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On the Mechanism and Kinetics of the CO–Oxidation Reaction on Polycrystalline Palladium

II. The Kinetics[1]

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The kinetics of the oxidation of carbon monoxide have been studied extensively over polycrystalline palladium foils which were prepared by exposure to relatively large amounts of oxygen at high temperatures. Reaction orders with respect to CO_2, CO and O_2 were determined over various intervals of partial pressure, total pressure and temperature; $0.1 \leqslant p_{CO}/p_{O_2} \leqslant 20$, $10^{-7} < p < 10^{-3}$ Pa, and $450 < T < 873$ K. The order with respect to CO_2 was zero under all the conditions tested. The orders with respect to O_2 and CO depended on the partial pressure ratio and showed very little dependence on total pressure. For $p_{O_2} < p_{CO}$ the rate was first order in oxygen and negative 0.5 to 0.8 order in CO below 473 K. When $p_{O_2} > p_{CO}$ in this temperature range, the orders with respect to oxygen and carbon monoxide were zero and unity respectively. The inhibitory effect of CO vanished at $T = 573$ K. In this case the orders were the same as above except when $p_{O_2} < p_{CO}$ the order with respect to CO was zero. The amount of adsorbed oxygen was measured under working conditions at 473 K using a CO-titration method. For $p_{O_2} > p_{CO}$, the amount of adsorbed oxygen is almost independent of p_{O_2}. The amount decreases sharply around $p_{O_2} = p_{CO}$ and is very small for $p_{O_2} < p_{CO}$. The kinetic behaviour can be explained in terms of a change in the rate determining step, depending on the amount of adsorbed oxygen.

I. INTRODUCTION

Several investigations of the overall reaction rate kinetics have been carried out in the case of oxidation of carbon monoxide over palladium (*1*–*8*). At high pressures (*2*–*7*) there is general agreement that the rate is proportional to oxygen pressure p_{O_2} and that the reaction is inhibited by adsorption of CO. Furthermore, the rate shows a strong dependence on substrate temperature.

At low pressures Ertl and co-workers have published several papers on this reaction (*8*–*11*) which discuss the kinetics of CO_2 formation in terms of an Eley–Rideal mechanism with some participation of a Langmuir–Hinshelwood mechanism under certain conditions. For a variety of single-crystal planes, (100), (110), and (111), and for polycrystalline wire they found no significant difference in the catalytic activity as a function of temperature and composition. Therefore, structural factors related to crystallographic orientation appear to be of minor importance for this catalytic system.

Close and White (*12*) have studied the reaction at low pressures using polycrystalline ribbon that was exposed to large amounts of oxygen prior to use. Their measurements suggest that relatively large amounts of oxygen are incorporated into the substrate in this process and that a

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catalytically stable substrate for this reaction probably involves a considerable amount of nonstoichiometric oxide near the substrate surface. This is consistent with the Auger spectra obtained by Ertl and Koch (*9*). Close and White (*12*) found that the reaction obeys three distinct rate laws depending on the temperature. Their results were limited in the sense that the partial pressure ratio p_{CO}/p_{O_2} was not varied systematically over a range wide enough to reveal any important dependence on composition. Our goal in the present work has been to thoroughly characterize the kinetics of the low-pressure CO-oxidation reaction in the three temperature regions reported by them: (1) below 473 K, (2) 473–700 K, and (3) above 700 K.

In these three regions our results show the order with respect to CO and O_2 depends on the partial pressure ratio as well as the temperature. The rather complicated kinetic phenomena can be explained using the amount of oxygen adsorbed under working conditions and by considering a change in the rate-determining step which is related to the amount of adsorbed oxygen which decreases sharply for $p_{CO} \geqslant p_{O_2}$. The amount of adsorbed oxygen in the course of the reaction was determined using methods outlined earlier (*13*). Our results, where comparable, are in general agreement with the work of Ertl and co-workers (*8–11*).

II. EXPERIMENTAL METHODS

The experimental apparatus and procedures were essentially the same as those reported previously (*12–13*). The palladium ribbon was exposed to 10^{-4} Pa of oxygen at 900 K for several hours prior to use. This conditioning procedure leaves a catalyst which is stable in the sense that CO_2 production rates are stable and reproducible.

In most of the experiments described in this paper the system was operated at steady-state. At a constant substrate temperature and constant partial pressures of CO and O_2, the CO_2 production was monitored mass spectrometrically. The observed $m/e = 44$ signal is proportional to the CO_2 production rate since the system is pumped continuously.

In other experiments the amount of adsorbed oxygen was determined under working conditions using transient CO_2 spectra induced by applying a large dose of carbon monoxide or by terminating the oxygen flow. These methods of procedure and analysis have been outlined in the previous paper (*13*).

All of these experiments utilize hot filament electron supplies in the ionization gauge and mass spectrometer. There is some background reaction on these filaments which, being independent of the substrate temperature, was determined separately with the substrate at room temperature and subtracted from measurements made at operating temperatures. Since the extent of background conversion varies with total pressure and partial pressure, a background measurement must be made for every operating condition.

III. RESULTS

1. Reaction Order with Respect to CO_2

It has generally been assumed that CO_2 interacts so weakly with the kind of catalytic surface employed here that the partial pressure of CO_2 exerts no influence on the rate of the reaction. In at least one case however CO_2 has been reported as adsorbing on PdO (*14*). We have determined the order of the CO_2 production rate with respect to the partial pressure of CO_2 under conditions similar to those reported below which were used to determine the dependence on O_2 and CO. Typical data are shown in Fig. 1 for 450 and 573 K and these plots show no variation in the rate of CO_2 production as the background pressure of CO_2 is increased over the range

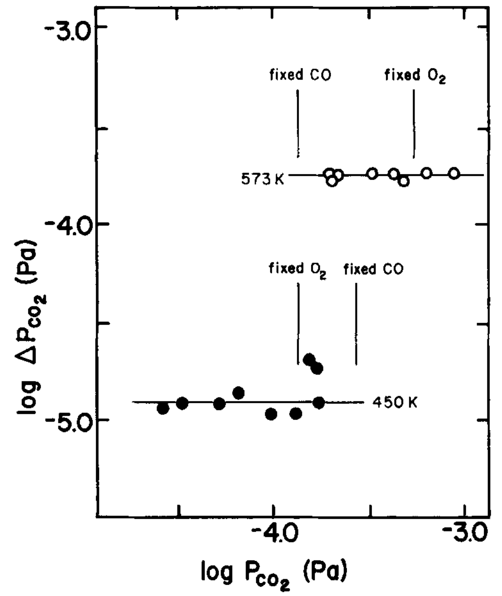

FIG. 1. Variation of the rate of CO_2 production with CO_2 pressure at fixed O_2 and CO pressures. The vertical lines indicate the fixed pressures at the two temperatures 450 and 573 K.

10^{-5}–10^{-3} Pa. Thus the reaction is zero order with respect to CO_2. Table 1 summarizes CO_2 reaction orders for a wide variety of situations at 450 and 573 K. Within experimental error, the reaction order is always zero. Based on these results we have determined reaction orders with respect to CO and O_2 by varying either the oxygen or carbon monoxide partial pressure with no attention given to the carbon dioxide pressure.

TABLE 1

REACTION ORDER WITH RESPECT TO CO_2

T (K)	Fixed pressures (10^{-4} Pa) CO	O_2	Range of CO_2 pressure (10^{-4} Pa)	Order
450	1.3	1.3	0.012–0.12	-0.06 ± 0.18
450	1.3	1.3	0.6–5.2	0.0
450	2.6	1.3	0.3–1.7	0.0
450	1.3	5.2	0.6–2.4	-0.07 ± 0.20
573	1.3	1.3	2.0–6.5	0.0
573	2.6	1.3	2.4–7.8	0.0
573	1.3	5.2	2.0–7.8	0.0

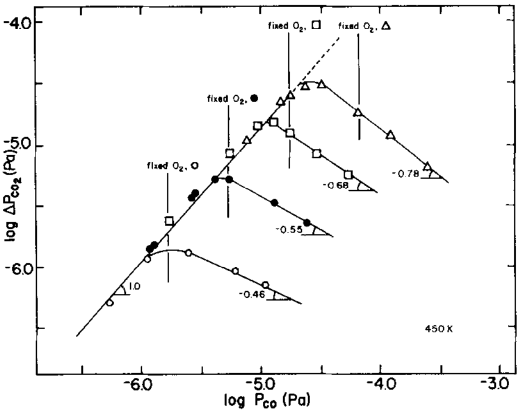

FIG. 2. Variation of the rate of CO_2 production with CO pressure at 450 K and various fixed oxygen pressures. The vertical bars indicate the fixed oxygen pressures and the reaction orders with respect to CO are indicated along the linear portion of each curve. 1.7×10^{-6} Pa (○); 5.3×10^{-6} Pa (●); 1.9×10^{-5} Pa (□); and 6.65×10^{-5} Pa (△).

2. *Reaction Order with Respect to CO*

Figures 2–5 summarize the measured CO_2 formation rates as a function of CO pressure for several fixed temperatures and several fixed oxygen pressures. The reaction orders with respect to carbon monoxide are shown for each linear portion of the figures. The measured rates are independent of the sequence of pressures

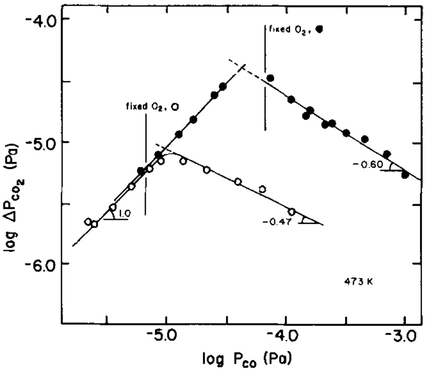

FIG. 3. Variation of the rate of CO_2 production with CO pressures at 473 K and two fixed oxygen pressures: 6.71×10^{-7} Pa (○); and 6.65×10^{-5} Pa (●). Reaction orders are indicated on the linear portion of each branch of the curves.

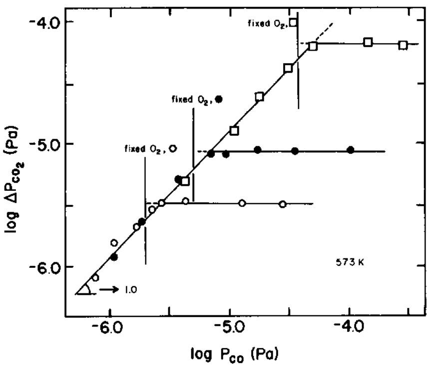

FIG. 4. Variation of the rate of CO_2 production with CO pressure at 573 K and three fixed oxygen pressures: 2.0×10^{-6} Pa (○); 5.05×10^{-6} Pa (●); and 3.7×10^{-5} Pa (□). There is a zero order dependence at high CO pressure and a first order dependence at low CO pressure in each case.

used with a substrate prepared as described in Sect. II.

These figures are all characterized by a first order dependence when p_{CO} is less than p_{O_2} and by a sharp break when $p_{CO} \simeq p_{O_2}$. Above the break where $p_{CO} > p_{O_2}$, the observed orders depend on the temperature and the pressure. At 473 K and below, the high pressure region, $p_{CO} > p_{O_2}$, is characterized by negative orders which measure the extent of inhibition of the reaction by carbon monoxide. According to Fig. 2, the magnitude of these negative orders is larger when the carbon monoxide and oxygen pressures are relatively high. In light of the discussion below, most of this change is due to variation in CO(a) which is controlled by p_{CO}. At 573 K there is no longer inhibition in the high pressure region; rather, the zero order dependence noted in Fig. 4 indicates a saturation condition which is reactive. At even higher temperatures, 873 K, the break still occurs but there is neither saturation nor inhibition; as the carbon monoxide pressure increases the reaction order passes from unity to 0.45 when the oxygen and carbon monoxide pressures are about equal. The CO_2 production rate depends strongly on temperature in the same fashion as observed by others (*8–12*). There is a sharp onset beginning near 450 K, a maximum near 470 K, and a slow decline of the rate at higher temperatures.

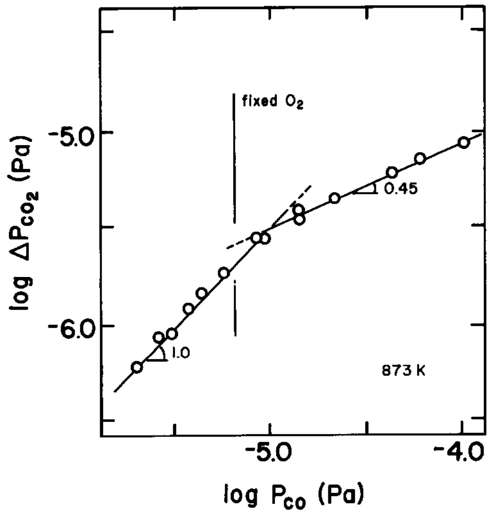

FIG. 5. Variation of the CO_2 production rate with CO pressure at 873 K and a fixed O_2 pressure of 6.7×10^{-6} Pa. Orders are indicated along the two linear portions.

These results clearly break into the three temperature regions reported by Close and White (*12*) for $p_{CO} > p_{O_2}$. At temperatures below 473 K they found negative orders with respect to CO. Between 473 and 700 K they reported a first order dependence on CO while at high temperatures above 700 K they found a half-order dependence on CO. Excepting the intermediate temperature region our data agree quantitatively. At 573 K where we found a zero order dependence on CO, Close and White (*12*) reported a first order dependence. Unfortunately they did not have independent control of the CO and O_2 partial pressures and chose to work with $p_{CO}/p_{O_2} \simeq 1$. The latter choice was particularly unfortunate since the order undergoes a drastic change near this pressure ratio. The turnover from positive to negative order is an interesting phenomenon which has been noted on Pt (*15*) for the CO-oxidation reaction. Our results at 573 K are

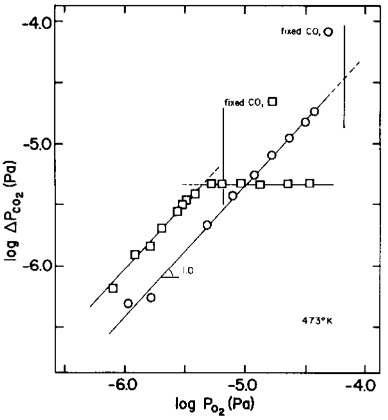

FIG. 6. Variation of the CO_2 production rate with O_2 pressure at 473 K and fixed CO pressures of 6.7×10^{-6} Pa (□) and 6.7×10^{-5} Pa (○). As indicated the low pressure regions are both first order. The high pressure region for the 6.7×10^{-6} Pa case is zero order.

in agreement with the data of Ertl and coworkers at 523 K (*8–10*).

3. Reaction Order with Respect to O_2.

Holding the carbon monoxide pressure constant, we determined the order of the carbon dioxide production with respect to oxygen at 450, 473, 573 and 873 K. The results excepting 450 K are graphically displayed in Figs. 6–8. The data for 450 K are not shown since they are nearly identical to those at 473 K. Like carbon monoxide, the oxygen dependence shows a sharp break when the CO and O_2 pressures are approximately equal. For $p_{O_2} < p_{CO}$ the order with respect to oxygen is unity at all temperatures we studied except 873 K where the order drops to 0.68. When p_{O_2} is somewhat larger than p_{CO}, the order drops to zero in every case indicating a saturated surface but one which is quite reactive. The data given here for 473 and 573 K are in excellent agreement with that of Ertl and co-workers at 523 K (*8–10*).

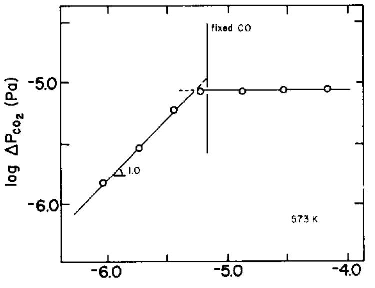

FIG. 7. Variation of the CO_2 production rate with O_2 pressure at 573 K and a fixed CO pressure of 6.7×10^{-6} Pa. The system shows first order behavior at low pressure and zero order behavior at high pressure.

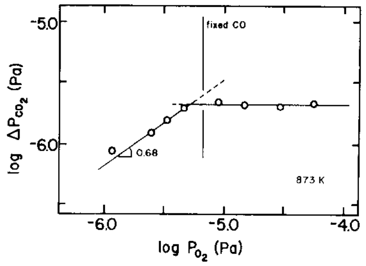

FIG. 8. Variation of CO_2 production rate with O_2 pressure at 873 K and a fixed CO pressure of 6.7×10^{-6} Pa. The low pressure region is 0.68 order with respect to O_2 while the high pressure region is zero order.

IV. THE AMOUNT OF ADSORBED OXYGEN

In the preceding paper (*13*) it was concluded that the oxidation reaction occurs by two major reaction paths depending on the experimental conditions. In some cases an Eley–Rideal process, $CO(g) + O(a) \rightarrow CO_2(g)$, predominates while in others a Langmuir–Hinshelwood process, $CO(a) + O(a) \rightarrow CO_2(g)$, is most important. In either case it is kinetically important to determine the amount of adsorbed oxygen. Two methods of analysis are available (*13*), one useful at high pressures, the other at low. In the latter, O(a) is titrated by applying a large dose of CO and measuring the total amount of CO_2 produced. In the former, analysis of the CO_2 decay after terminating the oxygen flow provides the amount of adsorbed oxygen.

Figure 9 shows, for three fixed CO pressures, how the amount of adsorbed oxygen

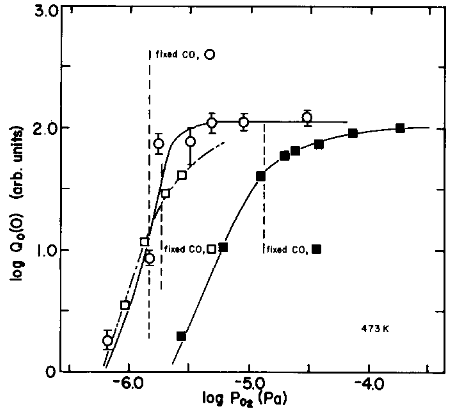

FIG. 9. The variation of the amount of adsorbed oxygen with ambient oxygen pressure at 473 K and several fixed CO pressures, 1.5×10^{-6} Pa (○); 1.9×10^{-6} Pa (□); and 1.3×10^{-5} Pa (■). The data at 1.5×10^{-6} Pa were obtained by the CO titration method, whereas the other two sets were obtained from analysis of CO_2 decay curves.

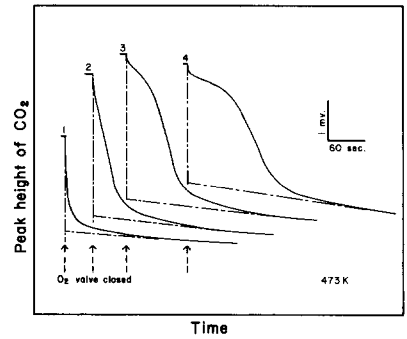

FIG. 10. Details of the CO_2 decay curves plotted in Fig. 9 as open squares. Origins are arbitrarily shifted in time for better viewing. At the vertical broken line the oxygen flow was terminated in each case. Peak areas were determined by the decay curve and the broken boundaries shown. For each case the O_2 dose was for 420 s with the substrate at 473 K. The oxygen pressures were as follows: (1) 9.3×10^{-7} Pa; (2) 1.3×10^{-6} Pa; (3)2.0×10^{-6} Pa; and (4) 2.8×10^{-6} Pa.

under working conditions, Q_0(O), varies with the ambient oxygen pressure. Both methods of analysis were employed. The open circles were determined by titration while the open and filled squares were determined by analysis of decay curves. In the titration method a steady-state CO–O_2–CO_2 system was established at 473 K. Then oxygen flow was terminated and after a variable period the carbon monoxide pressure was increased about two orders of magnitude. The amount of CO_2 produced was measured as the area beneath the transient CO_2 versus time curve. Extrapolation gives Q_0(O). In the decay curve analysis method, the steady-state CO–O_2–CO_2 system was established after which the oxygen flow was terminated. The CO_2 decay was carefully monitored afterward. Figure 10 shows how the CO_2 pressure varied after a 420 s and 473 K oxygen dose at various pressures where the CO pressure was fixed at 1.9×10^{-6} Pa. The area beneath the curves, which is bounded on the left and bottom by the borken lines, clearly increases with oxygen pressure. These areas are plotted in Fig. 9 as open squares.

Comparing the open circles and squares in Fig. 9 indicates the generally good agreement between the two methods. The decay curve method is subject to more error than the titration method under conditions where both can be used and in general the decay curve area determination underestimates the amount of surface oxygen (*13*). Nevertheless, such data can be used in a semiquantitative sense.

The filled squares in Fig. 9 show the amount of adsorbed oxygen at 473 K when the CO pressure is raised to 1.3×10^{-5} Pa. The saturation amounts do not vary between 10^{-6} and 10^{-5} Pa, however the oxygen pressure required to reach saturation increases with the carbon monoxide pressure. The saturation point is reached when the CO and O_2 pressures are about equal. Using as a standard the maximum amount of CO adsorbed as determined by flash desorption, the saturation level shown in Fig. 9 is about a monolayer. When p_{O_2} drops below p_{CO} the amount of adsorbed oxygen rapidly diminishes.

V. DISCUSSION

Kinetic Behavior in Terms of Adsorbed Oxygen

The data reported in Sect. III strongly suggests that a change in the rate-determining step occurs when the pressure ratio p_{CO}/p_{O_2} is changed from a value below to a value above unity. The data of Sect. IV facilitates understanding the kinetic behavior of the overall reaction rate. At 450 and 473 K and under conditions where $p_{O_2} > p_{CO}$, the surface is covered fully with O(a). Recalling that CO(a) is readily replaced by O(a) at the temperature used in our experiments here (*13*), we know that when O(a) is large CO(a) is small (*16*). Under these conditions the reaction proceeds through an Eley–Rideal process involving CO(g) and O(a). The rate-determining step in this reaction path is the collision rate of CO with the oxygen-saturated surface. The key steps are

$$O_2 \rightarrow 2O(a),$$
$$CO(g) + O(a) \rightarrow CO_2(g),$$

with the latter rate-determining. Thus the reaction is first order in CO and zero order in O_2.

On the other hand, when $p_{O_2} < p_{CO}$ the oxygen adsorption data shows that the amount adsorbed is markedly less than the saturation amount. The surface is then partially covered with CO (*16*), and $CO(a) \gg O(a)$. Two reaction paths, the Eley–Rideal and Langmuir–Hinshelwood processes (*13*), become available in principle since the amount of CO(a) is significant and both processes occur readily at these temperatures. The reactions of interest are:

$$CO(g) \rightleftarrows CO(a),$$
$$O_2(g) \rightarrow 2O(a),$$
$$CO(a) + O(a) \rightarrow CO_2(g),$$
$$CO(g) + O(a) \rightarrow CO_2(g).$$

Under a significant oxygen pressure below 473 K, adsorbed carbon monoxide can be desorbed as CO_2 via the Langmuir–Hinshelwood process rather than desorption as CO (*11,17*). This process can thus contribute to the CO_2 production rate along with the Eley–Rideal process (9). It also bears importantly on the discussion of CO inhibition (see below) because it participates in the removal of CO(a). The amount of adsorbed oxygen is much smaller than CO(a) implying that the oxygen adsorption rate is smaller than the consumption rate of O(a) by reaction with CO(a) and CO(g). Hence O(a) cannot accumulate at the surface and the oxygen adsorption step is rate limiting for CO_2 formation. Thus the reaction should be first order in oxygen as observed and the rate law takes the form:

$$R = kp_{O_2}p_{CO}{}^{\alpha}.$$

We have already shown (*13*) that below 393 K the rate of the reaction $O_2(g) + CO(a) \rightarrow CO_2 + O(a)$ is very slow and CO(a) prevents adsorption of oxygen. The negative order with respect to CO reported here at temperatures up to 473 K is consistent with the idea that higher CO pressures give larger amounts of CO(a) which lowers the amount of surface area available for oxygen. In recent work (*16*) we have found that CO(a) under working conditions of the substrate is very small for $p_{CO} < p_{O_2}$ while it is significant, for temperatures below 450 K, when $p_{CO} > p_{O_2}$. The magnitude of the negative order depends on the quantitative amount of adsorbed carbon monoxide.

Above 523 K, CO does not adsorb on palladium and our results at 573 K and higher show that inhibition by CO does not occur when $p_{CO} > p_{O_2}$. Under these conditions both CO(a) and O(a) are very small. The experimental data still imply that the adsorption of oxygen is the rate-determining step since the kinetics give a first order dependence on O_2 and a zero order dependence on CO.

At 573 and 873 K when $p_{CO} < p_{O_2}$, our data indicate the same kinetics as for lower temperatures, i.e., zero order with respect to oxygen and first order with respect to carbon monoxide. The reaction path is therefore attributed to the Eley–Rideal process. For the case $p_{CO} > p_{O_2}$ at 873 K, no simple kinetic pathway can be assigned. At this temperature oxygen previously incorporated into the substrate probably begins to be released to the surface where it either reacts or desorbs. Other processes such as the dissociative adsorption of CO and subsequent reactions of the resulting adsorbed species may also occur. The data of Close and White (*12*) appear to indicate that oxygen uptake continues to occur even at temperatures up to about 973 K. This interesting, but complex problem is presently being investigated in detail. The rate measured at 873 K is much smaller than at 573 K and follows closely the data of Close and White (*12*).

The CO Inhibition Effect

Our experiments show that at low temperatures and for $p_{CO} > p_{O_2}$ the overall CO_2 production rate is retarded by increases in the pressure of carbon monoxide. This inhibition is attributed to adsorption of CO which lowers the available surface area for oxygen adsorption, the latter being needed for carbon dioxide production. The amount of O(a) is determined kinetically, depends on the rate of O_2 adsorption and the rate of loss of O(a) through the reactions $CO(a) + O(a) \rightarrow CO(g)$ and $CO(g) + O(a) \rightarrow CO_2(g)$, and is very small compared to CO(a). The inhibition becomes larger as the temperature decreases not because the heat of adsorption of CO is larger than that of oxygen, since just the reverse is true (*8,18*). Rather, it arises because the reaction $CO(a) + O(a) \rightarrow CO_2(g)$, which plays a role in eliminating CO(a) from the surface, is slow as compared with the reaction $CO(g) + O(a) \rightarrow CO_2(g)$. The latter needs little, if any, activation energy while at low temperatures the former requires a significant activation energy (*4,11,13,17*). At low temperatures the reaction $O_2(g) + CO(a)$ does not occur (*13*). Thus the surface becomes covered with CO(a) and the reaction to produce CO_2 is very slow. As the temperature is increased to values above 400 K there is a significant decrease in the amount of adsorbed CO and the reaction CO(a) + O(a) occurs readily. Since the relative amounts of CO(a) and O(a) are controlled by the ratio p_{CO}/p_{O_2}, there is an inhibitory effect when $p_{CO} > p_{O_2}$. This is observed in our experiments at 450 and 473 K. The reaction $O_2(g) + CO(a)$ may occur at these temperatures but it is too slow to overcome the inhibition by CO. At 573 K and above, carbon monoxide does not adsorb, the reaction CO(a) + O(a) does not occur, and the inhibition effect vanishes. The above observations mean that the CO adsorption isotherm under working conditions will differ significantly from the isotherm obtained using CO alone (*16*).

For the situation where $p_{O_2} > p_{CO}$ the rate is limited by the reaction $CO(g) + O(a) \rightarrow CO_2(g)$ (*13*) which has at most a very small activation energy. This is confirmed by the fact that the overall rates at 450, 473, and 573 K are almost equal when $p_{O_2} > p_{CO}$ and p_{CO} is fixed at the same value for all three temperatures.

SUMMARY

The catalytic oxidation of CO over polycrystalline palladium substrates which were previously exposed to large amounts of oxygen has been investigated over the temperature range 450 to 873 K using a variety of pressure ratios, $0.1 \leq p_{CO}/p_{O_2} < 20$, and total pressures 10^{-7}–10^{-3} Pa.

The order with respect to CO_2 was determined to be zero at 450 and 573 K. At 450 and 473 K two rate laws are operative. For $p_{O_2} < p_{CO}$ the rate was first order in oxygen and negative 0.5 to 0.8 order in carbon monoxide depending on the oxygen partial pressure. When $p_{O_2} > p_{CO}$ the reaction was first order in CO and zero order in O_2.

At 573 K the same rate laws apply except the inhibitory effect of CO vanished

for $p_{O_2} < p_{CO}$ and the order with respect to CO became zero. At 873 K the low temperature kinetics scheme is still valid for $p_{O_2} > p_{CO}$. When $p_{O_2} < p_{CO}$ the orders with respect to CO and O_2 are 0.45 and 0.68, respectively. The observed kinetic behavior can be explained in terms of a change in rate-determining step, depending on the amount of adsorbed oxygen. The amount of adsorbed oxygen under working conditions was determined using a titration method and a CO_2 decay method (*13*).

REFERENCES

1. McKinney, P. V., *J. Amer. Chem. Soc.* **54,** 4498 (1932).
2. Baddour, R. F., Modell, M. K., and Heusser, V. K., *J. Phys. Chem.* **72,** 3621 (1968).
3. Baddour, R. F., Modell, M., and Goldsmith, R. L., *J. Phys. Chem.* **74,** 1987 (1970).
4. Daglish, A. G., and Eley, D. D., *Proc. Int. Congr. Catal., 2nd, 1960,* **2,** 1615 (1961).
5. Schwab, G. M., and Gossner, K., *Z. Phys. Chem. N. F.* **16,** 39 (1958).
6. Tajbl, D. G., Simons, J. B., and Carberry, J. J., *Ind. Eng. Chem. Fundam.* **5,** 171 (1966).
7. Langmuir, I., *Trans. Faraday Soc.* **17,** 621 (1922).
8. Ertl, G., and Kau, P., *Surface Sci.* **15,** 443 (1969).
9. Ertl, G., and Koch, J., *Z. Phys. Chem. N.F.* **69,** 323 (1970).
10. Ertl, G., and Koch, J., *Proc. Int. Congr. Catal., 5th, 1972* p. 969 (1973).
11. Ertl, G., and Neumann, M., *Z. Phys. Chem. N.F.* **90,** 127 (1974).
12. Close, J., and White, J. M., *J. Catal.* **36,** 185 (1975).
13. Matsushima, T., and White, J. M., *J. Catal.* **39,** 265 (1975).
14. McKinney, P. V., *J. Amer. Chem. Soc.* **55,** 3626 (1933).
15. Bonzel, H. P., and Ku, R., *J. Vac. Sci. Technol.* **9,** 663 (1971).
16. Mussett, C., Matsushima, T., and White, J. M., unpublished data.
17. Matsushima, T., and White, J. M., unpublished data.
18. Ertl, G., and Koch, J., "Adsorption–Desorption Phenomena" (F. Ricca, Ed.), p. 345. Academic Press, New York, 1972.