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Oscillatory Oxidation of H_2 over a Pt Catalyst

P. K. TSAI AND M. B. MAPLE

Department of Physics and Institute for Pure and Applied Physical Sciences, University of California, San Diego, La Jolla, California 92093

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Oscillatory oxidation of hydrogen over a polycrystalline platinum wire has been systematically studied near atmospheric pressure in a clean flow reactor. Oscillations in the temperature of the catalyst and the composition of the exit gas stream were observed for inlet gas compositions, $1.5\% \leq P_{H_2}/P_{O_2} \leq 15\%$, where P_{H_2} and P_{O_2} are the respective partial pressures of hydrogen and oxygen in the gas stream. The oscillations occurred for gas temperatures from 106 to 190°C. Waveforms, which had up to several peaks per cycle, varied in shape from the relaxation type to nearly sinusoidal. Their behavior as a function of time, gas flow rate, and gas temperature is characterized for different ranges of P_{H_2}/P_{O_2}. Changes in oscillatory behavior were seen after the catalyst was reetched.

INTRODUCTION

As part of a continuing study of oscillations in the rates of chemical reactions between gases over transition metal catalysts, we report our recent observations of the oscillatory oxidation of hydrogen over a polycrystalline Pt catalyst. To our knowledge, these experiments are the first in which the waveforms and oscillatory characteristics were investigated while the gas temperature and H_2–O_2 gas composition were varied systematically.

Oscillatory behavior in oxidation reactions occurring over transition metal catalysts has been summarized in review articles (*1*, *2*). The most widely studied of these systems has been the oxidation of CO over Pt (*3–13*):

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2$$

From the standpoint of kinetics, this is expected to be the simplest oscillatory reaction because of the molecular chemisorption of CO on Pt. Nonetheless, there has been considerable variety in the oscillations reported. Earlier work in our laboratory involved a systematic study of oscillations in the oxidation of CO over Pt (*5*), Pd (*14*), and Ir (*14*) catalysts. Reproducible oscillations were obtained, and certain oscillatory characteristics as a function of the temperature and composition of the gas stream were established. Subsequently, a model which accounts successfully for the waveforms and their characteristics was developed (*15*).

Oscillations in the oxidation of hydrogen:

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O$$

have been observed over Ni (*16–20*), Pd (*21*), and Pt (*3, 4, 16, 22–24*) catalysts. Although this reaction has the same stoichiometry as CO oxidation, the kinetics is complicated by the dissociation of the hydrogen molecule on the metallic surfaces. In addition, evidence from studies on single crystal samples of Ni (*25*), Pd (*25, 26*), and Pt (*25*), shows that hydrogen atoms, unlike CO molecules, can occupy sites between the first and second surface layers. Fewer reports have been published on oscillations involving hydrogen and a wide variety of waveforms has been observed even during the course of one experiment (*22*).

Below we present the results of a systematic study of H_2–O_2 oscillations. We include a discussion of the initiation and evolution of the waveforms. The region of

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experimental parameters over which oscillations occurred is shown.

METHODS

Experiments were carried out at atmospheric pressure in a flow reactor described in Ref. (5). Since the H_2–O_2 reaction is exothermic, we were able to monitor the reaction rate by measuring the increase in temperature of the catalyst. A flow-through leak valve in the exhaust line enabled us to analyze the product gas stream with a mass spectrometer.

The catalyst, which had been used in Ref. (5), was a single loop made by spot-welding together the ends of a polycrystalline Pt wire (Matthey-Bishop, 99.999% purity) with a length of 2.5 cm and a diameter of 0.05 cm. Before oscillations were initiated, the wire loop was etched in hot acid (3 HCl : 1 HNO_3). Two Chromel–Alumel thermocouples were spot-welded to the loop so that we could monitor the catalyst temperature, T_c. A thermocouple located near the catalyst was connected to a programmable power supply and was used to regulate the gas temperature, T_g. The oven controller was frequently used in a mode in which the temperature varied linearly as a function of time, with typical scan rates of approximately 5°C per hour.

We attempted to keep the experimental system as clean as possible. Electropolished stainless steel tubing was used for all gas handling and the use of elastomer gaskets was limited to two ungreased Viton "O" rings at the ends of the mullite flow reactor tube.

Gases were from Matheson: H_2, ultrahigh purity (99.999%); O_2, ultrahigh purity (99.95%); and He, Matheson grade (99.9999%). The hydrogen gas was passed through a Matheson hydrogen purifier; the oxygen and helium were used without additional purification. Solenoid valves and electronic mass flowmeters were used to regulate gas flow rates to a precision of 0.3% or better. Generally, an oxygen flow rate between 10 and 30 cm^3/min was selected and the hydrogen flow rate was adjusted to change the H_2–O_2 gas composition. Helium, employed as an inert diluent, was usually used at flow rates comparable to the O_2 flow rate.

RESULTS

Initiation of Oscillations

We were able to obtain oscillations over the freshly etched Pt wire loop by slowly increasing the gas temperature until anomalies developed in the reaction rate. The gas mixture used to initiate the oscillations contained helium and had a hydrogen–oxygen ratio of 4% by volume, which was in the intermediate range of oscillatory gas compositions studied. The oscillations began readily once an appropriate gas temperature was attained. The shape of the waveforms evolved substantially in the first 10 h; the period showed much less variation.

Once oscillations had been obtained, they could be stopped and restarted. The waveforms were extinguished when hydrogen was eliminated from the gas stream or when the gas temperature or flow conditions were changed abruptly. When we reestablished external conditions conducive to oscillations, they generally developed in less than half an hour. After we found that alternately oxidizing and reducing the catalyst several times at 270°C delayed the development of the waveforms, we did not use an oxidation–reduction procedure to pretreat the catalyst surface before restarting the oscillations under new operating conditions.

Figure 1 shows waveforms that developed after having been extinguished due to a variety of changes in external conditions, given in the figure caption. These oscillations occurred under the flow rates: H_2, 1.200 cm^3/min; O_2, 30.0 cm^3/min; and He, 35.0 cm^3/min. In all cases, the basic shape of the oscillations emerged within a few cycles, but some time was required before the amplitude and period stabilized. In general, the periods and amplitudes increased as a function of time. At higher gas tempera-

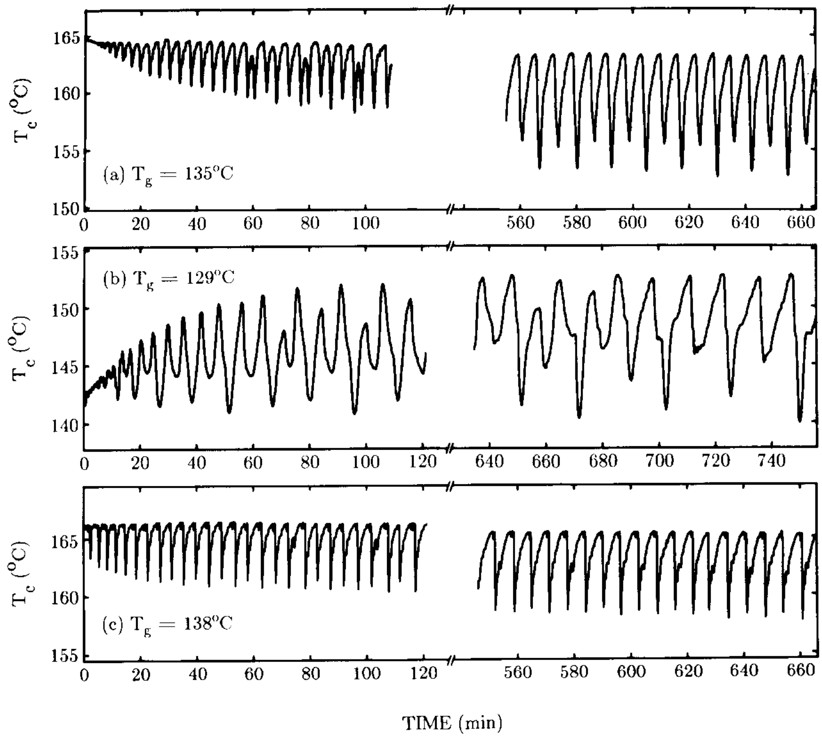

FIG. 1. Initiation and stabilization of oscillations for P_{H_2}/P_{O_2} = 4.00%. Time scales reflect elapsed time under constant gas temperature and stable flow conditions. Identical flow rates were used: H_2, 1.200 cm³/min; O_2, 30.0 cm³/min; and He, 35.0 cm³/min. (a)–(b) Oscillations recorded near the beginning of our experiments: (a) T_g = 135°C; at t = 0, the H_2 and O_2 flow rates were increased from their former values of 0.800 and 20.0 cm³/min, respectively. (b) At t = 0, T_g was decreased from 135 to 129°C. (c) Oscillations recorded near the end of the run. T_g = 138°C; at t = 0, the H_2 flow rate was decreased from 1.500 cm³/min.

tures, the maximum reaction rate attained in each cycle reached a constant value quickly while the minimum rate dropped with time, as shown for T_g = 135 to 138°C in Figs. 1a and c. In contrast, at lower gas temperatures, the minimum reaction rate became established first and the maximum rate increased with time, as shown for T_g = 129°C in Fig. 1b.

Gas Flow Rates

Moderate values of the hydrogen and oxygen flow rates were chosen so that the reaction rate was large enough to be accurately measured, but the amplitudes of the oscillations remained small compared to the ambient temperature. The maximum reaction rate, $T_c - T_g$, was approximately 35°C. In addition, we found that gas flow rates affected the periodicity of the oscillations. We investigated this effect briefly during the first week of the oscillations.

Figure 2 shows three sets of oscillations recorded under differing flow rates with a fixed gas temperature, T_g = 143°C, and a fixed hydrogen–oxygen ratio, P_{H_2}/P_{O_2} = 4.00%. The total flow rate was reduced in stages from 141 to 70.8 cm³/min, corresponding to a reduction in linear velocity from 27.8 to 14.0 cm/min. Note that all the waveforms show periodicity extending over more than one peak. Lowering the flow rate of the gas stream increased the uniformity of the waveforms; in addition, the frequency of the oscillations and the number of peaks per cycle decreased. The

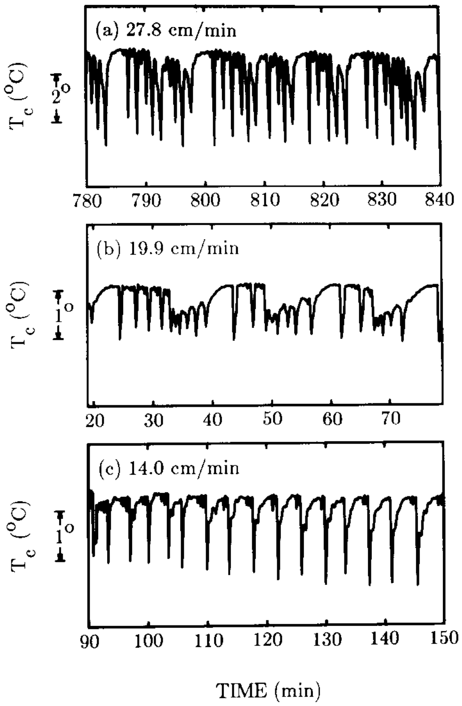

FIG. 2. Effect of total flow rate on oscillations for P_{H_2}/P_{O_2} = 4.00% and T_g = 143°C. Time scales reflect elapsed time under stable flow conditions. (a) H_2, 1.600 cm^3/min; O_2, 40.0 cm^3/min; He, 99.5 cm^3/min; linear velocity given in the figure. (b) H_2, 0.80 cm^3/min; O_2, 20.0 cm^3/min; He, 80.0 cm^3/min. (c) H_2, 0.80 cm^3/min; O_2, 20.0 cm^3/min; He, 50.0 cm^3/min.

waveforms changed from having 5–10 peaks of varying characteristics in each cycle in Fig. 2a to two nearly identical peaks per cycle in Fig. 2c.

The bulk of the data presented in this paper was recorded with a total flow rate of approximately 60 cm^3/min, which corresponds to a linear velocity of 12 cm/min. Since the total flow rate was approximately constant, the ratio P_{H_2}/P_{O_2} could be treated as an experimental parameter. For P_{H_2}/P_{O_2} $\leq 10\%$, we used the flow rates: H_2, 0.450 to 3.00 cm^3/min; O_2, 30.0 cm^3/min; and He, 35.0 cm^3/min. We adjusted the flow rates for $10\% \leq P_{H_2}/P_{O_2} \leq 15\%$ so that the maximum reaction rates would be comparable to those for lower values of P_{H_2}/P_{O_2}. We used: H_2, 1.000 to 1.500 cm^3/min; O_2, 10.0 cm^3/min; and He, 45.0 cm^3/min.

Evolution of Oscillations

As the experiment proceeded, the time required for the waveforms to stabilize decreased. For example, we compare the oscillations in Figs. 1a and c, which occurred, respectively, near the beginning and end of the run under identical flow conditions and similar gas temperatures. For the oscillations in Fig. 1a, more than 8 h were required before the waveforms stabilized to a drift of less than 5% per hour in period and in amplitude. In contrast, for the data shown in Fig. 1c, the oscillations stabilized to the same degree after roughly 80 min. Drifts in the oscillatory characteristics were still noted after several hours, but were much reduced. When the gas temperature and flow conditions had been held constant for 5 to 10 h, the amplitude and period increased by 2 to 3% per hour.

An indication of the long-term reproducibility of the waveforms can be obtained by comparing the stabilized waveforms in the latter parts of Figs. 1a and c. After 10 h under constant conditions, the individual peaks are similar in shape, and the average maximum amplitudes are comparable: 10.1°C for the oscillations in Fig. 1a and 7.0°C for those in Fig. 1c. The periods are in excellent agreement: 6.3 ± 0.2 min per single peak in Fig. 1a, and 6.4 ± 0.3 min per single peak in Fig. 1c. The most striking difference between the two sets is the degree of multipeak behavior shown. The earlier waveforms have cycles containing two and sometimes four peaks. In contrast, the later set of oscillations shows only a mild double-peaked behavior.

Characterization of Oscillations

When the catalyst had been oscillating for 4 to 6 weeks, we attempted to examine systematically the variation in waveforms over the range in oscillatory gas temperatures and compositions. We found a variety of waveforms with periods from under 1 min to more than 40 min. The oscillations occurred for gas compositions P_{H_2}/P_{O_2} =

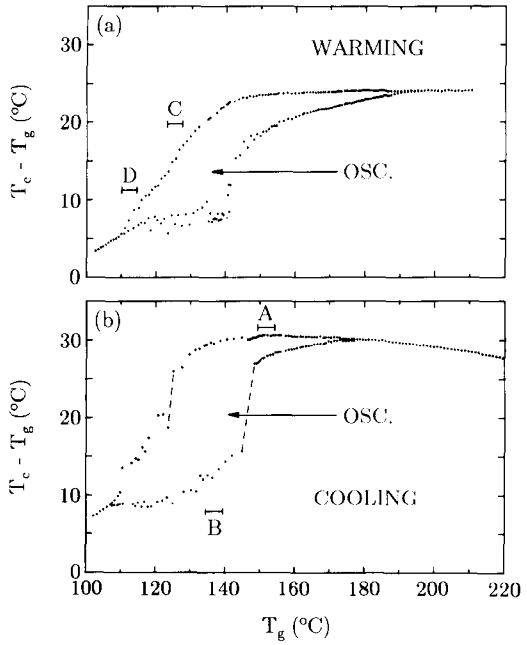

FIG. 3. Reaction rate vs gas temperature for P_{H_2}/P_{O_2} = 4.00%; flow rates are given in Fig. 1. The minimum and maximum reaction rates attained in each oscillation are plotted. (a) T_g increasing at 4.4°C/h. (b) T_g decreasing at 5.0°C/h. The dashed lines indicate abrupt changes in the minimum and maximum oscillatory reaction rates.

1.50 to 15.0% and gas temperatures T_g = 106 to 190°C. For a fixed gas composition, the range of oscillatory gas temperatures was defined by the minimum and maximum values at which an oscillation in catalyst temperature was clearly discernible. An example of an oscillation at the lower boundary appears at t = 4 min in Fig. 4d. Occasionally, the onset of oscillations at the upper boundary was not distinct; in these cases, the high temperature limit was taken where the small, rapid oscillations seen at all hydrogen concentrations attained an amplitude of approximately 0.25°C. Outside the oscillatory limits, the reaction rate was single-valued. The reaction rate had a small value below the low temperature limit, and a large value above the high temperature limit.

While we were surveying the waveforms throughout the oscillatory region, we ramped the gas temperature continuously for each fixed gas composition in order to minimize the effects of slow changes in the condition of the catalyst surface. Typical scan rates averaged about 5°C per hour. Each type of oscillation was also observed under conditions of constant temperature, with two exceptions which are noted below.

In the remainder of this section, we characterize the oscillatory behavior as a function of gas temperature in two ranges of hydrogen concentrations.

For gas compositions up to P_{H_2}/P_{O_2} = 5.00%, the O_2 flow rate used was 30.0 cm³/min and the He flow rate was 35.0 cm³/min. In Fig. 3, the minimum and maximum reaction rates attained in each oscillation are plotted for P_{H_2}/P_{O_2} = 4.00% as a function of both increasing and decreasing gas temperature; different temperature regions, labeled A–D in order of decreasing gas temperature, are marked. This figure illustrates that there seem to be two branches of low and high reactivity, which coexist in the oscillatory region. Near the low and high gas temperature limits of the oscillations, the amplitudes were small; the largest amplitudes occurred at intermediate temperatures.

In this range of hydrogen concentrations, the waveforms went through several distinct stages as the gas temperature was varied. Representative oscillations, corresponding to regions A–D in the previous figure, are shown in Fig. 4. Near the high temperature limit, the reaction rate remained on the high reactivity branch during most of each cycle, and the oscillations looked like downward spikes of high frequency, as shown in Fig. 4a. As the gas temperature decreased, oscillations spent more time in a state of lower reaction rate, as reflected in Figs. 4a–d as well as Figs. 1a and b. Oscillations at intermediate temperatures were usually more complex in shape, as was also found in Ref. (*22*). Cycles containing multiple peaks occurred frequently, predominately with two or four peaks, but also with three or five peaks. Near the low

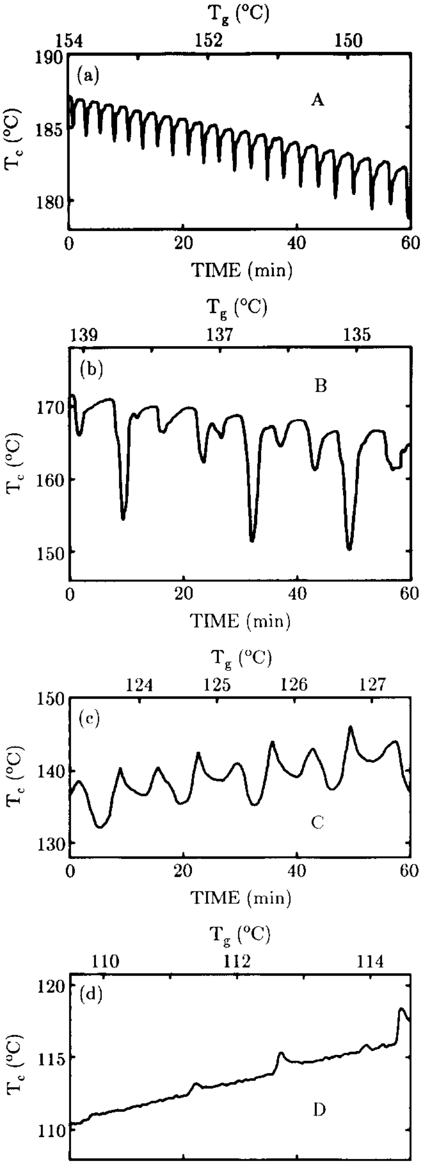

FIG. 4. Oscillations for P_{H_2}/P_{O_2} = 4.00%, corresponding to regions A–D in Fig. 3. (a) Region A, gas temperatures 154.0 to 149.1°C. (b) Region B, 139.2 to 134.2°C. (c) Region C, 123.1 to 127.5°C. (d) Region D, 109.5 to 114.6°C.

temperature limit, the oscillations resembled upward peaks of low frequency, illustrated in Fig. 4d. We did not observe this type of waveform under conditions of constant oven temperature.

In Fig. 5, oscillations for gas compositions P_{H_2}/P_{O_2} = 1.50 to 5.00% can be compared for a fixed gas temperature, T_g = 138°C. These waveforms, which were allowed to stabilize for several hours, were obtained in order of decreasing hydrogen concentration. At smaller values of P_{H_2}/P_{O_2}, the oscillations spent more time on the lower reaction rate branch, as was also noted in Ref. (*4*). In addition, as shown in Fig. 6, the amplitude of the oscillations decreased and the period increased.

We also studied oscillations for gas compositions P_{H_2}/P_{O_2} = 10.0 to 15.0%. In Fig.

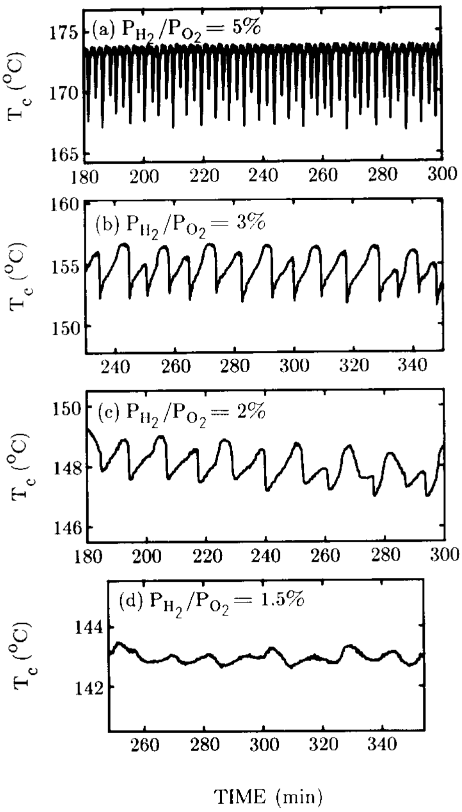

FIG. 5. Oscillations for P_{H_2}/P_{O_2} = 1.50 to 5.00% and T_g = 138°C. Time scales reflect elapsed time under a given hydrogen concentration. Flow rates used were: O_2, 30.0 cm³/min; He, 35.0 cm³/min; (a) H_2, 1.500 cm³/min; (b) H_2, 0.900 cm³/min; (c) H_2, 0.600 cm³/min; (d) H_2, 0.45 cm³/min. The oscillations shown in Fig. 1c with a H_2 flow rate of 1.200 cm³/min are part of this series.

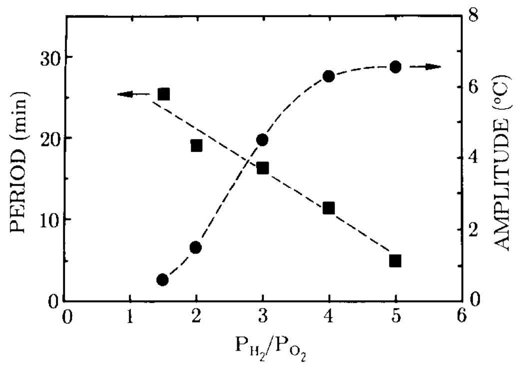

FIG. 6. Oscillatory characteristics (period, amplitude) vs hydrogen concentration, P_{H_2}/P_{O_2}. The characteristics of the four double-peaked cycles in Fig. 5 occurring just before a stabilization time of 300 min were averaged for the values in the graph. An oscillatory period is defined as the time taken for each double-peaked cycle. The amplitude is defined as the maximum excursion in catalyst temperature attained in one double-peaked cycle.

7, the dependence of the reaction rate on the gas temperature for $P_{H_2}/P_{O_2} = 10.0\%$ is plotted for consecutive increasing and decreasing temperature scans. The flow rates were: H_2, 1.000 cm^3/min; O_2, 10.00 cm^3/min; and He, 45.0 cm^3/min. Again, two branches of low and high reactivity were clearly distinguishable. The range of oscillatory gas temperatures was considerably narrower than for lower hydrogen concentrations.

Examples of oscillations obtained for $P_{H_2}/P_{O_2} = 10.0\%$ are shown in Fig. 8. Oscillations near the high gas temperature limit are shown in Fig. 8a. The flow rates used to obtain these data were: H_2, 3.00 cm^3/min; O_2, 30.00 cm^3/min; He, 35.00 cm^3/min. Waveforms corresponding to the data plotted in Fig. 7a are presented in Fig. 8b. As these figures illustrate, typical oscillations at the low and high gas temperature limits resembled the waveforms at the corresponding limits for lower hydrogen concentrations. At intermediate temperatures, large amplitude oscillations resembling square waves switching between the two reaction branches occurred. The square waves were the second type of waveform which we were unable to sustain when the gas temperature was fixed.

Oscillatory Region

The range of experimental parameters over which we found oscillations is summarized by the data labeled "Run I" in Fig. 9. The limits of oscillatory gas temperatures are plotted as a function of P_{H_2}/P_{O_2} for total flow rates near 60 cm^3/min. Results from scans in both directions are shown. On the average, the limits of the oscillations were reproduced within 8°C for consecutive scans made in opposite scan directions. However, for the gas composition $P_{H_2}/P_{O_2} = 5.00\%$, the high T_g limit decreased by as much as 30°C approximately 10 days after the initial measurements were made. Nevertheless, the oscillatory temperature ranges still overlapped considerably. This temperature difference gives a rough idea of the long-term reproducibility of the limits

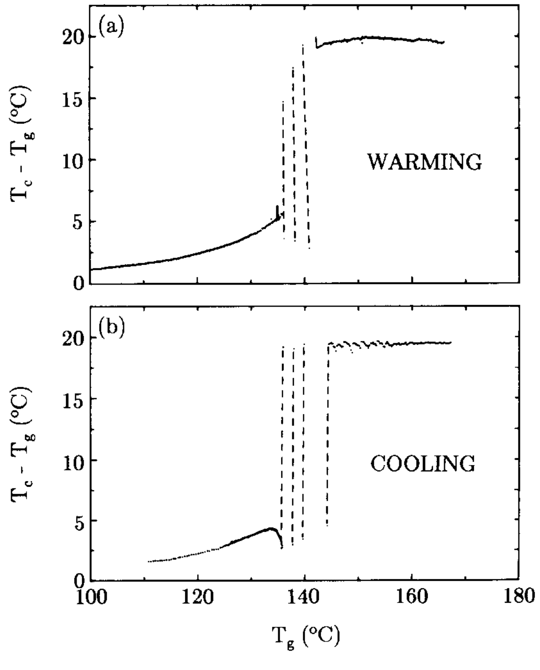

FIG. 7. Reaction rate vs T_g for $P_{H_2}/P_{O_2} = 10.00\%$. Flow rates: H_2, 1.000 cm^3/min; O_2, 10.00 cm^3/min; He, 45.0 cm^3/min. The dashed lines indicate minimum and maximum reaction rates during one oscillation. (a) T_g increasing at 5.3°C/h. (b) T_g decreasing at 5.8°C/h.

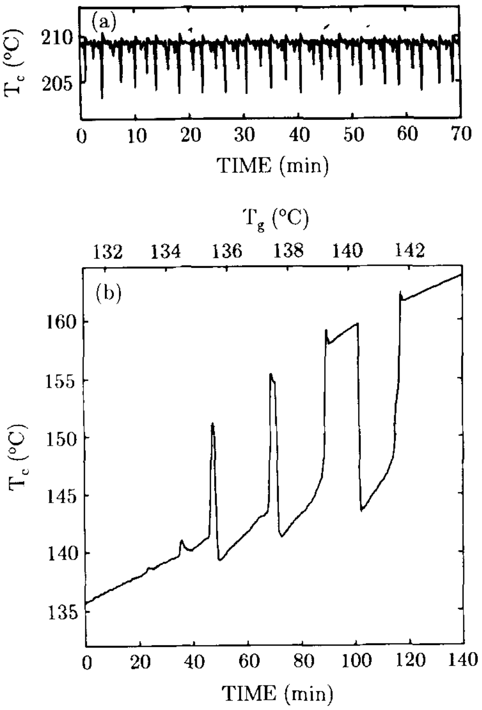

FIG. 8. Oscillatory waveforms for P_{H_2}/P_{O_2} = 10.0%. (a) Oscillations at T_g = 150°C, near high temperature limit. Flow rates: H_2, 3.00 cm³/min; O_2, 30.0 cm³/min; He, 35.0 cm³/min. (b) Oscillations recorded during the increasing temperature scan in Fig. 7a.

of oscillatory gas temperatures. Belyaev *et al.* (*16*) also noted shifts in the oscillatory temperature range during prolonged work with the same catalyst.

The largest range in gas temperatures over which oscillations occurred continuously was from 110 to 190°C during an increasing temperature scan for P_{H_2}/P_{O_2} = 4.00%. The smallest range was from 134 to 142°C during an increasing temperature scan for P_{H_2}/P_{O_2} = 10.00%. The low gas temperature limits of the oscillations increased linearly with the hydrogen concentration. The high gas temperature limits of the oscillations decreased and then increased with increasing hydrogen concentration.

Results after Reetching the Catalyst

At the end of the set of measurements just described, we reetched the catalyst. In this section, we present data recorded within a few days of reetching. After the gas composition of P_{H_2}/P_{O_2} = 5% and an initial gas temperature of T_g = 145°C were chosen, T_g was lowered until oscillations developed. The shape of the waveforms stabilized quickly, but the period decreased substantially during the first 48 h.

The oscillations that we observed differed in several ways from those occurring previously. Oscillatory gas temperatures shifted to much lower values. The waveforms were much smoother, often almost sinusoidal in shape, and showed a new set of trends in their evolution. In general, the periods decreased and the average reaction rate increased as a function of time. Oscillatory amplitudes both increased and decreased under constant external conditions.

Observations of oscillations for P_{H_2}/P_{O_2} = 5.00% were made when the gas temperature was scanned and held constant. We used similar flow rates to facilitate comparisons with data recorded before we reetched the catalyst. Typical flow rates were: H_2, 1.500 cm³/min; O_2, 30.0 cm³/min; and He, 25.0 cm³/min.

The reaction rate as a function of gas temperature is plotted for consecutive increasing and decreasing temperature scans in Fig. 10. The oscillatory region has a sau-

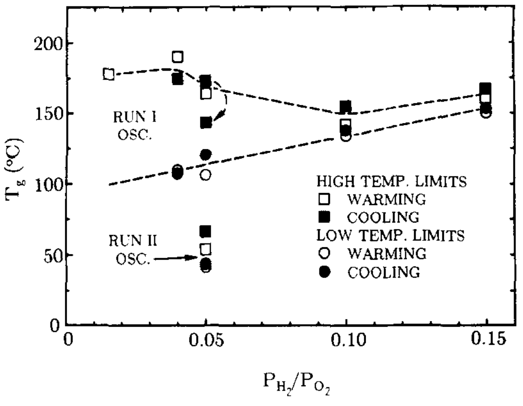

FIG. 9. Oscillatory region: gas temperature vs gas composition. "Run I" and "Run II" refer to data taken before and after reetching the catalyst.

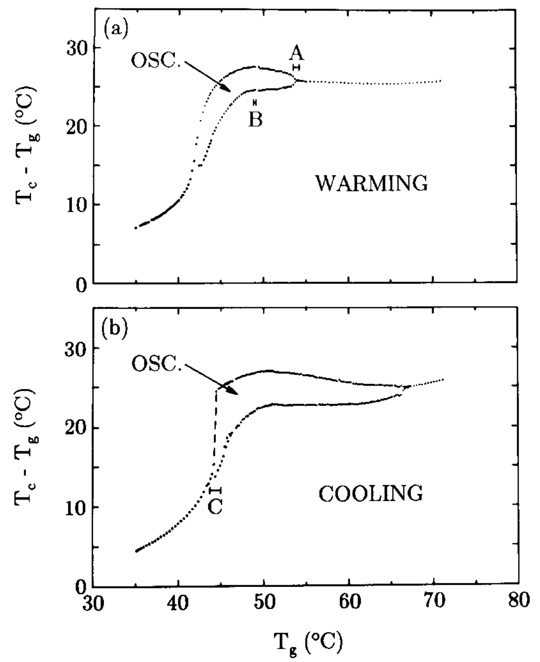

FIG. 10. Reaction rate vs T_g for $P_{H_2}/P_{O_2} = 5.00\%$ after reetching the catalyst. Flow rates: H_2, 1.500 cm³/min; O_2, 30.0 cm³/min; He, 25.0 cm³/min. (a) T_g increasing at 3.0°C/h. (b) T_g decreasing at 2.6°C/h. The dashed line indicates an abrupt change in the maximum oscillatory reaction rate.

sage-like shape that is quite different from the regions in Figs. 3 and 7. Waveforms from the temperature scans are presented in Fig. 11. One similarity between the oscillations that occurred before and after reetching is that the smallest amplitudes occurred at the limiting oscillatory gas temperatures. An additional similarity is that the oscillations at lower T_g have lower frequencies and spend a proportionately longer amount of time in a state of low reaction rate.

The limits of oscillatory gas temperatures for $P_{H_2}/P_{O_2} = 5.00\%$ after the catalyst was reetched are presented in Fig. 9 as data for Run II. Note that there was no overlap between the oscillatory regions before and after reetching.

Four weeks after reetching, experiments were terminated when the waveforms began to show signs of what we interpret as catalyst poisoning. We note that the nearly sinusoidal waveforms in Fig. 11 as well as the waveforms observed near the end of our experiment resembled oscillations of CO, O_2, and 1-butene over a supported Pt catalyst (*7, 27*).

DISCUSSION

Oscillations in the rate of production of water over a polycrystalline Pt catalyst have been characterized at atmospheric pressure over a range of H_2–O_2 compositions and gas temperatures, T_g. In the

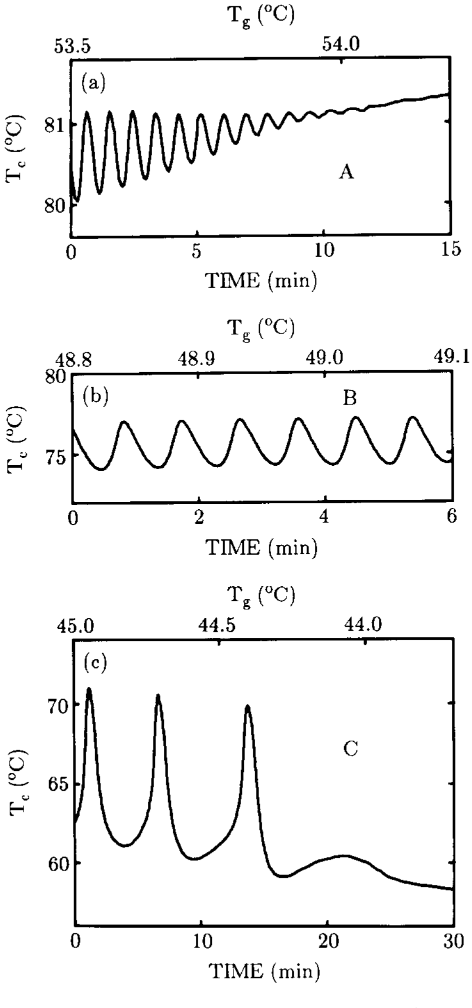

FIG. 11. Oscillations for $P_{H_2}/P_{O_2} = 5.00\%$, corresponding to regions A–C in Fig. 10. (a) Region A, gas temperature, 53.5 to 54.2°C. (b) Region B, 48.8 to 49.1°C. (c) Region C, 45.0 to 43.7°C.

course of experiments over a 2-month span, we studied oscillations in the catalyst temperature for gas compositions from $P_{H_2}/P_{O_2} = 1.5$ to 15%. Oscillatory gas temperatures ranged from 106 to 190°C. The periods varied from less than a minute to approximately an hour. Oscillations occurred with and without helium in the gas stream.

For a given gas composition, oscillations occurred between two limiting gas temperatures. Outside these limits, the reaction rate was single-valued. Graphs of the minimum and maximum reaction rates attained in each cycle as a function of T_g suggest two branches of reactivity: one of high reactivity at high gas temperatures, and another of low reactivity at low temperatures. The oscillations occur as periodic transitions between the two branches in the region where the branches coexist. The switching nature was particularly evident in the square wave oscillations for higher hydrogen concentrations. At lower values of T_g, oscillatory frequencies decreased and the catalyst spent more time on the low reaction rate branch.

At the beginning of our experiments, we varied the flow rate of the gas stream. The shapes of individual peaks observed under different flow conditions were comparable, but the periodicity of the waveforms was affected by the gas velocity. When the total flow rate was lowered, the waveforms became more uniform and decreased in frequency. Most of the oscillations presented in this paper were recorded using a fixed total flow rate. Although we have no explanation for the effects of the gas velocity on the oscillations, mass spectrometer output agrees with calculations showing that all of the hydrogen which could diffuse to the catalyst surface was not reacted.

Once oscillations were initiated, the shape of the individual peaks emerged rapidly. The amplitudes and periods stabilized more quickly each time oscillations were restarted. A variety of waveforms was observed. We found relaxation oscillations that looked like spikes and square waves. Waveforms with single as well as multiple peaks per cycle occurred. At intermediate oscillatory temperatures, waveforms typically had two to four peaks per cycle. The same qualitative behaviors occurred when the gas temperature was scanned and held constant. Thus, we believe that the general trends exhibited by our results were independent of ramping the gas temperature. However, the observed shifts in the oscillatory temperature limits may have been related to our scanning T_g.

In previous work by this group, oscillations in the oxidation of CO over polycrystalline Pt (*5*), Pd (*14*), and Ir (*14*) catalysts were systematically studied. The waveforms were well approximated by square waves, and a single peak per cycle occurred. A kinetic model was developed in which the oscillations were driven between two reaction branches by the alternate formation and reduction of a species of oxygen strongly bound to the catalyst surface (*15*). The model accounted successfully for the waveforms and their characteristics as a function of gas temperature and CO concentration.

Oscillatory gas mixtures for the H_2–O_2 reaction were somewhat higher in the concentration of the reducing gas and somewhat lower in temperature than for the CO–O_2 reaction. Oscillations for both reactions had comparable time scales and appeared to be transitions between two branches of the reaction rate. The major qualitative differences were the greater variety exhibited by the H_2–O_2 waveforms and their poorer reproducibility.

We believe that the oscillations involving hydrogen, like those involving carbon monoxide, are probably driven by a mechanism involving the formation and reduction of a strongly adsorbed O species; this is consistent with experimental results in Ref. (*24*). We have not attempted to model the H_2–O_2 oscillations due to the complexities introduced by the dissociation of hydrogen and its migration below the first surface layer (*25*). The H_2–O_2 kinetics involve two atomic chemisorbed species and two subsurface species, in contrast to the CO–O_2 reaction, where the reducing species is molecularly chemisorbed. In addition, the mechanism of the oxidation of hydrogen over Pt has been interpreted both as the combination of an adsorbed H with a hydroxyl intermediate (*28*, *29*), as well as the combination of two adsorbed H atoms with an adsorbed O (*30*). We suspect that the complexity of the reaction kinetics is responsible for the complexity of the waveforms.

ACKNOWLEDGMENTS

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