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Kinetics of the Reaction of Oxygen with Carbon Monoxide Adsorbed on Palladium[1]

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A study of the kinetics of the reaction of adsorbed carbon monoxide with oxygen on polycrystalline palladium is reported in which a pressure jump method was used to induce transients in the carbon dioxide production. Through an analysis of these transients under a variety of conditions of temperature and oxygen pressure, some details of the kinetics have been delineated. At relatively low temperatures and under a significant O_2 pressure, CO(a) is desorbed more readily as CO_2, via the reaction $CO(a) + O(a) \rightarrow CO_2$, than as CO. The reaction is first order in oxygen and the rate is limited by the rate of adsorption of oxygen onto sites which are in close proximity to CO(a). Oxygen adsorption at sites which are further than a critical distance from CO(a) are unreactive. The critical distance increases with temperature reflecting increased mobility. Under conditions where both CO(a) and O(a) are significant and both CO(g) and O_2(g) are small the rate is limited by the mobility of CO(a) and/or O(a). The amount of CO(a) during the course of the steady-state oxidation reaction can be determined by analyzing the transient CO_2 production which occurs following a pressure jump in carbon monoxide.

I. INTRODUCTION

In previous papers (*1,2*) it has been shown that the CO oxidation on polycrystalline palladium can occur through two reaction paths, an Eley–Rideal reaction, $CO(g) + O(a) \rightarrow CO_2$, and a Langmuir–Hinshelwood reaction, $CO(a) + O(a) \rightarrow CO_2$. Similar results have been reported on single crystals of Pt (*3*) and Pd (*4,5*). The former path is relatively simple kinetically (*1,2*) and plays the major role in the steady CO_2 formation when the partial pressure ratio, p_{O_2}/p_{CO}, is greater than unity. On the other hand, the latter involves more complicated kinetic behavior (*1,4*) which has not been studied in detail.

Below about 523 K, the rate of steady CO_2 formation is retarded by adsorption of CO when $p_{CO} > p_{O_2}$ (*2*), and the inhibition becomes larger as the substrate temperature is decreased. The process $CO(a) + O(a) \rightarrow CO_2$ can, under these conditions, play a role in elimination of CO(a) from the surface. Therefore, the kinetics of this process is not only interesting as a fundamental surface process, but may also play an important role in maintaining the activity of the catalyst under conditions where relatively large amounts of CO can be adsorbed.

The purpose of this paper is to report and interpret experimental data, obtained using pressure jump methods (*3,4*), which are related to the process, $CO(a) + O(a) \rightarrow CO_2$. By analyzing transients, induced by a pressure jump in CO or O_2, as a function of ambient pressure, gas phase composition, and substrate temperature, we are able to delineate certain aspects of the kinetics and determine the amount of CO(a) and O(a) present during CO_2 formation.

II. EXPERIMENTAL METHODS

Some aspects of the apparatus and experimental procedures have been re-

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ported previously (*1,6*). The system was a bakeable ultrahigh vacuum apparatus used in a routine fashion such that the base pressures achieved were less than 5×10^{-7} Pa, the principal residual being CO. The pressures, total and partial, were monitored with a Bayard-Alpert ionization gauge and a quadrupole mass spectrometer. During experiments the system was continuously pumped by an ion pump.

The substrate was a rectangular Pd foil ($20 \times 5 \times 0.13$ mm). Prior to the experiments it was exposed to oxygen at a pressure of 10^{-4} Pa at 900 K. This treatment is sufficient for establishment of stable catalyst behavior (*6*). During a series of measurements, the oxygen-dosed substrate was heated to 900 K for about 5 min prior to each experiment.

Reactant gases O_2 and CO were introduced through two continuously variable leak valves. Temperatures were measured with an iron–constantan thermocouple spot-welded to the substrate.

III. RESULTS AND DISCUSSION

1. Transients Observed When a Steady-State O_2/Pd System Was Dosed with CO

A typical experiment is outlined in Fig. 1; a steady-state flowing O_2/Pd system was established at some temperature T and then dosed with a relatively large pressure of CO. For the case shown in Fig. 1, the initial O_2 pressure was 3.3×10^{-5} Pa, the CO dose pressure was 7.6×10^{-5} Pa, the dose time was 5 min, and the temperature was 393 K. The CO valve was rapidly closed to end the dose period. As shown in Fig. 1, the initial and final CO pressure jumps induced transients in the O_2 and CO_2 pressures.

At the beginning of the dose period, the CO pressure increased to a steady value through an initial plateau. The plateau is attributed to two processes: first, there is some consumption of CO by the reaction $CO(g) + O(a) \rightarrow CO_2$ and second, there is adsorption of CO onto unoccupied sites left after this reaction. During this period the oxygen pressure showed a small drop, due to adsorption upon similar unoccupied sites, while CO_2 peaked (peak I of Fig. 1). After passing through a peak in the early stages of the CO dose, the CO_2 pressure slowly approached a steady-state value, which was, at 393 K, much lower than the maximum of peak I. During the CO dose, the behavior of CO_2 is interpreted as follows. The initial sharp CO_2 peak shows the occurrence of the Eley–Rideal reaction (*1*), $CO(g) + O(a) \rightarrow CO_2$. A short time after the CO dose began, the CO_2 decreased because at this temperature the surface coverage of oxygen cannot be maintained for $p_{co} \gg p_{O_2}$. This occurs since the reaction $CO(g) + O(a) \rightarrow CO_2$ is fast, allowing CO(g) to rapidly replace O(a) as it is used. The reaction $O_2(g) + CO(a) \rightarrow CO_2 + O(a)$ either does not occur or is very slow.

When the CO flow was stopped as shown in Fig. 1, the CO partial pressure dropped very rapidly, while O_2 and CO_2 pressures changed characteristically with much longer time constants. The formation rate of CO_2 dropped from its steady value to a little lower background level and then increased slowly, went through a maximum, and decreased to a new steady value which was dictated by the background pressures of CO and O_2. The general shape is depicted in Fig. 1 as peak II. During the CO_2 peak, the O_2 pressure dropped reflecting the adsorption of oxygen on sites made available by the removal of CO as CO_2.

When the substrate was heated just before finishing the CO dose, a significant amount of CO, but only a small amount of CO_2, was desorbed. Thus, the CO_2 which appears after the CO valve is closed is formed by the reaction of CO(a), and does not arise from desorption of adsorbed carbon dioxide, such as Kobayashi and

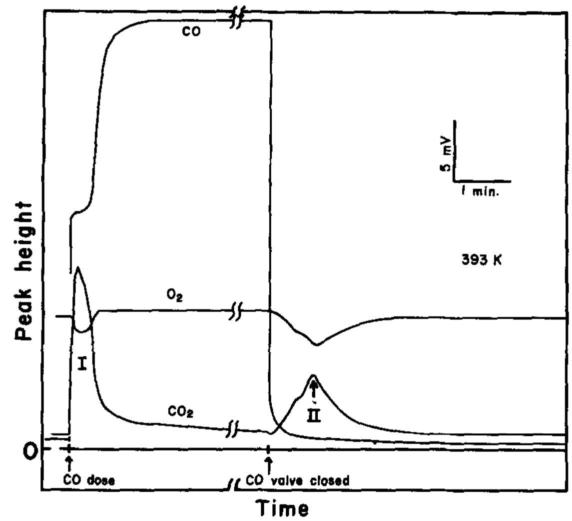

FIG. 1. Application of CO pressure jump method to induce transients, peaks I and II, in the CO_2 production at 393 K. Variations in CO, O_2, and CO_2 are shown for a CO dose pressure of 7.5×10^{-5} Pa for 5 min. The initial O_2 pressure was 3.3×10^{-5} Pa.

Kobayashi (*8*) reported on Cr_2O_3 by a similar method.

This behavior shows that under these conditions CO_2 is formed by the reaction of adsorbed carbon monoxide with adsorbed oxygen. Oxygen reacting directly from the gas phase to form CO_2 does not predominate because if the process $CO(a) + O_2 \rightarrow CO_2 + O(a)$ were most important, the maximum CO_2 pressure should always appear during the CO dose, since the coverage of CO(a) is largest during that period; that is, the CO_2 pressure should obey a first order decay after closing the CO valve. Actually the CO_2 rate was relatively small when CO was flowing. As pointed out by Bonzel and Ku (*3*), the transient CO_2 appearing after the CO valve was closed can be accounted for on the basis that a small part of CO(a) is desorbed as the CO pressure drops; after that O_2 is adsorbed as O(a) which reacts with CO(a) to produce CO_2.

In what follows we discuss the dependence of CO_2 peak II upon background O_2 pressure, the substrate temperature, and the coverage of CO(a) and O(a). The CO_2 transient often showed two or more local maxima, especially at low temperatures. Most of our discussion is based on the second peak because it was always much larger than the others.

2. O_2 *Pressure Dependence*

The magnitude and shape of the CO_2 peak II is very sensitive to the background O_2 pressure. Figure 2 shows the dependence of the maximum peak height, $(\Delta p_{CO_2})_{max}$, on p_{O_2} at 413 K. The difference between the height of peak II and the final CO_2 background defines $(\Delta p_{CO_2})_{max}$. As illustrated in Fig. 2, the height shows a first order dependence on p_{O_2} whereas the time required to reach the maximum after the CO valve was closed, t_{max}, decreased with first order dependence. Similar results were obtained at 433 and 393 K.

As summarized in Table 1, the area under peak II was constant independent of p_{O_2} except when $p_{CO} \gg p_{O_2}$ or $p_{CO} \lesssim p_{O_2}$. In the former case there was a considerable opportunity for making significant error in computing the peak area due to the very broad peak which became difficult to distinguish from the CO_2 background. The

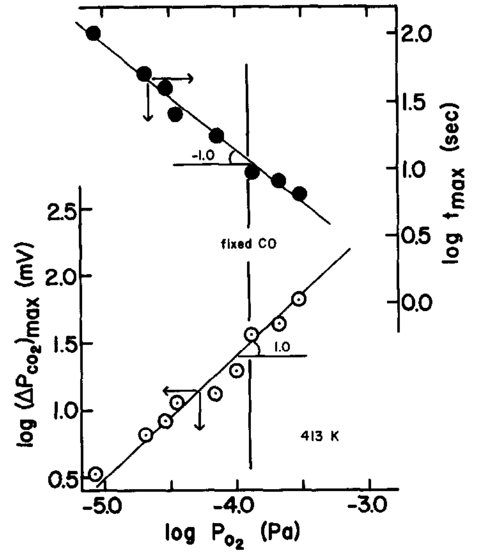

FIG. 2. Variation with O_2 pressure of the height of peak II (see Fig. 1) and the time, t_{max}, required to reach the maximum at 413 K. The CO dose pressure was 1.2×10^{-4} Pa and the dose period was 5 min.

decrease of the peak area for $p_{CO} < p_{O_2}$ indicates that the steady-state CO(a) grew smaller as the oxygen pressure increased (*2,7*). These results show that under a significant p_{O2} almost all of CO(a), which can react with oxygen, is desorbed as CO_2 through the Langmuir–Hinshelwood process, rather than being desorbed as CO. Hence the amount of CO(a) under working conditions can be determined from the CO_2 peak area. In passing it should be noted that the contribution of gas phase CO to CO_2 production during peak II was subtracted as a background level. This background includes the contribution of $CO(g) + O(a) \rightarrow CO_2$ and production of CO_2 at the mass spectrometer and ion gauge filaments.

TABLE 1

RELATIVE AREA OF CO_2 PEAK UNDER VARIOUS BACKGROUND O_2 PRESSURES AT A FIXED CO OF 1.2×10^{-4} Pa AT 413 K[a]

p_{O_2} (10^{-5} Pa)	Relative area
0.85	0.87
2.0	1.0
2.9	1.0
3.4	1.0
6.9	0.98
9.6	1.0[b]
12.8	1.0
21.3	0.92
28.2	0.90

[a] The CO dose period was 300 sec.
[b] Standard.

3. Temperature Dependence

The temperature dependence of peak II, as shown in Fig. 3, is quite different from that observed on single crystal Pt (*3*) and Pd (*4*). The latter two systems showed a single peak, while our transients were characterized by two (and in some cases more) peaks, especially at low temperatures. These different peaks may be due to different kinds of adsorption of CO, depending on crystal planes. It would be very interesting to try to resolve these CO_2 peaks. However, except at temperatures below 375 K, they are strongly overlapped and at low temperatures our data are subject to rather large experimental error.

The logarithm of the peak height of the second maximum, which was always predominant, is plotted versus $1/T$ in Fig. 4 for temperatures between 371 and 478 K. Over this range, the activation energy is estimated to be about 21 kJ $mole^{-1}$, which is smaller than the value of 29 kJ $mole^{-1}$ reported on Pd(111) (*4*) for comparable experimental conditions.

The characteristic shape and area of peak II is quite dependent on the substrate temperature as shown in Fig. 3. For temperatures above 500 K there is actually no peak and the CO_2 signal decays away rapidly. This is attributed to the small amount of CO adsorbed at these temperatures and, as outlined below, the relatively large amount of O(a) available for reaction with CO(a) under these conditions. At lower temperatures, especially below 460 K, one or more pronounced peaks occur in the CO_2 production after termination of the CO dose. These are attributed to the reac-

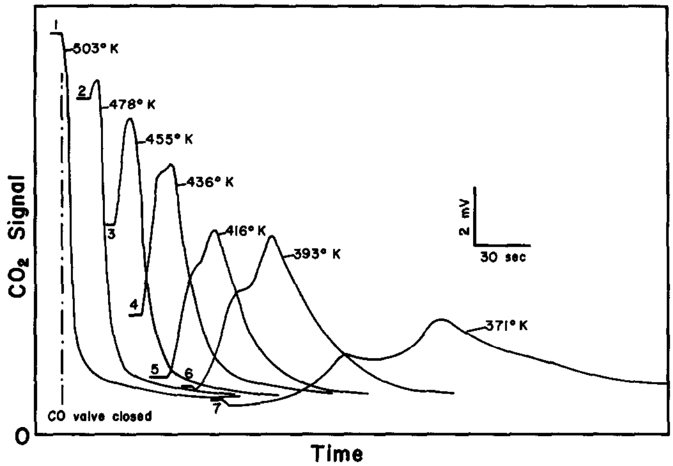

FIG. 3. The temperature dependence of peak II for a fixed CO dose of 7.6 × 10^{-5} Pa for 5 min and a fixed initial oxygen pressure of 3.3 × 10^{-5} Pa. The short flat step at the beginning of each curve indicates the steady-state CO_2 production rate prior to the sharp pressure drop in CO (see Fig. 1). The pressure drop occurred at the right end of the step.

tion $CO(a) + O(a) \rightarrow CO_2$, the rate of which appears to be limited by oxygen adsorption onto sites which are in close proximity to CO(a). The CO_2 pressure increases with time after the CO dose is terminated because the amount of adsorbed oxygen increases with time. The maximum rate is expected when both the CO(a) and O(a) are about half of full coverage. These considerations are discussed in further detail in Sect. IV.

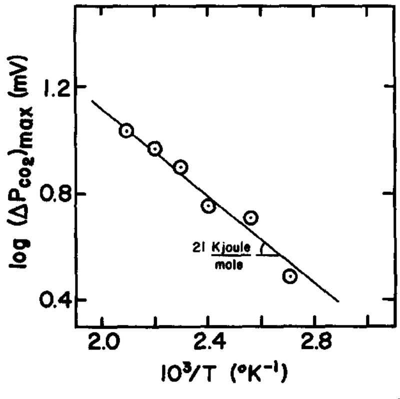

FIG. 4. Arrhenius plot of the temperature dependence of the height of peak II. Experimental conditions are those referred to in Fig. 3. When the CO_2 transient showed more than one peak the largest was used as the maximum.

4. *Amount of CO(a) and O(a) during CO_2 Formation*

In order to elucidate the kinetic behavior of the CO_2 formation during peak II, the amounts of CO(a) and O(a) were determined while CO_2 peaked, using a CO-titration method (*1*). A typical experiment is shown in Fig. 5. The $CO/O_2/Pd$ system was allowed to reach steady state. To observe a transient peak A, the CO valve was closed. After a period t_1, the O_2 valve was closed and following a delay t_2 a relatively large dose of CO was applied. After the CO valve was closed at the beginning of the transient experiment, the CO_2 pressure followed the expected course. When the O_2 flow stopped, it decreased immediately, as shown by the solid curve in Fig. 5. The broken line portion of the curve shows the decay of CO_2 that would have been observed if the oxygen flow had continued. Dosage with CO after the delay t_2 gave a sharp pulse, peak B, of CO_2 due to the reaction, $CO(g) + O(a) \rightarrow CO_2$. The area of peak B gives the amount of oxygen adsorbed on the substrate at time t_2 (*1*).

Generally the area of peak B decreased with t_2, and the decrease is dominated by

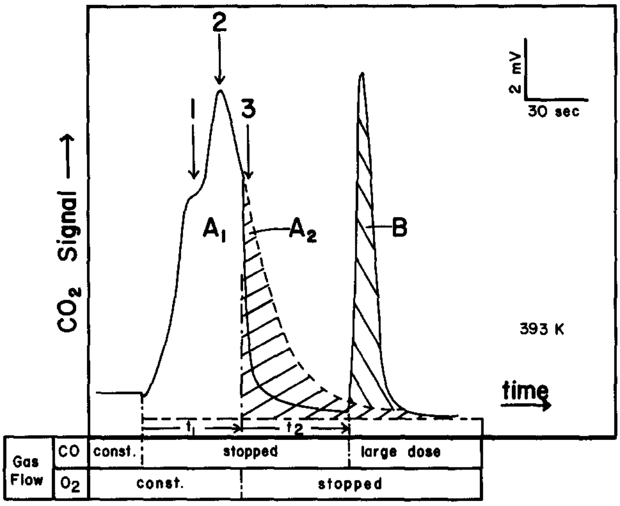

FIG. 5. A typical transient peak II monitored by pressure jump techniques to determine the amount of CO(a) and O(a) present. For this case, the O_2 pressure up to the close of period t_1 was 3.7×10^{-5} Pa while the CO dose prior to t_1 was 8.7×10^{-5} Pa for 5 min.

the reaction between O(a) and the background CO. Hence the amount of O(a) at $t_2 = 0$ was estimated by extrapolation of a plot of the logarithm of the area of peak B versus t_2 (*1*). The results are summarized in Table 2. The times $t_2 = 28$, 35, and 43 sec correspond to the points 1, 2, and 3 shown in Fig. 5. Peak B in Table 2 represents the extrapolated area ($t_2 \rightarrow 0$) of peak B relative to that obtained at $t_1 = 200$ sec. For $t_1 > 200$ sec, CO_2 was produced at a constant background level indicating all available CO(a), except that due to background, has been removed from the substrate. Thus the area of peak B at $t_1 = 200$ sec may be considered to correspond to the saturation value of adsorbed oxygen. Peaks A_1 and A_2 in Table 2 show, respectively, the amounts of CO(a) desorbed as CO_2 during t_1 and the CO(a) remaining at the end of period t_1 relative to the full CO_2 peak which would be observed if the O_2 flow was not terminated until $t_1 > 200$ sec.

TABLE 2

AMOUNT OF CO(a) AND O(a) DURING CO_2 FORMATION

t_1 (sec)	Peak			Peak B/peak A_1
	A_1	A_2	B	
28	0.35	0.65	0.10	0.20[a]
35	0.51	0.49	0.21	0.30
43	0.75	0.25	0.63	0.55
200	1.0[b]	0.0	1.0[b]	0.80

[a] This ratio is calculated using actual peak areas, not the relative areas shown in the other columns.

[b] Standard.

The composite of Table 2 and Fig. 5 reveals some important details concerning the reaction to produce CO_2 under these conditions. First, as indicated by the areas of the A_2 peaks, stopping O_2 flow at any time less than 200 sec leaves a significant amount of CO on the surface. Second, during period t_1, a significant amount of oxygen is adsorbed as indicated by the area of peak B. From Fig. 5 it is, however, clear that CO_2 production drops dramatically when O_2 flow is terminated even though significant amounts of O(a) and CO(a) are present. Thus not every O(a) is readily available for reaction with CO(a) under these conditions. Further, note that the sum of the areas of peak A_2 [residual CO(a)] and peak B [amount of O(a)] is always less than unity which suggests that some of the sites vacated by CO during t_1

are not occupied by oxygen at the beginning of period t_2.

5. *Effect of Heating a Substrate Partially Covered with CO(a) and O(a).*

In a somewhat different kind of experiment, the O_2 flow was stopped at point 2 of Fig. 5 and, instead of dosing with CO, the substrate was heated gradually to about 670 K. During this heating a significant amount of CO_2 was desorbed whereas by comparison the amount of CO desorbed was very small. This result suggests that O(a) and CO(a) are relatively immobile at low temperatures. This point is discussed further in Sect. IV especially as it relates to the rate when the O_2 pressure is large.

IV. KINETIC MODEL

In the previous section we have presented experimental observations for a variety of conditions and a brief discussion of those observations in anticipation of the general conclusions drawn in this section. The observations under conditions of significant O_2 pressure can be explained on the basis of a model in which O_2 adsorption is rate limiting and for which there are two classes of adsorbed oxygen, reactive and nonreactive. The distinction between these two classes is related to the distance between CO(a) and O(a); if this distance is small the O(a) is reactive. The critical distance which divides the reactive and nonreactive classes increases with the temperature reflecting higher mobility as the temperature increases. However, mobility plays only a small part in determining the rate at any given temperature so long as the O_2 pressure is significant. Rather, the rate is dominated by oxygen adsorption onto unoccupied sites in the neighborhood of CO(a) as indicated by the first order dependence on O_2(g) shown in Fig. 2.

When both CO(g) and O_2(g) are low the rate is determined by the mobility since there is no gas phase oxygen which can populate sites which are close to CO(a).

On the basis of this model we can account for the observations of Sect. III. For example, the last column of Table 2 shows that the ratio of the areas of peak B and peak A_1 increases markedly with t_1. From this observation we conclude that when t_1 is small, CO(a), removed as CO_2, is not immediately replaced by adsorbed oxygen. This suggests that oxygen adsorption is under these conditions rate limiting.

Even when the amounts of adsorbed oxygen and adsorbed CO are significant, the CO_2 formation rate is very small in the absence of gas phase oxygen as shown by the data of Fig. 5 and Table 2. This confirms the notion that the mobility of CO(a) and O(a) is limited and, especially at low temperatures around 400 K, there is a relatively large amount of O(a) which is not close enough to CO(a) to react and produce CO_2. Thus the CO_2 production rate is limited by the rate of oxygen adsorption onto the reactive class of sites and a first order depencence on the O_2 pressure is expected. Figure 2 shows that the maximum rate of CO_2 production during the transient peak II does indeed follow a first order dependence on O_2.

The number of reactive O(a) sites should increase as CO(a) decreases until the coverage reaches about half of its maximum value after which the number should decrease. Thus the maximum CO_2 production rate plotted in Fig. 2 corresponds to a CO coverage of about 0.5. Assuming that the amount of adsorbed CO is the same at the termination of the CO dose, regardless of the O_2 pressure, $t_{\max}$ measures the time required to reduce the initial amount to one half the maximum value. According to the above model a first order dependence of the rate on O_2 pressure implies that $t_{\max}$ should follow a negative first order dependence on O_2 pressure which is in agreement with Fig. 2.

As pointed out in Sect. III the temperature dependence of the transient induced by the CO pressure jump is quite strong. At temperatures above 500 K the maximum rate of CO_2 production occurs at the beginning of the transient. This occurs because the amount of CO(a) at steady state is quite small under these conditions (*7,9,10*) and the number of reactive O(a) sites is relatively large at these temperatures where the critical distance distinguishing reactive and nonreactive sites is relatively large. As the substrate temperature decreases the steady-state CO(a) increases and the number of reactive O(a) sites diminishes. Referring to Fig. 3, at 478 K the steady-state CO(a) is about half its maximum value. As the temperature decreases $t_{\max}$ increases because more CO(a) must be removed before the amount of CO(a) reaches half its maximum value and because the rate of oxygen adsorption onto reactive sites declines.

A model in which the rate of CO_2 production is proportional to the product of the amount of adsorbed oxygen and the amount of adsorbed carbon monoxide has been proposed as an explanation of some data on single crystal Pt (*3*) and Pd (*4*). Such an expression cannot be successfully applied to the results reported here because it fails to account for the very low reaction rate observed when both CO(g) and O_2(g) are low even though CO(a) and O(a) are significant. According to the model presented here, the number of sites which are both available for O_2 adsorption and are in close proximity to CO(a), i.e., a reactive O(a), depends on the mobility of CO(a) and/or O(a). The activation energy of the maximum rate of CO_2 production, Fig. 4, is thus influenced by the temperature dependence of the mobility of CO(a) and/or O(a) on polycrystalline Pd. At the same time the rate is, at a given temperature, limited by the oxygen adsorption rate onto reactive sites, the number of which for a given amount of CO(a), increases with temperature.

SUMMARY

The kinetics of the reaction $CO(a) + O(a) \rightarrow CO_2$ on polycrystalline palladium was studied by means of a pressure jump method. Under a significant O_2 pressure, CO(a) is desorbed as CO_2 rather than CO. The rate is first order in O_2, is limited by O_2 adsorption, and has an activation energy of about 21 kJ mole^{-1}. The amount of CO(a) during the course of the steady-state oxidation reaction can be determined through analysis of the transient CO_2 peak produced by the pressure jump method.

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