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at Atmospheric Pressure Over Platinum Single Crystals :
Surface Analysis and Pressure Dependent Mechanisms

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ABSTRACT

The oscillatory behavior of the catalyzed oxidation of carbon monoxide has been studied over platinum single crystals of (111), (100), and (13,1,1) orientation. Surface properties were examined in ultra high vacuum, before and after the reaction, using Auger Electron Spectroscopy (AES), Low Energy Electron Diffraction (LEED), and a Kelvin probe for work function measurements. The oxidation of carbon monoxide was carried out at both low pressure (10^{-4} torr) and atmospheric pressure. The mechanism for the oscillations was different at high and low pressures. A model is presented for the oscillations appearing in the high pressure reaction. This model invokes the formation of platinum oxide, the presence of which was determined experimentally. At atmospheric pressure, silicon was always present on the platinum surfaces and was necessary to detect oscillatory behavior.

INTRODUCTION

Oscillatory reactions have a long and distinguished history in chemical sciences (1). One such reaction which has been studied in great detail is the catalyzed oxidation of carbon monoxide by oxygen to form carbon dioxide. Temporal oscillations in the reaction rate have been observed over platinum, palladium, and iridium catalysts (2,3). This behavior was first reported by Bensch et. al. in 1972 using a supported platinum catalyst (4). Since then, this reaction has been studied over a variety of platinum surfaces including wires, foils, deposited films and single crystals (5-12), and the temporal oscillations have been shown to be a surface mediated phenomenon rather than the result of mass transfer effects(4).

The research carried out to date on this reaction over well characterized single crystal surfaces focused on the oscillatory behavior at low pressure (11-12), in which the surface was exposed to a flowing mixture of carbon monoxide and oxygen at a total pressure of $\sim 5 \times 10^{-4}$ torr. Low energy electron diffraction observations and work function measurements showed that, over the Pt(100) surface, the oscillations are associated with a surface phase transition from the hexagonal (hex) structure ((5 X 20) structure) to the square (1 X 1) and c(2 X 2) structures. It was found that a maximum in the rate coincides with the presence of the hex phase and a high coverage of atomic oxygen while the minimum rate is observed coincidentally with the (1 X 1)/c(2 X 2) phase and a high concentration of adsorbed carbon monoxide.

The most detailed kinetic modeling of the reaction at

atmospheric pressure has performed done by Sales, Turner, and Maple (STM) in conjunction with their experimental studies (13). This model includes the formation of an oxide in the near-surface region of the catalyst. In the two branches of the CO oxidation reaction, the surface is alternately oxidized and reduced, thus changing the surface oxide coverage. This oxide coverage determines in which of the two branches the reaction will be. This model, however, does not include an autocatalytic step, necessary to drive the transition between the two branches.

The work presented here combines surface science techniques, available in ultra high vacuum, with an in situ high pressure cell. Such surface science techniques were not available to STM in their high pressure reaction studies. We have also used platinum single crystals with three different orientations : (111), (100), and a stepped (13,1,1). Since the (100) surface reconstructs and the (111) surface does not, we were able to study the role reconstruction plays in the oscillations observed at high pressure.

We were able to reproduce the results obtained by Cox et. al. (11) for the reaction at low pressure. It appears that their surface reconstruction model explains the oscillatory behavior in the low pressure regime. At atmospheric pressure, however, we have observed oscillations over both the (111) and the (100) platinum surfaces. Also, the surfaces examined after sustained oscillations were heavily oxidized and silicon impurities had segregated from the bulk to the surface. These results indicate that the mechanism at low pressure is different from that at high pressure.

We present a model based on the kinetic equations of STM which also takes into account the non-isothermal behavior of the reaction. The introduction of a temperature that depends on the reaction rate into the model provides a mechanism for the transition between the two reaction branches, similar to the non-autocatalytic non-isothermal systems discussed by Gray and Scott (15) and Uppal, Ray, and Poore (16).

EXPERIMENTAL

Experiments were carried out in an ultra-high vacuum system equipped with low energy electron diffraction (LEED) optics, Auger electron spectrometer (AES), a UTI-100C quadrupole mass spectrometer, a Delta-Phi-Electronix Kelvin probe, and an isolation cell allowing in situ reaction studies at atmospheric pressure. Details of the chamber and high pressure cell have been reported previously (14). A 2000 eV electron beam was used as the excitation source for AES. The 4-grid LEED optics were used as a retarding field analyzer with a modulation voltage of 8 V.

Platinum single crystals were obtained from the Material Science Research Center at Cornell University. Crystals of (111), (100), and (13,1,1) orientations were prepared by standard crystallographic methods. To mount the crystals, gold wire was spot welded to two opposite edges of the sample and then attached to the copper feedthroughs with copper barrel connectors. The impurities present before cleaning were silicon, calcium, sulfur, carbon and oxygen. The crystal surface was cleaned by argon ion sputtering with the crystal heated to 1000 K, sputtering at room

temperature and then heating the crystal to 1000 K in 10^{-7} torr of oxygen. This cycle was repeated until no further impurities could be detected with AES. The platinum sample was usually heated by passing a current through the crystal. While work functions measurements were performed, however, it was necessary to heat the crystal radiatively with a tungsten filament placed behind of the crystal. Sample temperatures were measured with a chromel-alumel thermocouple which was spot welded to the edge of the crystal.

The low pressure oxidation of carbon monoxide was carried out in 1×10^{-4} torr of CO and 4×10^{-4} torr of oxygen at a temperature of 425 K. Changes in the work function of the platinum surface, monitored using a Kelvin probe, were up to 300 mV. The high pressure carbon monoxide oxidation reaction was carried out in the high pressure cell in a continuous flow mode with a total flow rate of ~200 ml/min with gas compositions in the range of 1 - 30 % CO. The crystal was heated resistively in the range from room temperature to 700 K using a constant current. Since the reaction is very exothermic (-70 kcal/mole), it was convenient to follow the reaction rate by following the temperature of the platinum crystal. To establish the validity of this indirect rate measurement, the reaction gases were leaked into the UHV chamber and the CO, O₂, and CO₂ pressures were monitored with the mass spectrometer. As expected, an increase in temperature was associated with a decrease in CO and O₂ pressures and an increase in the CO₂ pressure.

RESULTS

A. Oscillatory Behavior

1. Low pressure experiment

The experiment reported by Cox et al (11) was repeated in order to compare the results which they obtained at low pressure with our results at atmospheric pressure. The work function of a clean, annealed Pt(100) crystal surface was monitored continuously during exposure to 4×10^{-4} torr of O_2 and 1×10^{-4} torr of CO at a temperature of 425 K. Oscillations in the work function of the platinum surface were as large as 300 mV. These oscillations were similar to those reported by Cox et. al.

2. High pressure experiments

When the clean, annealed Pt(100) surface was exposed to a mixture of O_2 and CO at atmospheric pressure no oscillations were observed in the composition range 1 - 30 % CO and the temperature range of 300 - 1000 K. In addition, oscillations were never observed using either clean, annealed Pt(13,1,1) or clean, annealed Pt(111) surfaces. However, when any of the crystals were sputtered for 20 min. at 1000 eV, small erratic oscillations of with a magnitude of about 2 degrees and a period ranging from 1 to 60 seconds were observed, although not reproducibly.

When a clean, annealed crystal was left in the high pressure cell for several days, without cleaning, oscillatory behavior in the reaction developed. This behavior was observed on all three Pt(111), Pt(100), and Pt(13,1,1) surfaces. These results are summarized in Table 1.

The typical oscillatory behavior obtained on the various crystal surfaces and under a variety of conditions is shown in figure 1. In general, as the temperature of the catalyst was increased, the period and magnitude of the oscillations decreased and the magnitude increased as the carbon monoxide concentration was increased. This behavior is the similar to that reported by other authors (13). Figure 2 shows a plot of temperature versus carbon monoxide concentration. The region between the two curves gives the conditions under which oscillations were obtained on a Pt(13,1,1) crystal surface. The shape of this oscillatory region is similar to that reported by Turner et. al. (13).

B. Surface Analysis

An Auger spectrum of the Pt(111) surface after the oscillating reaction is shown in figure 3. The platinum peaks are greatly attenuated relative to those for clean platinum. The peak at 81 eV is due to heavily oxidized silicon (15) and a large oxygen peak at 512 eV is present. This Auger spectrum is typical of the spectra obtained for all surfaces examined after oscillations had been observed, although calcium and sulfur were also present on some of the platinum surfaces. Due to the presence of several species on the surface, it is difficult to quantitatively determine the amount of silicon and oxygen present. Based on standard Auger spectra, however, it is clear that there must be sub-surface oxygen present to give an oxygen Auger peak of the magnitude observed and the amount of silicon present was about 1/2 of a monolayer.

The LEED pattern of the Pt(111) surface after oscillations had been observed is shown in figure 4. This is a slightly misfit $(\sqrt{3} \times \sqrt{3})$ -R30° surface structure. A $(\sqrt{3} \times \sqrt{3})$ -R30° structure has been reported for PtO₂ formed on platinum by high oxygen exposure at elevated temperatures (16). The LEED of the Pt(100) surface after oscillations showed a diffuse (1 X 1) surface structure which was relatively faint.

Because the copper support rods were heavily oxidized after the reaction, an accurate oxygen thermal desorption spectrum could not be obtained. It was noted, however, that desorption of oxygen began at ~ 800 K. It appears that the amount of near surface oxygen was substantial. Even after heating the crystal at 1000 K for one minute in vacuum, the decomposition rate of PtO₂ (as monitored by mass spectrometry) remained constant and the oxygen Auger peak had decreased by less than 10 %.

C. The Effect of Surface Oxidation and Reduction of the Oscillatory Reaction Behavior

Figure 5 shows the effect of pure carbon monoxide and pure oxygen treatments on the catalytic reaction behavior of a Pt(111) surface which had exhibited oscillatory behavior. After the reduction or oxidation of the surface, the reaction gas composition and current passed through the sample were restored to the values under which oscillations had been observed. Figure 5a shows the result of leaving the crystal in flowing CO at 550 K for a period of 40 minutes. When oxygen was introduced following this treatment the temperature of the crystal increased rapidly from 550 K to 630 K and began oscillating. The base temperature

drops off gradually to the value before the CO treatment. Figure 5b shows the result of a more severe reducing treatment. The oxygen flow was shut off and the crystal was heated to 720 K for 5 minutes. When the oxygen was reintroduced with the crystal at 550 K, the crystal temperature jumped to 670 K and then gradually dropped off to 600 K without beginning to oscillate for at least an hour. In general, a mild CO treatment resulted in an initial temperature jump when oxygen was introduced followed by oscillations. A more severe CO treatment resulted in a large temperature jump upon the addition of oxygen, with the resumption of oscillatory behavior re-occurring after a considerable time period, this period being longer the more severe the CO treatment.

Figure 5c shows the effect of an oxygen treatment of the crystal surface which had exhibited oscillations. The CO flow was shut off for a period of 5 minutes, exposing the crystal to pure oxygen, with the crystal at 570 K. When the CO flow was resumed, there was no increase in the temperature of the crystal for a period of at least 1 hour. In general, an oxygen treatment resulted in little or no temperature jump upon the addition of CO and the period of time which elapsed before the oscillations resumed was longer the more severe the oxygen treatment.

These results seem to be consistent with the model proposed by Sales, Turner, and Maple (STM) in which the oscillations are driven by a cyclic oxidation and reduction of the surface. A heavily oxidized surface results in a low reaction rate, while a high rate is observed on a reduced surface.

DISCUSSION

The results of these experiments indicate that the mechanism for the oscillatory behavior of the CO oxidation reaction at atmospheric pressure differs from that at low pressures. In the low pressure regime, the oscillations appear to be driven by a periodic phase transformation of the Pt(100) surface (11,12). At atmospheric pressure, the absence of observable oscillations on the clean, annealed Pt(100) crystal surface and their presence on the silicon contaminated Pt(111) and Pt(100) surfaces indicates that the mechanism of the oscillations at atmospheric pressure is not the same as that proposed for the reaction at low pressure. This is not surprising since it is doubtful that the surface would be reconstructed when exposed to a mixture of CO/O₂ at atmospheric pressure.

The kinetic model for this reaction is presented in the appendix. The model considers the presence of three surface species: molecular CO, atomic oxygen, and a platinum oxide which is only slightly reactive towards CO. The solution to these equations for a given set of parameters is shown in figure 6. When the reaction rate is high, the oxygen coverage is relatively high, the CO coverage is relatively low, and the oxide coverage is increasing. The converse is true when the reaction rate is low. The behavior of the reaction can be seen more clearly when the rate of CO oxidation is plotted versus the oxide coverage. A plot of this type is shown in figure 7 where the solid line indicates the path of the reaction and the dotted line is an unstable solution to the kinetic equations.

When the oxide coverage is such that the reaction is proceeding at a fast rate (in the upper branch), the time derivative of the oxide coverage is positive. Thus, the surface oxidizes while the rate of CO oxidation is slowly decreasing. This is due to a reduction in the number of sites on the platinum which are not oxidized. This continues until the cusp is reached, and at this point the reaction drops into the lower branch. The time derivative of the oxide coverage in the lower branch is negative, so the surface begins to reduce. The reaction rate gradually increases due to an increase in the number of platinum sites available. This process continues until the next cusp is reached, at which point the reaction jumps back to the upper branch and the cycle repeats itself.

In an attempt to experimentally verify this hypothesis of changing oxide coverage, the reaction was stopped at various points in the oscillation, the high pressure cell opened and the surface was examined by Auger spectroscopy. The spectra obtained were identical within experimental error. Several factors may have contributed to our inability to detect changes in the oxide coverage : 1) the surface present at atmospheric pressure is unstable under UHV; 2) the oxide is several layers thick; 3) the silicon is in the form of SiO_2 and remains oxidized; 4) adsorbed CO can react with the oxide before a measurement can be made; and 5) the absolute changes in the coverages are less than 5 % of a monolayer.

The parameters determining the length of time which the reaction spends in the upper and lower branches are the rate

constants for the oxidation and reduction of the surface. Within the context of the model, these parameters determine the point at which $d\theta_{ox}/dt = 0$ on the Z-shaped curve (fig. 7). Oscillatory behavior will occur if this point falls between the two cusps (on the dotted line). If the surface oxidation rate constant is too large relative to the surface reduction rate constant, the reaction will reach a steady state in the lower branch. If the surface oxidation rate constant is too small relative to the reduction rate constant, the reaction will reach a steady state in the upper branch.

Changes in the other rate constants affect the shape of the Z-shaped curve. As the rate of oxygen adsorption is increased, the change in θ_{ox} during an oscillation decreases, the magnitude of the temperature jump decreases, and the curve shifts toward higher oxide coverages. A similar effect is observed when the CO desorption rate is increased. An increase in the adsorption rate of CO has the opposite effect. As the CO oxidation rate constant is increased, the change in θ_{ox} decreases, the magnitude of the temperature jump increases, and the curve shifts to higher oxide coverages. These effects are summarized in the form of temperature versus time plots in figure 8.

For a given set of conditions, the rate of reaction clearly depends on the oxide coverage. If the amount of oxide on the surface is less than the amount of oxide present at the first cusp, the reaction will start off in the upper branch. This is illustrated experimentally in figure 5b where the crystal was treated in flowing CO at 630 K for 5 minutes, reducing the surface oxide coverages less than that of the oscillatory region.

When oxygen was introduced the temperature of the crystal jumped up 100 K very rapidly and remained in the high branch for at least one hour. Figure 5c shows the result of oxidizing the surface past the oscillatory region. When CO was introduced, there was no jump in crystal temperature and the reaction remained in the lower branch for at least one hour.

The silicon always present on the surface after the initiation of the oscillations appears to play an important role in the oscillatory behavior. While a clean, sputtered Pt(13,1,1) surface was found to yield only small, erratic oscillations (fig. 2d), the same surface with Si present yielded large, regular oscillations (fig. 2). It appears that this impurity either increases the sticking coefficient of oxygen or catalyzes the formation of the platinum oxide. We believe that the silicon provides an adsorption site with a higher sticking probability than that for platinum, and after adsorption, the oxygen can spill over to the Pt surface. These results are consistent with the earlier modeling results of STM and other independent studies of the formation and reduction of PtO_2 (17). Oxide formation rates measured over platinum black were an order of magnitude smaller than those necessary to sustain oscillations in the model. The presence of Si impurities which segregate to the Pt surface may increase this oxide formation rate to values which will support oscillatory behavior. This increase in the rate of oxide formation may be due either to an increase in the coverage of atomic oxygen (θ_{O}), or an increase in the rate constant for oxide formation.

While the Pt/Si/O system has not been extensively studied, work by Salmeron et. al. gives an indication of the instability of Si at a Pt surface when exposed to oxygen (18). This work shows that even low partial pressure of oxygen may induce either surface segregation or bulk diffusion of Si into Pt. Thus the Pt/Si/O system might be expected to be unstable in an UHV environment. Figure 9 shows the effect of exposure of an oscillating Pt crystal to UHV conditions. The gas composition and temperature are the same for the two sets of oscillations shown. The only difference was the the high pressure cell had been opened to UHV between the two. This change in oscillatory behavior may be ascribed to the instability of the Pt/Si/O system in vacuum. Changes in the surface which occur when the system is exposed to vacuum may result in a change of the surface oxidation or reduction rate resulting in the effect shown theoretically in figure 8d. Unfortunately, there was no observed change in the relative Auger intensities for these three species. Thus one may assume that induced changes probably do not involve large scale diffusion of species, but instead minor structural rearrangement in the near surface layers, or coverage changes too small to detect by AES.

An alternative explanation for the results of Figure 10 may be a slow diffusion of oxygen from the bulk of the Pt. One might assume that exposure of the Pt to UHV conditions results in the decomposition of the PtO_2 . This would certainly affect the CO oxidation kinetics on the surface and might result in the changes shown in figure 9. Thermodynamically PtO_2 would certainly

dissociate in UHV for temperatures higher than 400 K. From the standard heat of formation (41.8 kcal/mole) and the standard entropy of formation (48.9 cal/mole/deg) one can calculate that PtO_2 will dissociate for $P(\text{O}_2) < 1.3 \times 10^{-17}$ torr at 300 K and for $P(\text{O}_2) < 1.1 \times 10^{-2}$ at 550 K. Nevertheless, the kinetics of oxygen diffusion in Pt are very slow. Although the kinetic data for the diffusion of oxygen through Pt are not very precise, the data which is available ($D_0 = 9.3 \pm 1.8 \text{ cm}^2/\text{sec}$, $E = 78 \pm 25 \text{ kcal/mole}$) (19) indicate that, at 300 K, the diffusion of oxygen through 10 Å of Pt would require 6×10^{33} years and 200 seconds at 1000 K.

CONCLUSIONS

- 1) Oscillatory reaction rates have been observed for the catalyzed oxidation of carbon monoxide over platinum single crystal surfaces of (111), (100), and (13,1,1) orientations at atmospheric pressure.
- 2) The Pt(100) surface is known to undergo a (5 X 20) to (1 X 1) phase transformation upon the adsorption of carbon monoxide. Cox et. al. have proposed that oscillations which they have observed at low pressure (1×10^{-4} torr) are due to this surface phase transformation. Since the Pt(111) surface does not undergo any such reconstruction, this mechanism cannot be responsible for the oscillations at atmospheric pressure which are reported here.
- 3) Reaction rate oscillations at atmospheric pressure are believed to be driven by an cyclic oxidation and reduction of the

platinum surface. A model incorporating this process and including the temperature variation of the catalyst as the driving force of the transition between reaction branches step shows excellent agreement with experimental results.

4) While oscillations have been obtained over clean platinum single crystal surfaces, it appears that silicon impurities are usually present on a surface supporting oscillations. These impurities are believed to play an important role in the oscillatory behavior by either catalyzing the formation of the platinum oxide or by increasing the sticking coefficient of oxygen on the platinum surface.

APPENDIX

A Kinetic Model for the Oscillatory Behavior of the CO Oxidation Reaction Over Platinum

The following assumptions are made in the model :

1) The molecular adsorption rate of CO and the dissociative adsorption rate of O₂ depend only on the number of sites available for adsorption, the partial pressures of the gases, and the temperature.

2) CO₂ is produced from the reaction between adsorbed CO and adsorbed atomic oxygen and desorbs instantaneously upon formation.

3) The desorption energy of CO is independent of coverage. Desorption of oxygen is ignored.

4) The number of CO and O₂ adsorption sites are the same.

In the STM model, all calculations were made for isothermal conditions. In reality, due to the high exothermicity of the reaction, the crystal temperature, T , is dependent on the reaction rate. We have modified the STM model by assuming a temperature with a reaction rate dependence of the form : $T = T_0 + a r(\text{CO}_2)$. The magnitude of the constant 'a' would depend on the surface-to-volume ratio of the catalyst, the rate of thermal conduction from the sample, and other thermodynamic factors. It was not the intention of the authors to model the temperature exactly, and we feel that this simple model is sufficient.

There are three surface species whose coverages were considered : atomic oxygen (θ_o), molecular carbon monoxide (θ_{co}), and oxygen in the form of an oxide (θ_{ox}). The kinetic equations which define these coverages are as follows:

$$d\theta_o/dt = k_1\theta_s^2 - k_3\theta_o\theta_{co} - k_5\theta_o(1 - \theta_{ox}) \quad (1)$$

$$d\theta_{co}/dt = k_2\theta_s - k_4\theta_{co} - k_3\theta_o\theta_{co} - k_6\theta_{co}\theta_{ox} \quad (2)$$

$$d\theta_{ox}/dt = k_5\theta_o(1 - \theta_{ox}) - k_6\theta_{co}\theta_{ox} \quad (3)$$

where $\theta_s = 1 - \theta_o - \theta_{co} - \theta_{ox}$

and the rate constants are temperature dependent.

Values for the rate constants are shown in Table 2.

In eqn. 1 the first term represents the rate of dissociative adsorption of O_2 , the next term the reaction between adsorbed, atomic oxygen and adsorbed carbon monoxide, and the last term the formation of the oxide from adsorbed, atomic oxygen. Similarly, the terms in eqn. 2 describe the molecular adsorption of CO, the desorption of CO, the reaction between adsorbed CO and adsorbed, atomic oxygen, and the reaction of CO with the oxide to form CO_2 , respectively. The third equation consists of the rates of formation for the oxide from adsorbed, atomic oxygen and the reaction of the oxide with adsorbed CO to form CO_2 .

This set of equations was solved using two different methods. One was an iterative method in which the time increment was weighted inversely proportional to the sum of the rates of the individual simple processes involved in the reaction (rate of O_2 adsorption, rate of CO adsorption, etc.) with a proportionality constant on the order of 10^{-4} . The other method

was similar to the quasi-steady state solution reported by STM *. In this solution, the derivatives $d\theta_o/dt$ and $d\theta_{co}/dt$ were set equal to zero and the terms $k_5\theta_o(1 - \theta_{ox})$ and $k_6\theta_{co}\theta_{ox}$ were ignored. The justification for these approximations is the rates of adsorption, desorption and CO_2 production are much larger than the rates of oxidation and reduction of the surface ($k_1, k_2, k_3, k_4 \gg k_5, k_6$). The difference between our method and that reported by STM is that our solution is not isothermal. The solutions obtained by the iterative and quasi-steady state methods were very similar. The only difference between the solutions obtained by the two methods occurred when the reaction approached a point of transitions between branches. This is because $d\theta_o/dt$ and $d\theta_{co}/dt$ become relatively large at these points and the steady state approximation no longer holds. Since the later method required much less computer time, it was the primary method utilized in this work.

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TABLE 1

	Pt(111)	Pt(13,1,1)	Pt(100)
10 ⁻⁴ torr Clean Annealed	No Oscillations	No Oscillations	OSCILLATIONS
1 Atm Clean Annealed	No Oscillations	No Oscillations	No Oscillations
1 Atm "dirty"	OSCILLATIONS	OSCILLATIONS	OSCILLATIONS
1 Atm Clean Sputtered	?	Small Erratic Oscillations	?

TABLE 2

		A (sec ⁻¹)	E _a (Kcal/mol)
k ₁	Oxygen Adsorption	2.8 X 10 ⁶	0.5
k ₂	CO Adsorption	3.0 X 10 ⁴	0
k ₃	Langmuir-Hinshelwood	9.4 X 10 ⁹	10
k ₄	CO Desorption	1.0 X 10 ¹¹	20
k ₅	Surface Oxidation	0.275	1.0
k ₆	Surface Reduction	12	10

Figure Captions

- Fig. 1. Typical oscillations obtained on three platinum crystal surfaces under various conditions. Sample temperature is plotted versus time.
- Fig. 2. A plot of sample temperature versus carbon monoxide concentration showing the conditions for which oscillations were obtained over a Pt(13,1,1) crystal surface.
- Fig. 3. A typical Auger spectrum of the platinum surface, after the oscillatory reaction, showing the presence of silicon (80 eV) and oxygen (512 eV).
- Fig. 4. A schematic representation and photograph of the LEED pattern observed for the Pt(111) surface after the oscillatory reaction. This pattern indicates a misfit $(\sqrt{3} \times \sqrt{3})\text{-R}30^\circ$ surface structure.
- Fig. 5. Plots of sample temperature versus time under oscillatory conditions after treatments in (a and b) pure CO and (c) pure oxygen.
- Fig. 6. Solutions to the kinetic equations showing $\ln(\theta_o)$, $\ln(\theta_{co})$, and θ_{ox} as a function of time. See Table 2 for rate constant values.
- Fig. 7. Solution to the kinetic equations plotted as the rate of CO_2 production versus θ_{ox} . The solid line shows the reaction path and the dotted line is an unstable solution. Values for the rate constants are listed in Table 2.

Fig. 8. Theoretically generated oscillations of the sample temperature as a function of time. Values of the rate constants listed in Table 2 were used in the calculations except where indicated in the figure.

Fig. 9. Sample temperature as a function of time (a) before and (b) after exposure to UHV.

XBL 845-6976

Fig. 1

XBL 845-6975

Fig. 2

XBL 845-6976

Fig. 1

XBL 845-6975

Fig. 2

XBL 845-6976

Fig. 1

XBL 845-6975

Fig. 2

XBL 845-6974

Fig. 3

Pt (III) with Si and O after Oscillation Reaction

Fig. 4

XBB 845-3572

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Fig. 5

XBL 845-6972

Fig. 6

XBL 845-6971

Fig. 7

XBL 845-6970

Fig. 8

Pt (III) 30 % CO

XBL845-6969

Fig. 9

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