,\textsuperscript{38} water has been shown to be a common impurity. Water is not strongly bound to the platinum surface, since it desorbs at 100°C and can be displaced by carbon monoxide and most hydrocarbons. Although water adsorption has not been studied on stepped surfaces its effect in these systems is not considered to be important.

Of the great variety of impurities studied in presence of carbon and hydrogen are of primary importance on the different types of platinum surfaces that have been considered. Carbon and hydrogen may migrate from the bulk to the surface of the crystal and thus affect subsequent performance in surface reactions. Detailed examination of the platinum-carbon and the platinum-hydrogen systems is necessary to the understanding of the versatile catalytic properties of the metal. Carbon and hydrogen are also important, since their presence on the surface may be necessary in a wide range of the catalytic reactions of interest.
Techniques for Cleaning Metal Surfaces and their Application to Platinum

The advent of Auger Electron Spectroscopy (AES) has allowed a definition of an atomically clean surface. Since AES is sensitive to levels of contamination of less than 1-5% of a monolayer, where the variation is due to differences in Auger cross sections among the elements, we therefore define an atomically clean surface as one possessing less than 1-5% of a monolayer of any given contaminant.

In many studies it is necessary to generate a platinum surface with well defined atomic structure, for example, a low-index plane or a surface of ordered atomic steps. A satisfactory cleaning procedure will therefore allow cleaning of a surface which has been prepared to give a specified atomic structure without altering the initial geometry of that surface. Once a clean surface is generated it is important to maintain cleanliness for a suitable period of time to allow experiments to be performed. Calculations from the kinetic theory of gases indicates the need for pressures of the order of $10^{-9}$ torr to prevent surface contamination from the ambient.

Three principal techniques for clean, ordered surface generations are currently in use: ion bombardment, chemical cleaning and vaporization. Ion bombardment, principally used in LEED studies, involves collision of 300-500 Volt inert gas ions at a current of several micro-amps/cm² with the metal surface. Ions of this energy are generated by bombarding the gas, usually argon, at pressures of $5 \times 10^{-5}$ to $5 \times 10^{-4}$ torr with electrons. The high energy ions remove metal atoms from the surface by collision at a rate varying from 1 monolayer/minute to 1 monolayer/hour. The process introduces severe disorder at the metal surface,
which then must be reordered by annealing, usually at 500-600°C.

Ion bombardment is not very effective in removing impurities which diffuse to the surface from the bulk during the annealing process. This limitation is important in the case of platinum, where carbon diffusion renders ion bombardment ineffective for surface cleaning. Platinum crystals after an ion bombardment/annealing cycle typically show a ring-like diffraction pattern which is characteristic of the presence of graphite domains at the surface.

During chemical cleaning, the impurity is removed by an efficient chemical reaction of the surface impurity with a gas which does not react rapidly with the metal. Platinum surface carbon and hydrogen are readily removed by oxygen. In the case of an impurity which diffuses slowly from the bulk to the surface, the cleaning procedure is prolonged at a suitable temperature so that most of the impurity atoms may reach the surface from the bulk and be removed. Experiments over several years in more than one laboratory \(^{10,26}\) on many platinum crystals have indicated that chemical cleaning is very satisfactory in the case of platinum. \(^{39}\)

In cleaning by vaporization, the sample is heated to a temperature at which solid is removed at the rate of monolayers per second. Thus the material must have a vapor pressure of about \(1 \times 10^{-6}\) torr appreciably below its melting point. This is the case for silver and chromium. The method is not satisfactory for cleaning platinum, since the Pt-C bond has a disociation energy of 145 kcal/g-atom, greater than the heat of sublimation of platinum, (135 kcal/g-atom).
Removal of Contaminants from Platinum Surfaces

In earlier sections we examined three types of platinum surfaces and discussed the important impurities. We now suggest and discuss methods designed to generate atomically clean low index, stepped and polycrystalline platinum surfaces. We consider two experimental conditions for each class of crystal surface; 1) A surface which has not been cleaned in any way and requires a rigorous cleaning process and 2) one that has been cleaned many times and is contaminated only by a monolayer of carbon deposited during a surface reaction.

Surfaces prepared by these methods showed all of the characteristic features of atomic cleanliness, the Auger spectra showed no peaks other than those known to be due to platinum. The LEED patterns were always sharp with high intensity diffraction spots and low background intensities. Surfaces prepared in these ways showed reproducibility in chemisorption, and in studies of complex surface catalytic reactions.

a. Cleaning of the Platinum (100) Surfaces. We have indicated that the most important impurities on this face of platinum are carbon, present in the bulk of the crystal, and carbon monoxide, present at the surface.

If a newly prepared (100) crystal is heated in the vacuum chamber at 800°C a ring-like diffraction pattern due to graphitic carbon is produced, as shown in Fig. 5. The Auger trace is similar to that shown in Fig. 2. The carbon peak at 275 v is prominent while the platinum peaks are barely visible. The removal of carbon from the freshly prepared crystal (a disc of 10 x 5 x .5 mms) has been effected in our studies by heating at 1000°C for six hours at a pressure of 5 x 10^{-6}
torr of oxygen. After this treatment the LEED pattern that is characteristic of the well known (5 \times 1) mesh is observed. The auger spectrum is shown in Fig. 2. Oxygen treatment is also effective in removing hydrogen from platinum crystals.

The strong chemisorbed \( \beta_{\text{CO}} \) state on Pt(100) has a desorption temperature of 600°C. The platinum crystal temperature should therefore be held above 600°C until commencement of the experiment since the carbon monoxide sticking coefficient on this surface is known to be high.

Once the dissolved carbon has been removed from the platinum crystal, further contamination of the surface will be due solely to adsorption and reaction at the surface unless the crystal has been saturated with hydrogen. For a hydrogen-saturated crystal the procedure given above for a highly contaminated crystal should be used.

If the only contaminant is a layer of surface carbon it may be removed by heating the crystal to 800°C in \( 1 \times 10^{-6} \) torr of oxygen for five minutes. Monitoring the carbon auger peak while heating the sample in a pressure of \( 10^{-7} \) torr oxygen at 800°C indicates that the surface carbon can be removed in about 20 seconds. The procedure given above will remove all of the carbon normally encountered on platinum (100) surfaces. In a system equipped for LEED, but not for AES the appearance of the (5 \times 1) diffraction pattern may be used as a reliable indicator of an atomically clean platinum (100) surface.

b. **Cleaning of the Platinum (111) Surface.** For a freshly prepared platinum (111) surface the cleaning procedure given for the fresh (100) surface is satisfactory. The LEED Pattern should be that of Pt(111)-(1 \times 1) and the auger spectrum of the clean Pt(111) surface should be
identical with that of Fig. 2. Since carbon monoxide will not adsorb at a Pt(111) face above 200°C, the crystal may be cooled to 250°C before the commencement of experiments instead of the 600°C mandatory for the (100) face. To clean a slightly contaminated (111) surface a gentler procedure than that used for cleaning the (100) face may be adopted. Monitoring the carbon auger peak intensity as a function of time for a (111) crystal heated to only 400°C in $5 \times 10^{-7}$ torr of oxygen shows that the surface carbon can be removed in 3 hours. Such a treatment may be much more convenient than higher temperature heating for certain platinum surface geometries (e.g. polydispersed particles).

For a platinum (111) surface which has been saturated at an elevated temperature with hydrogen, the treatment for a freshly prepared (100) surface is applicable.

c. Cleaning of Stepped Surfaces of Platinum. Cleaning of the stepped surface may be complicated by oxygen adsorption at the steps. Stepped surfaces should therefore be heated at 800°-1000°C in vacuum, for at least one hour after removal of oxygen from the gas phase. With this proviso, the techniques for cleaning (100) surfaces will be applicable to surfaces with (100) terraces, and those for (111) crystals will succeed in cleaning surfaces with (111) terraces. Oxygen should not be removed by heating the hydrogen since hydrogen penetrates via the steps into the bulk of the crystal.\textsuperscript{22}

Polycrystalline and randomly oriented single-crystal platinum should be cleaned by the same methods which have been recommended for stepped surfaces, since hydrogen diffusion into the bulk lattice is likely in these cases.
Summary

Procedures for cleaning platinum (100), (111) and ordered stepped surfaces that are also applicable to the cleaning of polycrystalline samples have been developed. Important differences exist between the cleaning procedures necessary for the different crystal faces. It is hoped that the approaches outlined will be useful in laboratories where LEED and AES are not available.

Acknowledgment

This work was performed under the auspices of the U. S. Atomic Energy Commission. Support of this research by the Standard Oil Company of California is gratefully acknowledged. We are especially grateful to many workers in this laboratory, Dr. H. B. Lyon, Dr. A. E. Morgan, Dr. B. Lang, L. A. West, and Mr. F. J. Szalkowski, who, over several years have developed the methods and made many of the observations on which this paper is based.
Table I. Typical mass spectra of Pt single crystal content (ppm by weight).

<table>
<thead>
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REFERENCES

24. Materials Research Corp., Orangeburg, N. Y.
    ibid 38, 1885 (1967).
34. M. Fink, M. Martin and G. A. Somorjai, Surface Science, to be published.
39. It has been reported recently by Bouzel that carbon may be removed from the platinum (110) surface by heating in hydrogen. Since the authors had not carried out chemical cleaning of platinum in this manner the interested reader is referred to the original paper.
FIGURE CAPTIONS

Fig. 1 Diffraction pattern and schematic representation of the clean Pt(111)-(1 × 1) surface.

Fig. 2 Auger spectrum from the clean Pt(100)-(5 × 1) and from the carbon contaminated Pt(100)-(1 × 1).

Fig. 3 Diffraction pattern from clean Pt(100)-(5 × 1) and schematic representation of the Pt(100) surface with a hexagonal overlayer.

Fig. 4 A diagram of the Pt(S)-[6(111) × (100)] surface together with associated diffraction pattern.
Fig. 2

Platinum + Carbon and Carbon Monoxide

Clean Platinum

Auger Peak Height (arbitrary units)

Volts

0 100 200 300 400 500 600

x0.1 0.7

lx

Volts

XBL 719-7306
Reconstructed layer

Fig. 3
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