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Reaction rate oscillation of CO oxidation on Pt(210)

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We report on the occurrence of kinetic instabilities and regular oscillations in the rate of CO₂ formation as it results from the CO oxidation reaction carried out in ultrahigh vacuum and high vacuum on a platinum (210) surface. While the surface properties are characterized and controlled by combined low-energy electron diffraction, Auger electron spectroscopy, thermal desorption spectroscopy, and $\Delta\Phi$ measurements, the rate of reaction is monitored by measurements of the partial pressures of the reactants and/or of the work-function change of the Pt(210) surface. We have followed the reaction kinetics as a function of "external" parameters (P_{CO} , P_{O_2} , T) and have investigated the conditions under which oscillations occur. Likewise, the influence of some of the "internal" parameters (sample cleanliness, gas purity, surface structure) has been worked out. Finally, possible mechanisms for the occurrence of periodic oscillations are discussed, including the local oscillation as well as the process of synchronization.

I. INTRODUCTION

Ever since the discovery of rate oscillations in the catalytic oxidation of CO over supported platinum catalysts,¹ this phenomenon has been observed to take place under a variety of conditions including well-characterized single-crystal surfaces.² There are several aspects of this phenomenon which have interested and challenged researchers in the field of surface physics and catalysis, the main source of interest being that of finding the origin and cause of instabilities in reactions.

Another aim of this research has been to differentiate between elementary steps involved in the reaction and in the kinetic processes (which may be dominated by the nonlinearity of this reaction). An interesting feature of the heterogeneously catalyzed CO oxidation is that under a steady flow of reactants it represents an example of an irreversible dynamical system which exhibits nonlinear characteristics and transition to chaos. Recent experiments on platinum and palladium (110) surfaces have shown transition from regular periodic behavior to chaos.^{3,4}

Despite the large number of studies performed on rate oscillations of CO oxidation, very few oscillating systems have been well characterized, whether under high-pressure conditions on polycrystalline surfaces or at low pressures on single-crystal surfaces. The main difficulty in characterizing these systems has been that of preparing and maintaining ideal reaction conditions with reproducible surfaces that are free of impurities and defects. Although the single-crystal surfaces under UHV conditions are not completely free of the problems normally associated with higher pressures, they offer a larger degree of reproducibility with respect to the adsorption and reaction properties of the reactants.

It has been well established that the CO oxidation reaction on platinum group metals is a Langmuir-Hinshelwood

process, regardless of surface structure or pressure range.⁵ However, the *reactivity* of each surface orientation toward CO oxidation depends to a large degree on the adsorption and/or desorption properties of reactants, as will be shown in this article.

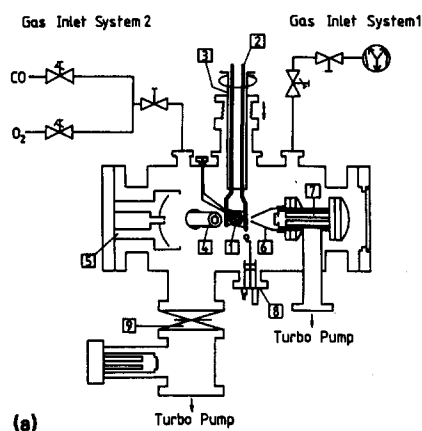
Among single-crystal surfaces of platinum group metals, Pt(100), Pt(110), Pt(210), and Pd(110) have shown oscillating reactions.^{4,6-8} Each of the above surfaces shows oscillations under different pressure and temperature conditions, and they also exhibit different oscillatory behavior. This difference can be traced back to the adsorption and phase transition properties of CO and oxygen on each surface. For example, a clean and well-annealed Pt(210) surface shows fairly reproducible oscillations in the rate of CO oxidation at oxygen pressures above 1.0×10^{-4} Torr. At constant oxygen pressure and sample temperature (P_{O_2}, T), however, oscillations occur *only* over a narrow region of CO pressure.

In the next section, the experimental procedure to establish and monitor oscillations will be explained. This will be followed by a presentation of results on the dependence of oscillations on P_{O_2} , P_{CO} , and temperature, as well as on surface conditions. Finally, the results will be compared to other single-crystal surfaces that exhibit oscillatory behavior, and a mechanism for the origin of the oscillations will be proposed.

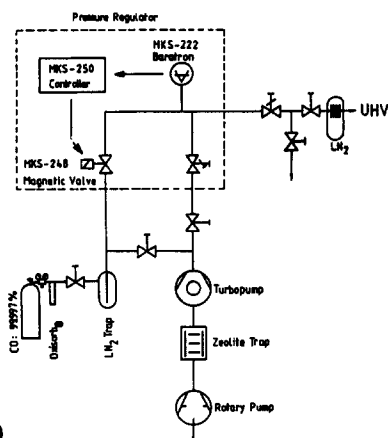
II. EXPERIMENT

A. The UHV apparatus and facilities

Our experiments were performed in a standard stainless-steel reaction chamber which was equipped with a four-grid low-energy electron diffraction (LEED) optics (Varian) serving as a probe for the structure (in the LEED



(a)



(b)

FIG. 1. (a) The UHV system used as the reaction chamber for the pressure range of 10^{-10} – 10^{-2} Torr. The numbers on the figure indicate the following components: (1) the single-crystal sample; (2) the tungsten rods used for sample mounting; (3) the liquid-nitrogen-cooled sample holder; (4) ion gun; (5) Auger/LEED optics; (6) cone of the mass spectrometer chamber; (7) mass spectrometer; (8) vibrating capacitor (Kelvin probe); (9) the gate valve used for varying the pumping speed. (b) The pressure regulation system for CO and O₂ prior to admission to the reaction chamber.

mode) and for the chemical cleanliness (in the retarding-field Auger mode) of the Pt(210) surface. Also attached to the chamber were a differentially pumped quadrupole mass spectrometer (Balzers QMG 311) with a cone for partial pressure and thermal desorption measurements, a Kelvin vibrating capacitor operated in a self-compensation mode for measuring work-function changes, and an ion sputter gun (Leybold) for sample cleaning. The system was pumped by a 330 liter/s turbomolecular pump (Balzers); the base pressure after appropriate bake-out was routinely obtained in the low 10^{-10} Torr range. The system is schematically shown in Fig. 1(a).

B. The gas inlet system

The gases were admitted to the chamber via all-metal bakeable leak valves (Varian). A schematic drawing of the gas-inlet system is given in Fig. 1(b). The pressures of CO and oxygen before admission to the system were regulated to better than 0.5%. A constant flow rate could then be adjust-

ed with the leak valves rather accurately and reproducibly. The pressures were measured using a spinning rotor gauge and a Bayard–Alpert ionization gauge from UHV to high-vacuum range (10^{-10} –1 Torr). During the reaction experiments the pressures of CO and oxygen were stable at better than 0.1% (as judged by the measurement done with the spinning rotor gauge). All the gas lines had to be baked periodically, and very-high-purity gases of CO and oxygen had to be used. Further purification of CO with Oxisorb® (Messer–Griesheim, CrII compound supported on silica-gel⁹), and a liquid-nitrogen (LN₂) trap was necessary in order to get long and reproducible oscillations. In order to check the effect of gas purity, different bottles of CO were used; each showed a different level of purity, which was indicated by the long-term stability of oscillations (oscillations lasted normally 2–3 h with a new Oxisorb and the purest gas). The best results were obtained with gases from Linde (CO: 99.997% and O₂: 99.999% purities); together with a liquid-nitrogen trap, oscillations could be sustained over 24 h.

C. Sample preparation

The samples were cut in the form of disks (8 mm diameter; 1.0 mm thickness) from high-purity (99.999%) single-crystal rods of platinum and oriented and polished in the [210] direction. The sample was mounted to a liquid-nitrogen cooling manipulator via two parallel-running Ta wires which were used for resistive (dc) heating. By means of a temperature controller, the sample temperature could be regulated within wide limits (80–1200 K) or kept constant (to within 0.1 K) with very small drift. The temperatures were measured using a Chromel–Alumel thermocouple spot-welded to the rear of the sample.

The cleanliness of the surface was absolutely critical for getting reproducible oscillations. Prior to each experiment the surface was cleaned with a combination of Argon ion sputtering (Ar⁺, 1 keV, 1000 K) and by annealing at elevated temperatures (1200 K, 15 min) followed by oxygen treatment (800 K, 1.0×10^{-5} Torr). The flow of oxygen for 20–30 min prior to the start of reaction helped to stabilize the background pressures by removing H₂, H₂O, and other residual gases from the surface of the reactor (vacuum system) or by reacting them with oxygen.

D. Experimental techniques to monitor rate oscillations

The majority of oscillating reactions studied on single-crystal surfaces occur at pressures above 10^{-5} Torr. Most nondestructive surface-sensitive techniques that use electrons or ions reach their operating limit at pressures around 10^{-5} Torr. Low-energy electron diffraction (LEED) has been used by Ertl and co-workers to monitor the structural changes during the reaction.⁶ However, this technique is limited to the low 10^{-4} Torr region. In addition, low-beam energies and currents are necessary in order to minimize the electron damage to the surface adlayer or cathode failure.

The direct way to monitor the reaction rate is through CO₂ partial pressure change in the gas phase. This can be accomplished easily by using a differentially pumped mass

spectrometer [Fig. 1(a)] with an orifice to the reactor chamber. With this arrangement, the partial pressure variation for both the product and the reactants can be monitored.

At high oxygen pressures, above 10^{-2} Torr, the sensitivity of detection decreases due to a decrease in the mean free path of gas molecules. At low temperatures ($T < 350$ K), the amount of CO_2 formation is below the background partial pressure of CO_2 ; detection at this end therefore also becomes limited.

For large work-function changes ($\Delta\Phi$) caused by the adsorbates, a Kelvin probe can be used as a monitor during the reaction over a wide pressure range (atmospheric to UHV conditions). As will be shown in the next section, work-function change is proportional to the rate of reaction during the oscillations.

Surface-sensitive techniques that use photons, such as infrared spectroscopy, can also provide additional information on single-crystal surfaces during oscillations.

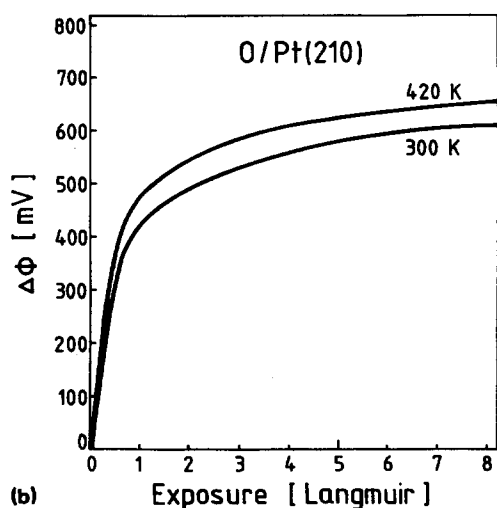
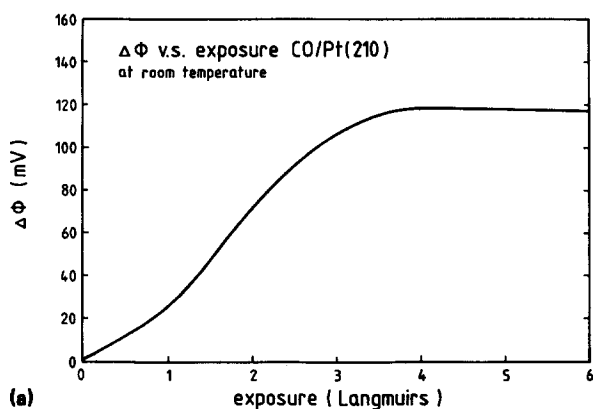


FIG. 2. (a) The work-function change ($\Delta\Phi$) of the Pt(210) surface as a function of CO exposure at room temperature. The exposure is given in langmuirs ($1 \text{ langmuir} = 1 \times 10^{-6} \text{ Torr s}$). (b) The work-function change ($\Delta\Phi$) of the Pt(210) surface as a function of oxygen exposure at 300 and 420 K.

III. RESULTS

A. Work-function changes caused by adsorbed CO and oxygen

Adsorption of CO on a clean Pt(210) causes a maximum work-function increase of 120 mV, which is proportional to the coverage of CO up to a coverage of 1.3 monolayers (ML) (maximum CO coverage, $\Theta_{\text{CO,max}} = 1.6 \text{ ML} \approx 1.0 \times 10^{15} \text{ molecules/cm}^2$) [Fig. 2(a)]. Adsorption of oxygen leads to a work-function increase as well. The $\Delta\Phi$ for an oxygen saturated surface [$\Theta_{\text{O}} = 0.8\text{--}1.0 \text{ ML}$, Fig. 2(b)] is 800 mV. Therefore, during the reaction, the work-function change is mostly representative of oxygen coverage. This means that the work-function change can in turn be taken as a reaction rate monitor (as will be shown later, the oxygen coverage is closely related to the reaction rate), as there is an oxygen coverage present on the surface which ranges from zero to $\sim 1.0 \text{ ML}$. We have controlled this behavior by simultaneously monitoring work-function changes and CO_2 partial pressures (i.e., mass spectrometer signals of 44 amu). The correlation between $\Delta\Phi$ and P_{CO_2} is documented in Fig. 3; $\Delta\Phi$ apparently follows the reaction rate in every detail. The $\Delta\Phi$ measurement has some advantages over a direct partial pressure measurement with a mass spectrometer, the main advantage being its compatibility with higher gas pressures ($P_{\text{O}_2} > 10^{-3} \text{ Torr}$), which are not easily accessible with a mass spectrometer. We have therefore mainly used $\Delta\Phi$ as a monitor for the reaction rate over a wide range of pressures.

B. Stationary measurements

Figure 4 shows the rate of reaction (P_{CO_2}) as a function of P_{CO} at constant sample temperature and oxygen pressure. This result was obtained in the following way: At constant P_{O_2} , the CO partial pressure was slowly increased and the

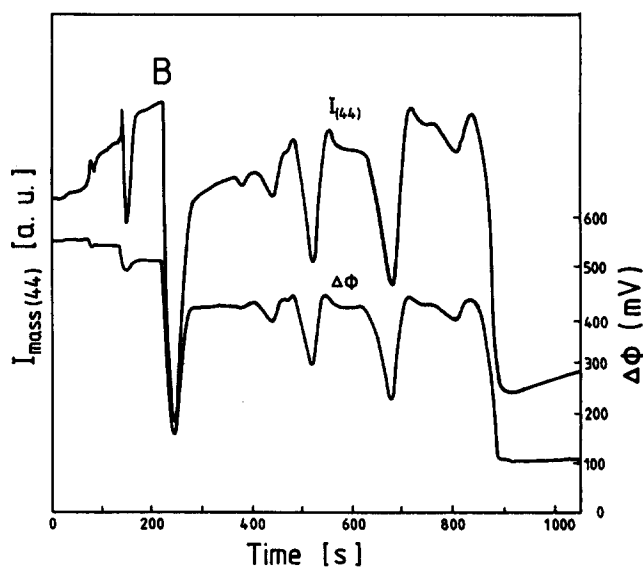


FIG. 3. Work-function change ($\Delta\Phi$) and the reaction rate followed simultaneously during the onset of oscillations. After point B (the transition point), $\Delta\Phi$ follows the reaction rate in every detail.

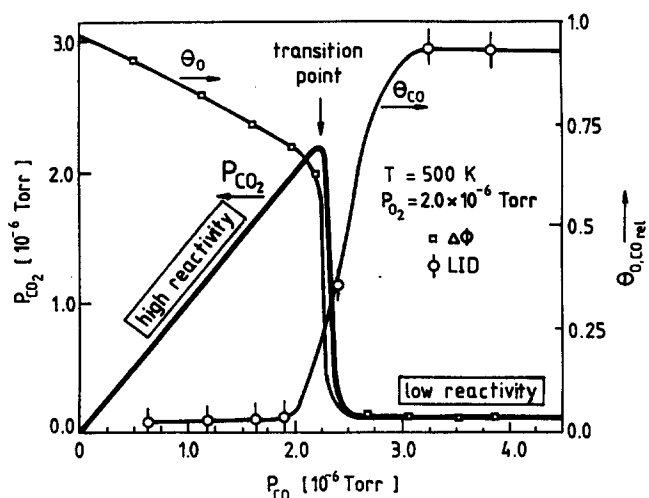


FIG. 4. The rate of reaction (P_{CO_2}) as a function of P_{CO} . The sample temperature and O_2 pressure were held constant (Ref. 20).

resulting work-function change monitored. Simultaneously, P_{CO_2} was determined mass spectrometrically, and oxygen coverage was measured using work-function changes. With the introduction of CO into the system, the reaction starts immediately. The rate of reaction increases linearly with P_{CO} up to the point of maximum reaction rate (transition point) where a slight increase in P_{CO} causes a partial or a complete poisoning of the surface with CO (low reactive region). The area between maximum and minimum reaction rate will be referred to as the *transition region*. Oscillations occur in the transition region from the high reaction rate to CO poisoning; they will be discussed further below. As shown in Fig. 4, the width of the transition region can be narrow (5%–10% of P_{CO}).

Figure 4 also shows the work-function change as a function of the CO partial pressure, P_{CO} , as the reaction proceeds. $\Delta\Phi$ initially decreases almost linearly with increasing P_{CO} from 800 meV (large oxygen coverage) to 600 meV. As will be shown later, this is in accordance with the removal of the oxygen β_1 binding state by reaction with CO (β_1 oxygen has a lower binding energy and a much smaller sticking probability than the β_2 oxygen which still persists on the surface at those P_{CO} values). Upon further increase of P_{CO} , however, $\Delta\Phi$ drops to values below 500 meV, thus indicating a steady depletion of surface oxygen and, at the same time, a rapid increase of the CO surface coverage. Any residual oxygen coverages (islands) are certainly very small in this range, since the work function has reached values as small as 70–30 meV. The dependence of the reaction rate on the CO partial pressure as monitored by CO_2 partial pressure can be divided into three regions: high reactive, transition, and low reactive, and it is the transition region which is responsible for kinetic oscillations or instabilities.

C. The procedure to start oscillations

At oxygen pressures above 10^{-4} Torr, the reaction can be brought into the oscillatory region. The following procedure was used: Once the sample was determined to be clean, the partial pressure of oxygen was set at a constant

level and was stabilized within 10–20 min. Then the sample temperature was adjusted to a constant value between 300–450 K. Thereafter, the CO was slowly introduced into the system in small steps. Intervals of several minutes were used between each adjustment to allow the reaction rate and the pressure of CO to stabilize.

The first observed rate oscillations on Pt(210) were obtained simply by setting CO and oxygen pressure to an appropriate level ($P_{\text{CO}} = 4.0 \times 10^{-5}$ Torr, $P_{\text{O}_2} = 4.0 \times 10^{-4}$ Torr) and by adjusting the sample temperature slowly, the reaction rate was brought into the oscillatory region. Figure 5 shows the start of oscillations on Pt(210) as monitored by work-function change ($\Delta\Phi$) measurements. The amplitude of oscillations decreased gradually, and after several cycles, the oscillations disappeared. They could be reestablished by readjusting one of the parameters (P_{CO} , P_{O_2} , T). However, the amplitude of these oscillations was smaller than that of the initial ones, and after a few cycles the oscillatory behavior ceased. The oscillations could be restarted only if the sample was cleaned with a combination of argon ion sputtering and annealing in oxygen.

Apparently, two processes affected the stability of oscillations: First, a drift in pressures of CO or O_2 which pushed the reaction to the outside of the oscillatory region; second, a gradual change in surface conditions caused by irreversible adsorption of impurities from the gas phase which could only be removed by sputtering of the surface. The first process (drift in externally set parameters) shows how sensitively the oscillatory region depends on P_{CO} , P_{O_2} , and T . The second process indicates a change in the adsorption, desorption, and reaction properties of the reactants (CO, O) caused by impurities and structural changes of the Pt surface. These factors and their influence on the reaction rate will be discussed later.

Figure 4, again, provides much evidence of dependence of the reaction rate on the CO partial pressure if P_{CO} is chosen close to the transition point from high to low reactivity. A detailed view can be obtained from Fig. 6. Near the reaction maximum (R_{max} , transition point), small increases in CO pressure resulted in a rapid drop of the reaction rate, followed by a recovery [Fig. 6(a)]. At this point even slight

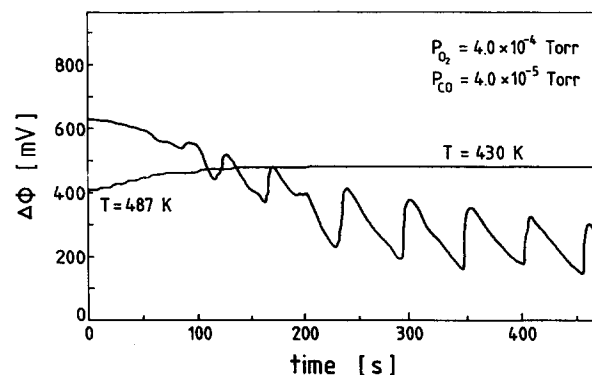


FIG. 5. Start of oscillation through temperature adjustment (smooth curve). Oscillations are monitored by the work-function change ($\Delta\Phi$) of the surface. Pressures of CO and oxygen were not regulated.

variation of CO pressure caused small and fast oscillations to appear (amplitude 30%–50% of R_{\max} , and period of 10–30 s). The oscillations grew gradually in amplitude and period and through several cycles of irregular oscillations, the amplitudes and periods reached a maximum limit until, finally, regular oscillations could self-sustain over several hours [Fig. 6(b)]. In Fig. 6(c) the amplitude of oscillations gradually decreases and the period increases due to the beginning of contamination of the system. After many cycles, oscillations disappear due to poisoning of the surface caused by the impurities which gradually adsorb from the gas phase.

D. Formation of regular oscillations

For low oxygen pressures ($P_{O_2} < 10^{-3}$ Torr), the commencement of regular oscillations is not immediate and can take as long as 30–60 min. Oscillations can start with the adjustment of one of the external parameters (P_{O_2} , P_{CO} , T) near the transition region either from a CO-covered surface or an oxygen-covered surface. Different situations are depicted in Fig. 7. Near the transition point, the “system” responds quickly to small increases in CO pressure and it can recover to the rate values near the constant background level

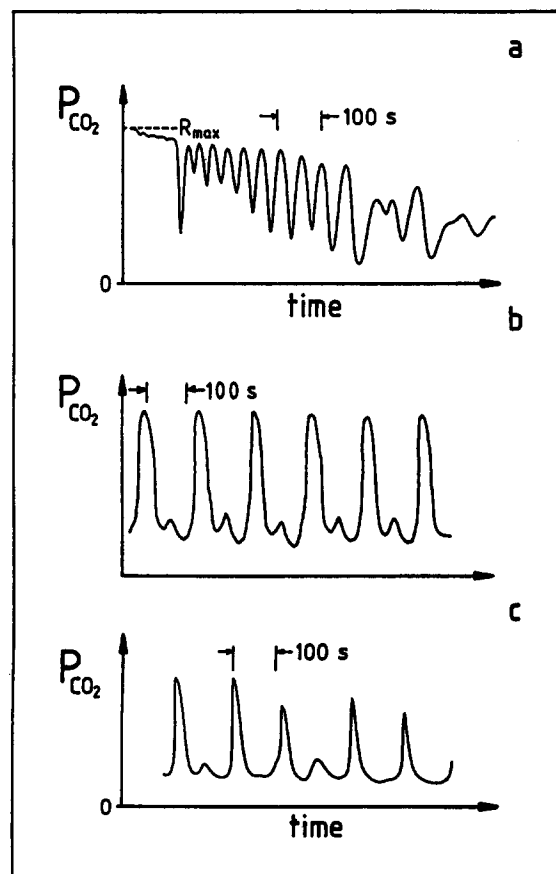


FIG. 6. Reaction-rate oscillations followed by the mass spectrometer at three different stages of evolution. Oscillations were started from the maximum reaction rate (R_{\max}) by small adjustment in CO pressure. (a) shows the beginning of the oscillations and (b) shows the commencement of regular oscillations; (c) shows the change in the oscillatory behavior caused by the adsorbed impurities from the gas phase.

[Fig. 7(a)]. At this stage, the reaction system behaves like a simple pendulum at rest. The pendulum is brought into motion by periodic forcing. If the interval between each forcing of the pendulum is long, the motion (oscillations) slowly decays. However, amplitude of oscillations in the experiment may increase beyond a certain level. The restoring force at this point seems to be sufficient (despite the damping force) to sustain the oscillations indefinitely. From the “high reactive side” (oxygen-covered system) as it is defined in Fig. 4, oscillations start with small amplitudes and periods; and as the nonreactive islands of CO grow in size, the reaction amplitude grows and the period increases. Indications are that islands of high CO coverage develop which continue growing in size. Figures 7(b) and 7(c) show that after several irregular cycles finally regular oscillations are established [Fig. 7(d)].

From the CO-covered (low-reactive) side, oscillations can start with higher frequency than from the oxygen (high-reactive) side. The amplitude of oscillations grows gradually and becomes limited at both ends and the period of oscillations increases (Fig. 8). Through several cycles of irregular oscillations, regular oscillatory behavior is sustained.

At low temperatures (around room temperature), oscillations start rather quickly with large amplitudes; however, after many cycles, the amplitude of oscillations gradually decreases and oscillations disappear [damped oscillator, Figs. 9(a) and 9(b)]. This is due to the narrowness of the

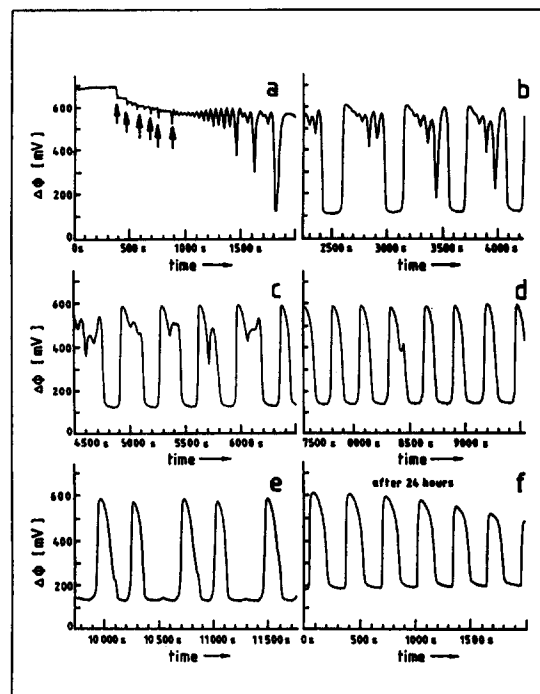


FIG. 7. Reaction-rate oscillations followed by work-function measurements. Oscillations are shown at different stages. Oscillations are started from the oxygen-covered side by small increases in CO pressures. Arrows indicate the point of CO pressure adjustments. (a), (b), and (c) show the process of self-organization. (d) shows regular oscillations and (e) the effect of structural change on the period of oscillations. (f) shows the effect of impurities on the oscillations by the removal of the liquid-nitrogen trap from the CO line. The oscillations were sustained over 24 h.

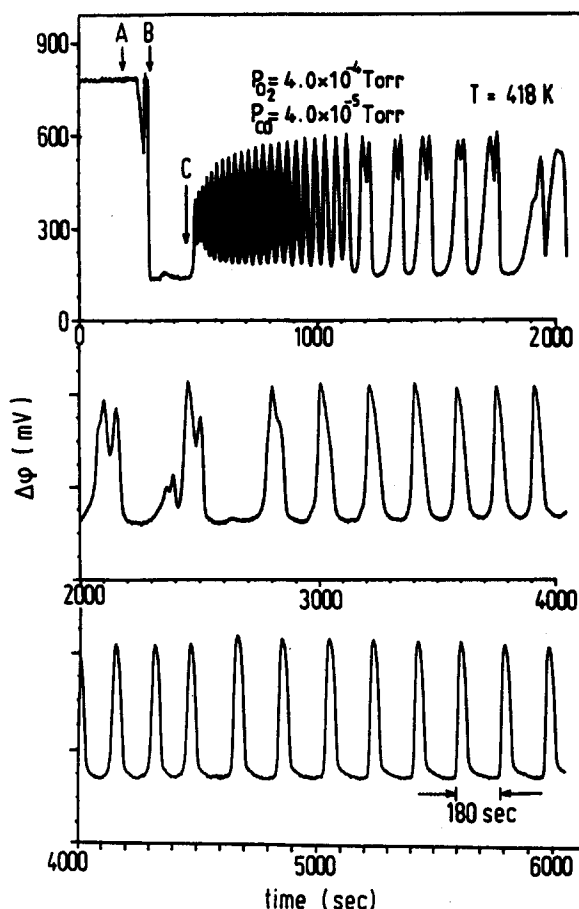


FIG. 8. Onset of oscillations and establishment of regular oscillations from a CO-covered surface. Oscillations were monitored through the $\Delta\Phi$ measurements.

existence region on one parameter and poor synchronization among various oscillatory regions.

At pressures above 10^{-3} Torr, the regular oscillations start rather quickly [Fig. 9(c)]. Due to the high rate of adsorption (high pressures), the *time* needed to reach a certain (critical) coverage of CO or oxygen is considerably reduced. The reactions occur more frequently due to a higher rate of CO and oxygen availability to the system. At these higher pressures ($P_{O_2} > 10^{-3}$), regular oscillations are established after a few cycles [Figs. 9(b) and 9(c)]. The measurement of oscillations could even be extended into the 10^{-2} Torr region [Figs. 9(b)–9(d)].

E. Mass spectrometric measurement

The differentially pumped mass spectrometer shown in Fig. 1(a) was calibrated to measure the turnover number (defined as product molecules per surface site per unit time) for the reaction. The reaction rate for the conditions shown in Fig. 4 gives a turnover number which is equivalent to the conversion of every impinging CO to CO_2 . The turnover was determined in the following manner: The reaction rate (P_{CO_2}) was calibrated for the complete conversion of one monolayer of CO (1 ML = 5.8×10^{14} CO molecules/cm²) to CO_2 from the titration of the CO-covered surface with oxygen. The P_{CO_2} signal which is proportional to the number

of CO_2 molecules formed per second was used to determine the number of CO_2 molecules formed during one oscillatory cycle. For large-amplitude oscillations shown in Fig. 7(d), the amount of CO_2 formation is larger than several hundred monolayers per cycle. This indicates that the oscillation mechanism is not simply an oxidation or reduction of a single adsorbed monolayer, but that there are two different reactive states that can either coexist (oscillations) or dominate (poisoning by adsorbate) over an appreciable period of time while the reaction is going on. The long period of oscillation shows the gradual conversion of reactivity from one state to another. Low reactivity is caused by the formation of dense CO islands, and high reactivity is associated with the presence of open oxygen islands. The conversion from low reactivity to high reactivity takes place at the boundary of the packed CO islands, and oscillations most likely indicate the growth and disappearance of CO islands (or reactive islands). This will be further clarified in Sec. IV.

Another type of measurement possible with the arrangement shown in Fig. 1(a) is the simultaneous measurement of partial pressure of CO and O_2 along with the rate of reaction (Fig. 10). The partial pressure changes of reactants are most sensitively measured near the surface by bringing the cone of the mass spectrometer close (0.5 mm) to the surface. However, the monitoring of partial pressures near the surface is more a measure of consumption rate than of the actual pressure change (caused by the reaction in the system). When the sample is placed more than a few centimeters away from the cone, the mass spectrometer indicates the partial pressures of reactants in the reaction chamber, whereas for small sample-to-cone distances of only a few millimeters, the cone is shielded by the sample and the mass spectrometer is more sensitive to the reflection or loss of CO from the surface. Therefore, under the condition of no reaction, CO and O_2 are reflected directly into the cone. When the reaction starts, parts of CO and O_2 are converted to CO_2 and the mass spectrometer shows a loss of their partial pressures, indication of a consumption of CO and O_2 .

No apparent phase shift could be seen between the reactants (P_{CO} , P_{O_2}) and the product. The stoichiometric balance for the reaction could also be obtained from these measurements ($CO + 1/2O_2 \rightarrow CO_2$), the increase in CO_2 signal is equivalent to the drop in CO pressure and twice the change in O_2 pressure (see Fig. 10). The fact that there are no phase shifts between the reactants and the product shows that reactivity of the surface changes through the formation of small islands and does not involve the formation and removal of complete reactive and nonreactive layers. Also, no reactive waves [which were reported to occur on Pt(100) (Ref. 6)] were observed by using the cone to scan different regions of the sample. In all cases no phase shift between different oscillatory regions on the sample was found.

F. Dependence of oscillations on P_{CO} , P_{O_2} , and T

The knowledge of conditions (existence region) for which the oscillatory behavior occurs can provide a direct way of differentiating among proposed mechanisms and can also provide a set of "realistic" parameters for model calculations or simulations.

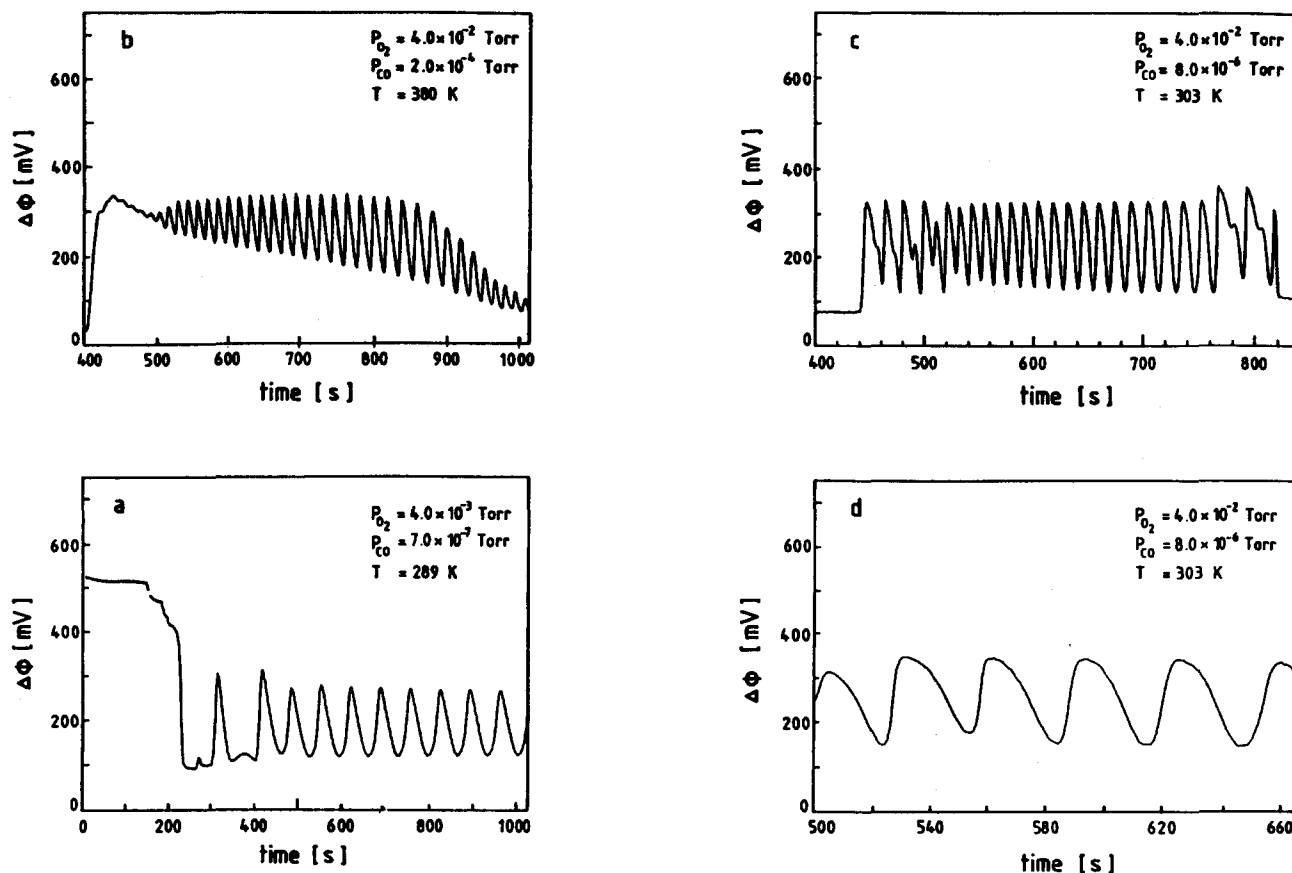


FIG. 9. Low-temperature oscillations at higher oxygen pressures monitored by $\Delta\Phi$. Oscillations were started by adjustment in CO pressure, (a)–(c). (d) shows room-temperature oscillations on an expanded time scale.

For *constant* values of oxygen pressure and sample temperature, oscillations occur over a narrow region of CO pressure [$\Delta P_{\text{CO}} \approx (0.1)P_{\text{CO}}$]. Figure 11 shows the oscillatory region at $P_{\text{O}_2} = 4.0 \times 10^{-4}$ Torr. Oscillations start at temperatures as low as 260 K with slow frequency and can be observed at temperatures as high as 470 K. At temperatures below 260 K, the low rate of oxygen dissociation and CO desorption limit the reaction probability; therefore, oscilla-

tions become hard to establish. At temperatures above 470 K, due to a high CO desorption rate, high coverages of CO cannot be reached anymore. The reaction therefore cannot be driven to a “CO-poisoned” state.

The width of the oscillatory region (ΔP or ΔT) is extremely narrow at low temperatures, and it expands somewhat as the temperature increases. It is important to note that the oscillatory region shown in Fig. 11 represents the transition region between two reactive states (low and high) (Fig. 4).

Oscillations have been observed at oxygen pressures as low as 1×10^{-4} Torr. Below this pressure, oscillations are difficult to establish on Pt(210). The low-pressure limit of oscillations is more dependent on oxygen pressure than on CO. Figure 11 shows that at 300 K the CO pressure is in the 10^{-7} Torr region. From Fig. 11, triples of values (P_{CO} , P_{O_2} , T_{osc}) can be obtained at which oscillations take place. Keeping one parameter constant (for example, P_{O_2}), $\log(P_{\text{CO}})$ can be plotted vs T^{-1} . Remarkably, for various oxygen pressures, the corresponding isosteric plots of the oscillatory region are linear with the same activation energy (Fig. 12). The shaded area shows the region for which the oscillations occur. For each oxygen pressure, the highest-temperature limit for oscillations is determined by strong desorption of the CO state that causes partial poisoning of the reaction. The dotted line, which shows this high-temperature limit,

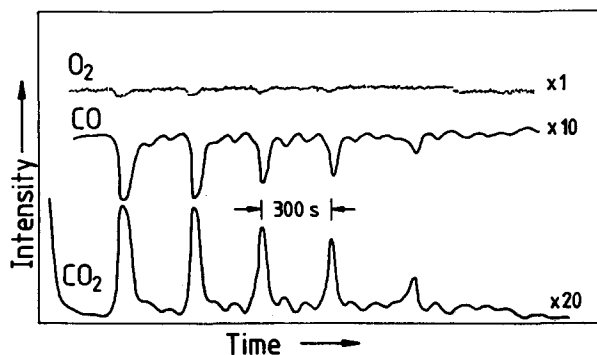


FIG. 10. A simultaneous monitoring of the partial pressure of reactants (P_{CO} , P_{O_2}) and the product (P_{CO_2}) near the surface. The increase in the CO_2 rate corresponds to a drop in partial pressures of CO and O_2 with no apparent phase shift.

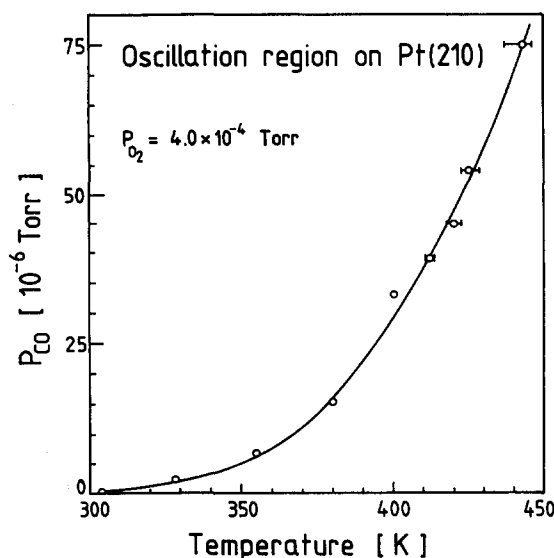


FIG. 11. The existence region for oscillations at constant oxygen pressure. The oscillatory region also represents the transition region between the two reactive regions.

gives an *activation* energy similar to the desorption of weakly bound CO (α) state [$E(\alpha)_{\text{CO}} = 25\text{--}30$ kcal/mol] (see Sec. IV).

From the set of data shown in Fig. 12, the oscillatory regions for constant CO pressures or sample temperature can be deduced as well. In a separate experiment, at a sample temperature of 420 K, the combination of CO and oxygen pressures that give rise to oscillations was determined. The results are shown in Fig. 13. The plot of $\log(P_{\text{CO}})$ vs. $\log(P_{\text{O}_2})$ yields a straight line with the following dependence:

$$P_{\text{CO}} = BP_{\text{O}_2}^{1/2}. \quad (1)$$

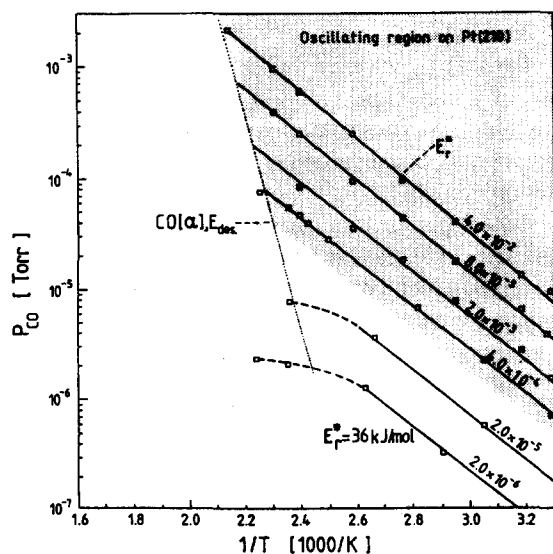


FIG. 12. "Isosteric" plot of the oscillatory region at constant oxygen pressures. The shaded area represents the region where oscillations appear; in the nonshaded region, only a rapid transition occurs (Ref. 20).

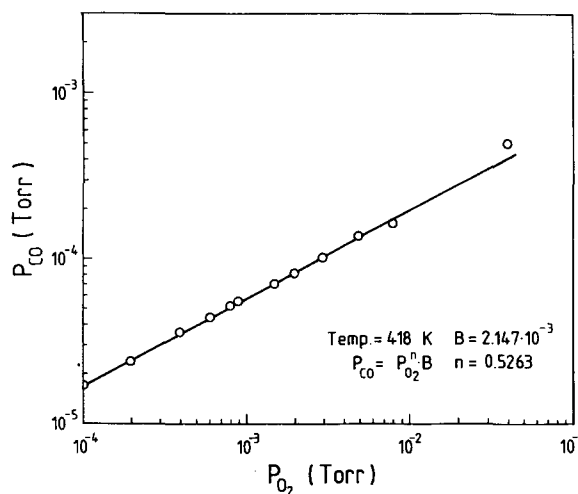


FIG. 13. Oscillatory region at constant sample temperature of 418 K. The parameters of Eq. (1) are noted in the figure.

IV. DISCUSSION

In this discussion we shall first investigate some phenomenological features of the oscillations, then comment on the physical conditions for their occurrence, and, finally, develop possible models and mechanisms that can lead to oscillating behavior.

A. Phenomenological aspects of rate oscillations on Pt(210)

Like any periodic functions, chemical oscillations are characterized by their shape, amplitude, and frequency. A detailed analysis of these properties is the key to any understanding of the origin of the oscillatory behavior, since the typical reaction sequence of ignition, reactivity increase, and gradual deactivation followed by restoration of activity is entirely reflected in the shape of one oscillatory cycle. On Pt(210) the observed oscillations are mostly regular with rather reproducible shape, amplitudes, and frequencies.

1. The shape of the oscillations

Figure 14 shows one full cycle of regular oscillations according to Fig. 8(d). This cycle shows the characteristics of a relaxation-type oscillator.^{2,10,11} Starting at point *A*, the reaction rate is at its lowest level and the reaction rate starts to increase slowly. At point *B*, the number of optimum sites for adsorption of oxygen has thus been enhanced, and the rate of reaction increases autocatalytically. At point *C*, the reaction rate approaches its maximum value, which is characterized by a high oxygen coverage. At this point, however, adsorption of CO becomes more competitive and gradually dominates, thereby removing the oxygen from the surface more and more until a near-saturated CO phase is reached (point *D*).

Under all conditions of temperature and pressure on Pt(210) the shape of oscillations is not sinusoidal but rather characterized by a sharp initial rise in reactivity and by a slower rate of recovery. Even at lower temperatures, the oscillations exhibit this shape, except that the ignition period is

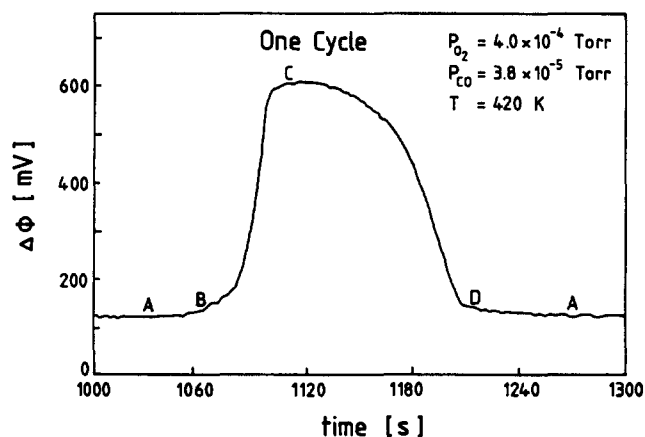


FIG. 14. A typical oscillatory cycle as monitored by the work-function change. The reactivity increases at point *A*; at point *B* the CO coverage drops below a critical level and allows rapid oxygen adsorption. At point *C*, oscillations reach their maximum amplitude and the reaction rate starts decreasing. At point *D* the surface becomes nearly covered with CO.

reduced and oscillations appear continuous and rather “harmonic” looking [Figs. 9(c) and 9(d)].

2. The amplitude and frequency of oscillations

The amplitude of oscillations on Pt(210) usually covers the entire region between the minimum and maximum rate of reaction. Near the boundaries of the existence region (cf. Fig. 4), the amplitude of oscillations becomes small and the oscillatory behavior is no longer regular. Inside the existence region and with extremely pure gases, the reactivity of the surface and hence the amplitude of oscillations remains constant even over a long period of measurement (over 24 h). Any structural changes caused by the adsorbates or small amounts of impurities do not seem to affect the amplitude [Fig. 7(e)]. However, the addition of larger amounts of impurities (mostly hydrocarbons) reduces the reactivity and hence the amplitude of the oscillations markedly [Fig. 7(f)].

As it is with any relaxation-type oscillator, the “time constant” of the system determines the frequency of oscillations.^{10,11} During the reaction, the surface interaction forces and the temperature control the time constant, thus leading to a rather complex dependence of the frequency on these parameters. Generally, the frequency of oscillations increases with temperature (at constant P_{O_2}). However, at higher temperatures, for some reason the ignition time increases and the frequency decreases. On Pt(210) the oscillations studied at lower pressures ($P_{O_2} < 10^{-3}$ Torr) show low frequencies (periods of several minutes and longer). In addition, structural changes caused by reaction or impurities increase the period of oscillations during a long-term experiment (more than several hours). At constant temperature, the frequency of oscillations increases with an increase in oxygen pressure. Figure 15 shows, based on the measurements displayed in Fig. 9, the frequency as a function of oxygen pressure. The frequency increases proportionally and to the square root of the oxygen pressure, and it is directly proportional to the CO pressure.

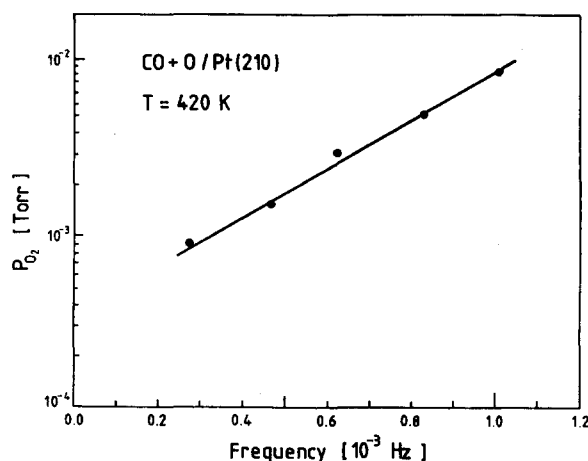


FIG. 15. The frequency of oscillations as a function of O_2 (and CO) pressure increases at a constant sample temperature. Note that for each oxygen pressure increase, CO pressure is also adjusted. The frequency of oscillations increases linearly with CO pressure, whereas the frequency of oscillations as a function of oxygen pressure follows a square-root law.

Although at high pressures ($P > 10^{-4}$ Torr) many processes such as adsorption can be very fast (a monolayer is achieved within a few seconds), due to the irreversible structural changes caused by the reactants or impurities, the dependence of this time constant on various parameters is difficult to determine. In contrast to Pt(110) and Pd(110) surfaces which show fast oscillations (frequencies up to 2 Hz) and period doublings and chaotic behavior,^{3,4} this phenomenon was not observed during regular oscillatory behavior on Pt(210) over the pressure range studied in this work.

B. The physical conditions for obtaining regular oscillations

The rate of reaction and the oscillatory behavior depend on two types of parameters. The first type will be referred to as *external parameters*. These are the pressures of CO and O_2 , sample temperature, and the flow rate (P_{CO} , P_{O_2} , T , and F). The second type of parameter is associated with the interaction of adsorbate with/on the surface, such as adsorption, desorption, diffusion, reaction, and other adsorbate-induced interactions. These parameters will be designated as *internal parameters*, because they reflect the chemical nature of the reaction system.

The external parameters can be varied and controlled rather accurately, whereas the internal parameters are structure sensitive and depend on the crystallographic orientation of the surface, long-range order and cleanliness of the surface. For a *clean* and *well-defined* Pt(210) surface, the occurrence of oscillations under a steady flow of reactants depends on a narrow range of external parameters (P_{CO} , P_{O_2} , T) as shown earlier in Sec. III (Fig. 11).

1. The dependence on “external” parameters (P_{CO} , P_{O_2} , T)

In Fig. 12, we have shown the correlation between P_{CO} and T at constant P_{O_2} . The plot of the pressure of one reactant (e.g., P_{CO}) vs reciprocal temperature with the partial

pressure of the other reactant being held constant represents sort of an isosteric plot. The fact that for most all of the plots shown in Fig. 12 a constant linear slope is obtained suggests that a phase equilibrium is indeed established for which a (modified) Clausius–Clapeyron formulation could be applied. The intriguing problem here is that we do not deal with the normal one-component phase equilibrium in which the chemical potentials of the gas phase and adsorbate phases, as well as their derivatives, are equal, which finally leads to the well-known evaluation of the isosteric heat of adsorption of this component at a particular surface coverage. Instead, we adjust conditions of *equal surface reactivity* of Pt(210) (namely, close to the transition region) by choosing P_{CO} , P_{O_2} , and T accordingly. From the foregoing, it is clear that the *surface reactivity* is almost entirely determined by the *number of empty sites* into which both CO and O₂ can adsorb and react. So, rather than keeping Θ_{CO} (or Θ_{O}) constant, we adjust our P and T values for *constant number of empty sites*, Θ_{empty} . The particle fluxes that are involved in the mass balance are (i) the adsorption of CO; (ii) the adsorption of O₂ with subsequent dissociation; (iii) the desorption of CO (desorption of oxygen can be neglected under the conditions chosen); and (iv) reaction to CO₂ and desorptive removal of the CO₂ formed.

The apparent isosteric “phase transition” enthalpy involved can contain either a (T -independent) activation energy for reaction between adjacent CO and O on the surface or, more likely, the isosteric heat of adsorption of the reaction product, CO₂. The magnitude of the experimentally determined heat, viz., 8.5 ± 1 kcal/mol, could point in this direction. Equation (1) showed a square dependence between P_{CO} and P_{O_2} at constant T . This condition arises from the fact that in or near the transition region the surface is nearly covered with CO, or CO and oxygen, and the number of empty sites is *quite low* ($\Theta_{\text{empty}} = 1 - \Theta_{\text{CO}} - \Theta_{\text{O}}$). As mentioned before, adsorption and reaction can only take place in the empty sites, and the reaction rate is determined by either the adsorption probability of reactants in these sites and/or their reaction probability. Assuming conditions right before the transition, under steady-state conditions (constant coverages), which would imply the adsorption rate for either species is equal to the rate of reaction:

$$\frac{S_{\text{CO}} P_{\text{CO}} \Theta_{\text{empty}}}{(2\pi m_{\text{CO}} kT)^{1/2}} = \frac{2S_{\text{O}} P_{\text{O}_2} \Theta_{\text{empty}}^2}{(2\pi m_{\text{O}_2} kT)^{1/2}} = R_{\text{CO}_2}, \quad (2)$$

where S_{O_2} and S_{CO} signify the initial sticking probability of O₂ and CO, respectively. Adsorption of CO is proportional to the number of empty sites (Θ_{empty}), whereas oxygen adsorption requires two sites and is proportional to $(\Theta_{\text{empty}})^2$. Solving for Θ_{empty} , P_{CO} becomes

$$P_{\text{CO}} = \frac{[2S_{\text{O}} R_{\text{CO}_2} m_{\text{CO}} (2\pi kT / m_{\text{O}_2})^{1/2}]^{1/2} P_{\text{O}_2}^{1/2}}{S_{\text{CO}}} \quad (3)$$

in agreement with the relation (1) found empirically:

$$P_{\text{CO}} = BP_{\text{O}_2}^{1/2}$$

and

$$B = \frac{[2S_{\text{O}} R_{\text{CO}_2} m_{\text{CO}} (2\pi kT / m_{\text{O}_2})^{1/2}]^{1/2}}{S_{\text{CO}}} \quad (4)$$

At higher temperatures, $T > 450$ K, the CO desorption becomes stronger; therefore, the exponent of relation (1) increases to compensate for CO desorption.

2. The dependence on “internal” parameters

During the course of this study, two different Pt(210) single crystals were used. These crystals were prepared from separate rods purchased from different suppliers. Both crystals showed identical LEED structure characteristic of a 1×1 surface with low background and sharp spots and exhibited identical behavior with respect to their surface interactions with oxygen and CO. The Auger electron spectroscopy (AES) on one crystal showed a small amount of oxygen impurity (slightly above the noise level). This “oxygen” or “oxide” impurity could not be removed even after extensive cleaning cycles and is possibly associated with the presence of silicon or calcium, both of which are frequently observed on platinum surfaces.¹² Interestingly, however, the presence of this impurity did not affect the adsorbate interactions and oscillations. A lower oxygen work function (~ 50 mV) was observed only on the crystal with oxide impurity.

The purity of gases, especially of CO, was crucial in maintaining a clean surface during the reaction. Open platinum surfaces are extremely active in dissociating hydrocarbons and hydrogen gas. Eiswirth, Schwankner, and Ertl have reported similar observations with respect to the purity of gases and have shown that the presence of hydrocarbons and hydrogen stops the oscillatory behavior on Pt(100).¹³ Figure 6 showed that the amplitude and frequency of regular oscillations decrease and oscillations disappear a few hours after their commencement. In this experiment no liquid-nitrogen trap was used to further purify CO. Impurities in this case also affected the *catalytic activity* and the *maximum reaction rate*. The oscillations could be established only after sputtering and annealing the sample. In another experiment the gases were purified over a LN₂ trap. Regular oscillations were established after 1 h and large amplitudes (covering the region between minimum and maximum reaction rate) were observed with periods of 3 min (Figs. 7 and 8). Oscillations were sustained over 24 h without any readjustment of parameters. The amplitude (catalytic activity) remained constant, but the period increased to 10 and finally to 15 min. By removing the LN₂ trap from the gas line, the amplitude of oscillations started to decrease and oscillations slowly decayed [Fig. 9(f)].

The above experiments show that by using very high-purity gases, the catalytic activity can remain constant; however, certain “structural changes” cause an increase in the period of oscillations. The same conclusion was reached by Ladas, Imbihl, and Ertl in their study of Pt(110) under reaction conditions.¹⁴ They reported formation of facets during the reaction at high CO and oxygen pressures. The Pt(210) surface did not show any apparent signs of facetting, only an increase in the LEED background was observed after the reaction. The structural transformation caused by reaction or a slight amount of impurities can reduce the domain size

of (210) islands or (as suggested by Imbihl, Sander, and Ertl¹⁵) create new adsorption states for CO or oxygen. Therefore, the presence of different crystallographic regions on the slightly faceted surface gives rise to a different reaction rate than that found on "pure (210) domains" and disturb the "single-phase" oscillatory behavior.

It is important to note that on both Pt(210) surfaces the same set of parameters (P_{CO} , P_{O_2} , T) gave rise to oscillations (Figs. 6 and 8), and that no noticeable change in the width of parameters was observed due to poisoning by impurities or structural changes. In other words, both Pt(210) surfaces investigated yielded identical existence regions for oscillations.

C. The origin of the oscillations

For the macroscopic observability of the oscillations, it is not sufficient that they occur somewhere locally on the surface; rather, the oscillating regions must be in phase on the entire surface. *Therefore, an appropriate physical explanation of the oscillations implies two aspects: (i) the origin of the local oscillation and (ii) the synchronization between various oscillators.*

1. Adsorption of CO and O₂ on Pt(210)

The difference in the existence regions and the oscillatory behavior among the various surfaces can be traced to their interaction with CO and oxygen. In order to understand the different oscillatory behavior and existence regions, the adsorption, desorption, and reaction of CO and oxygen have been measured and characterized on Pt(210) under UHV conditions. Using the adsorbate interactions with the surface, the conditions for instabilities and oscillations at higher pressures can be explained.

Pt(210) is an open surface with a hexagonal structure and only one symmetry plane along the $[1\bar{2}0]$ direction. The LEED pattern from the clean surface exhibits a 1×1 structure with no extra spots which are otherwise commonly observed with reconstructed Pt(110) and (100) surfaces.

The LEED pattern of adsorbed CO on the surface initially exhibits a 1×1 , and finally, a 2×1 structure. These structures have also been observed for CO on Pd(210).^{16,17} The thermal desorption of CO from the surface indicates two different binding states, β and α . The β is the strongly bound state with a first-order desorption kinetics and a binding energy of 40 kcal/mol. It reaches saturation at a CO coverage of 0.8–1.0 ML. The α is the weakly bound state with a second-order desorption kinetics and its binding energy (20–30 kcal/mol) decreases with an increase in the coverage. The formation of CO structures is accompanied by a large variation in the intensity of the substrate LEED spots. This indicates that there might be a relaxation or reconstruction of the substrate caused by CO adsorption.

Oxygen adsorption on this surface is similar to other open surfaces of platinum. Oxygen adsorbs into two different binding states, β_1 and β_2 . β_2 is the strongly bound state which has a very high sticking probability ($S_{\beta_2} = 0.6$) and the β_1 state is the weakly bound state with a very low sticking probability ($\beta_1 < 0.01$).¹⁶

2. The conditions for surface oscillations

As mentioned before, the reaction of CO with oxygen on platinum group metals follows the Langmuir–Hinshelwood (L-H) process ($\text{CO}_{\text{ad}} + \text{O}_{\text{ad}} \rightarrow \text{CO}_{2(\text{g})}$). For temperatures below 600 K oxygen desorption is negligible and coverage of CO is a sensitive function of sample temperature and P_{CO} . Both experimental and theoretical simulation of the L-H process (using either rate equations^{2,18} or a lattice-gas-type model^{19,20}) show three distinct reactive regions. In Fig. 4, for low P_{CO} , the surface is in the high reactive region and is covered mostly with oxygen (CO coverage is very low). Near the transition point, CO coverage increases gradually and the reaction rate reaches its maximum value at which the coverages of CO and oxygen are equal or comparable. At this point the number of the empty sites available for the reaction also is at its maximum. A slight increase in CO pressure at the transition point causes an oversupply of CO to the surface which in turn causes the rapid formation of large CO islands and blocking of the empty sites available for oxygen adsorption and reaction.

The sharp transition arises from the competitive adsorption between CO and oxygen. The occurrence of transition from the high reactive to low reactive region or vice versa can be enhanced by the interaction of the adsorbate on the surface. The effect of some of these processes such as different adsorption probabilities for reactants, desorption, diffusion, and adsorbate-induced phase transitions have been considered in a recent simulation study of this reaction.²⁰ From the experimental data on Pt(210) the following can be concluded about the conditions under which oscillations are found:

(i) *Oscillations occur in the transition region between the two reactive states.* In all cases, oscillations are observed in the transition region. Although sharp transitions occur on Pt(210) during the reaction experiments at pressures below 10^{-5} Torr or at temperatures above 500 K, oscillations are observed only at *higher pressures and lower sample temperatures* (see the existence region of oscillations, Fig. 12). Reaction experiments on Pt(111) also show sharp transitions; however, no oscillations had been observed for this surface under conditions similar to those for oscillations on Pt(100), Pt(110), and Pt(210) surfaces.^{6–8}

(ii) *Oscillations require rather high oxygen pressures to occur.* For O₂ pressures below 10^{-5} Torr, oscillatory behavior is not observed on Pt(210) [and is slow and unstable on other surfaces such as (110) (Ref. 7) and (100) (Ref. 13)]. However, during the oscillations the CO pressure can be as low as 10^{-7} Torr. This indicates that under reaction conditions, at low oxygen pressures ($P_{\text{O}_2} < 10^{-5}$ Torr) *high oxygen coverages cannot form within a comparable time scale*, in contrast to *high CO coverages*. The reason is that O₂ sticks less effectively than CO and reacts rapidly with coadsorbed CO. Also, the formation of a critical oxygen coverage is needed before the reaction rate becomes limited at the high reactive region.

(iii) *Oscillations occur at temperatures where the desorption rate of CO is low.* During the oscillations, the formation of high CO coverage is necessary to cause the reaction transition and the related drop in the reaction rate. On the

other hand, the back-transition (feedback or recovery) to the high reactive state from nearly CO-poisoned surface can only occur if there is an increase in the reaction probability caused by an increase in the oxygen sticking probability due to low oxygen coverage or presence of the newly formed CO states.

(iv) *At constant sample temperatures, the frequency of oscillations increases, with an increase in both CO and oxygen pressures.* This is in accordance with the rapid formation of either reactive states. The frequency of oscillations is mainly governed by the adsorption rate of CO and oxygen, and the desorption rate of CO. Any time scale provided by the diffusion of CO, or time necessary for the occurrence of phase transition on domain sizes of less than a few hundred angstroms, would be much smaller than the observed period for the oscillations.

(v) *Rather high rate of flow is necessary to start and sustain oscillations.* Experiments with very low flow rates (pumping speed of 5 liters/s or less) in the oscillating region show only rapid transition and large hysteresis and no oscillations. As was shown earlier in the Sec. III E, for the available pumping speed in the reactor chamber of 50–100 liters/s, the consumption rate (the sample selective pumping rate of mostly CO) due to reaction can be significant (5%–10% of the total pumping rate of the system). Therefore, the start of reaction from the CO-covered side (low reactive) is accompanied by a drop in the CO pressure due to CO consumption (Fig. 10). Its rate of recovery in the gas phase depends on the flow rate of CO. This provides the necessary pressure change for the modulation of CO coverage. If the flow rate is too slow or too fast, the necessary delay time (phase shift) which the system needs does not match the time constant of the surface inertia (determined by the size, adsorption, desorption, and reaction rate of reactants).

3. The synchronization process

As to the origin of the synchronization process on the surface, an analogy can be made to an unmixed Belousov–Zhabotinsky reaction where small oscillations can nucleate in an unmixed reactor and periodic oscillations are observed only when the reactor is mixed.¹⁰ On Pt(210) during the start of the oscillations, several processes can play a role in synchronizing various oscillating regions. First, during the production of CO₂ the sample behaves (mainly for CO) like a selective pump. Therefore, an initial drop in the gas pressure of CO results when the rate of reaction increases (P_{O_2} is usually 10 or 100 times larger than P_{CO} and the corresponding drop in oxygen pressure is by far lower). This drop causes a shift in the CO adsorption–desorption equilibrium and hence reduces primarily the CO coverage of islands with high coverage to lower values. While these islands had been in the CO poisoned state, this process can immediately make most islands reactive, since the CO gas-phase pressure is felt by the whole single-crystal surface simultaneously. A similar mechanism for the synchronization on Pt(110) and on polycrystalline surfaces has been suggested recently by Eiswirth *et al.*⁷ and Tsai, Maple, and Herz.²¹ Recent experiments on two separated Pd(110) samples under vacuum conditions also show clearly that the coupling between the two surfaces

takes place entirely via the pressure variation of CO.²²

The second process that can affect the size of the islands is concerned with the strength and range of mutual adsorbate interactions which can also be responsible for certain adsorbate phases or surface reconstruction phenomena. The process of self-organization and the “in-phase” oscillation greatly influence the shape and the frequency of the oscillations.

There is no evidence for the formation of reactive waves across the surface on Pt(210). This indicates that under isothermal conditions the mechanism of synchronization on large or separated (210) regions must be through the gas phase. Regardless of the process which provides the feedback, a high saturated CO surface (α state) is a very sensitive function of pressure (at constant T). Under this condition, the surface lends itself well to modulation due to changes in CO pressure. Also, any change in P_{CO} in the system is reflected immediately throughout the reaction chamber (at low pressures $P < 10^{-2}$ Torr, the mean free paths of the molecules are on the order of the system dimensions, and the rather high molecular speed provides a well-mixed reaction system, in a time scale much smaller than the period of an oscillation). Therefore, the CO pressure change provides a mechanism for synchronization of various oscillatory regions.

Another important conclusion is that the high-temperature limit of oscillating region coincides with the complete desorption of the weakly bound CO, α state. This indicates that conditions (iii) and (iv) mentioned in Sec. IV C 2 cannot be satisfied for the nonoscillating region.

D. Mechanism of oscillations

Simulation of the basic L-H process using rate equations or a lattice-gas model does not give rise to an oscillatory reaction rate.^{2,18,20,23} However, it predicts a region of instability or a rapid transition between the two reactive states. The rapid transition provides a sufficient gain when coupled to other nonlinear processes on the surface; oscillations in the reaction rate can occur.

In order to start oscillations, the formation of a critical oxygen coverage in the high reactive region initiates the transition; the feedback from the low reactive region occurs by the removal of the high oxygen coverage. The poisoning and recovery of the reaction needs to take place in a similar time scale, in addition, a slight phase shift (delay) is needed to separate the two processes. When the two processes occur on different time scales or are in phase, an intermediate steady state can occur or the reaction settles in either reactive states.

On Pt(100), due to an activated adsorbate-induced reconstruction with an appreciable mass transfer involved in the process, a large hysteresis is observed with either reactants alone, which may be sufficient to provide the necessary delay. On Pt(210) and Pt(110) surfaces no apparent hysteresis is observed to occur during the adsorption–desorption of reactants. However, the unreacted species or empty sites on the surface and a limited flow rate can provide the necessary delay.

Recent experiments on Pd(110) surface clearly show

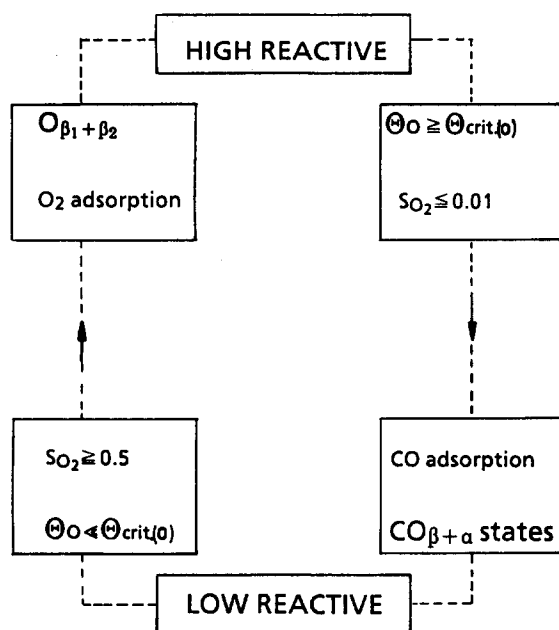


FIG. 16. Proposed cycle for the oscillatory mechanism on Pt(210).

the influence of the flow rate and its effect in the oscillatory behavior.²²

Based on the experimental observations on Pt(210), an oscillatory cycle (shown in Fig. 16) can be suggested as follows.

(a) The formation of strongly bound O_{β_2} state in the high reactive region causes a drop in sticking probability of oxygen. This, in turn, causes an increase in the effectivity of CO adsorption, and hence leads finally to a high CO coverage.

(b) Interestingly, the recovery of the system is also initiated by the depletion of high oxygen surface coverage, because the decrease of Θ_O below a critical value makes the sticking coefficient of O_2 rise again. This is aided by slight CO desorption from its α state and by a drop in P_{CO} which is converted to CO_2 by the ongoing reaction. The apparent drop in the CO pressure is clearly evident from Fig. 10. The simulation of the above cycle using a cellular automata technique shows similar oscillatory behavior as experimentally observed on single-crystal surfaces.²³

The above model is different from the one suggested by Ertl and co-workers for Pt(100),⁶ which requires a reconstruction of the substrate by CO and an increase in the sticking probability of O_2 . There, the delay is caused by the hysteresis of the surface.

E. Comparison with previous reports on oscillation

Studies of oscillating reactions in catalytic oxidation of CO can be divided into two groups. The first group includes work done on polycrystalline surfaces (supported catalysts, wires, ribbons) performed at relatively high pressures (1–1000 mbar). The second group consists of studies of oscillatory behavior on single-crystal surfaces under high-vacuum (HV) and UHV conditions.

1. High-pressure oscillations

Razoń and Schmitz have recently reviewed various aspects of experimental and theoretical studies done on *high-pressure oscillations*.² The oscillations under high pressures are mostly *nonisothermal* (due to exothermicity of the reaction); and in some cases, the change in sample temperature is used to monitor the oscillations. The amplitudes are usually “small” (5%–30% of the total conversion rate) and are superimposed on top of a steady rate. Most oscillations have complex forms and the periods of oscillations are usually of the order of minutes or longer. The anisotropy of the sample and the condition of the flow at high pressures affect the reaction conditions considerably.

There are several factors that complicate these studies; for example, the experimental conditions are different for most of the reported works. In addition, the catalyst preparation and the reactor type vary in most cases, and a direct comparison of results is not possible. Another complication arises from the fact that there are different crystallographic orientations on polycrystalline samples. The CO-oxidation reaction is structure sensitive, especially on platinum surfaces.⁵ Therefore, different reactive phases (multiplicities) can exist on the polycrystalline surfaces. And, finally, it is difficult to monitor the adsorption–desorption properties of the catalyst surface with respect to CO or oxygen, before or after the reaction.

The above limitations make the characterization of the oscillatory behavior quite difficult. However, despite the enormous experimental difficulties, a number of excellent studies have characterized the effect of various parameters on oscillatory behavior and on the existence region of oscillations.^{18,24,25}

2. Low-pressure oscillations

Since Ertl and co-workers observed rate oscillations on polycrystalline platinum at ultrahigh vacuum conditions (10^{-4} Torr), a number of single-crystal surfaces have shown oscillations in their rate of reaction with CO. These surfaces include platinum (100), (111) stepped, (110), (210), and, most recently, Pd(110). It is important to make a clear distinction between the oscillatory behaviors observed at low pressures (10^{-2} – 10^{-6} Torr) and at high pressures (1–1000 Torr). The oscillations under low pressures are *isothermal*. At UHV and HV conditions, the sample temperature can be held constant to within 0.05 K. The resulting heat of reaction at these conditions is too small to raise the sample temperature during the reaction.⁷ On Pt(210) oscillations can take place at temperatures lower than 300 K, where the reaction rate and the heat of reaction are 2–3 orders of magnitude lower than at temperatures above $T = 420$ K. And, finally, no detectable temperature gradient would exist across the sample.⁷ At room temperature, the oscillations were observed without the use of a temperature regulator or heating current. The sample temperature was in equilibrium with the holder and well insulated inside the vacuum system.

Remarkably, each of the single crystals noted above shows a slightly different oscillatory behavior, especially

with respect to the conditions (P_{CO} , P_{O_2} , T) under which oscillations occur.

Oscillations on the Pt(100) surface were often irregular; and for constant CO and oxygen pressure they occur over a wide range of temperatures ($\Delta T = 50$ K), whereas oscillations on Pt(110) and (210) and Pd(110) exist only over a narrow range of temperature (5–10 K) and are quite regular.^{3,4,8} The occurrence of the oscillations on these surfaces satisfies the same conditions as in Secs. IV C 2 and IV C 3 and exhibit similar oscillatory regions.

V. CONCLUSION

Oxidation of CO on the Pt(210) surface shows reproducible oscillatory behavior under constant flow of reactants and sample temperature. The occurrence of oscillations can be traced and correlated to the adsorption, desorption, and phase transition properties of the reactants.

The reaction between CO and oxygen, under sufficiently high pressure of reactants, can drive the phase transitions on the surface and in turn cause oscillations.

The temperature, pressure dependences, and the activation energy determined from the oscillatory regions provide additional information on the kinetics of the reaction and the condition of instabilities.

A major difficulty in the study of these phenomena is the direct monitoring of the surface, adsorbates, and phase transitions under dynamical conditions at higher pressures. A possible facetting of the platinum surface under higher pressures can cause additional complications for the characteri-

zation of the time constant of the system and frequency of oscillations.

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