

The Adsorption of Carbon Monoxide on Palladium during the Catalyzed Reaction $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$ ¹

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The amount of carbon monoxide adsorbed on palladium in the course of the catalyzed reaction, $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$ at 450 K was determined through analysis of the transient CO_2 formation which occurs following a carbon monoxide pressure jump. The results were compared with CO adsorption data obtained by flash desorption. The results of the two methods are in good accord. The amount of CO adsorbed when $p_{\text{CO}} > p_{\text{O}_2}$ is almost equal to that determined in the CO/Pd equilibrium system (nonworking conditions). A sharp decrease in CO(a) is noted around $p_{\text{CO}} \simeq p_{\text{O}_2}$ and CO(a) becomes very small when $p_{\text{CO}} < p_{\text{O}_2}$. The inhibitory effect of CO(a) on the steady-state CO oxidation reaction is discussed on the basis of these CO adsorption isotherms determined under working conditions.

I. INTRODUCTION

The adsorption of carbon monoxide on palladium has been the subject of numerous investigations (1) using several methods, i.e., infrared spectroscopy (2-7), flash desorption (8-12), work function measurements (8-11), LEED (8-11, 13-15), and electrical resistance measurements (15-17). One of the major reasons for the widespread use of CO in adsorption problems is that it is adsorbed reversibly and nondissociatively at relatively low temperatures (1-17). A second impetus for the investigation of the adsorption-desorption behavior of CO over Pd is the well-known inhibitory effect of adsorbed CO on the catalyzed reaction $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$ (6, 8, 9, 12, 14, 18-23). With a few exceptions (6, 7), all the adsorption studies utilize no gas-phase oxygen other than background, i.e., a CO/Pd system under nonworking conditions.

Recently the kinetics of the CO oxidation reaction on Pd under low pressures have been studied extensively (8, 9, 12, 14, 23-26). The CO-inhibition effect appears only when $p_{\text{CO}} > p_{\text{O}_2}$ and at 450-473 K (23). The inhibition effect probably extends below 450 K; however, it vanishes above about 523 K (14, 23). The amount of adsorbed oxygen during the course of the reaction, i.e., a CO/O₂/Pd system, (i) is constant independent of p_{O_2} when $p_{\text{O}_2} > p_{\text{CO}}$, (ii) decreases sharply around $p_{\text{O}_2} = p_{\text{CO}}$, and (iii) is very small for $p_{\text{O}_2} < p_{\text{CO}}$ (23). Taken together these results suggest that the CO adsorption isotherm for a catalytically active CO/O₂/Pd system probably differs significantly from that for the CO/Pd system.

CO adsorption in a CO/O₂/Pd system has been compared with that for a CO/Pd system by Ertl and Neumann (24), using laser-induced thermal desorption. Their results however were restricted to fixed pressures of CO and O₂ and to conditions

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where the difference in the coverage of the two systems was small.

The purpose of this work was to determine the amount of adsorbed carbon monoxide, CO(a), during the course of the CO oxidation reaction and for various partial pressure ratios. Both a flash desorption technique (12) and a pressure jump method (24-27) were used. Experimental data from the two methods are in good agreement. In Section II, the experimental techniques are briefly presented. The results and discussion are presented in Sections III and IV, respectively. Briefly at 450 K we find that: (i) when $p_{\text{CO}} > p_{\text{O}_2}$ the amount of adsorbed carbon monoxide is relatively large and nearly equal to that obtained for a CO/Pd system, (ii) CO(a) decreases sharply around $p_{\text{CO}} \simeq p_{\text{O}_2}$ and (iii) CO(a) is very small when $p_{\text{CO}} < p_{\text{O}_2}$. The magnitude of the CO-inhibition effect (23) is discussed in terms of these isotherms in Section IV.

II. EXPERIMENTAL

The experimental apparatus and procedures were essentially the same as those reported previously (12, 23, 25, 26). The system was a bakeable ultrahigh vacuum apparatus such that the base pressure achieved was less than 2×10^{-7} Pa. The pressures, total and partial, were monitored with a Bayard-Alpert-type ionization gauge and a quadrupole mass spectrometer. During experimentation the system was continuously pumped by an ion pump.

The substrate was a Pd foil. Prior to the experiments it was exposed to 10^{-4} Pa of oxygen at 1000 K to establish a stable catalyst (12). During a series of measurements, the oxygen-exposed substrate was heated to 1000 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. Resistive heating was used to vary the substrate temperature.

III. RESULTS

III.1. CO Adsorption in a CO/Pd System

To determine CO adsorption isotherm for nonworking conditions a flash desorption technique was used. The flowing CO/Pd system was allowed to reach equilibrium at some temperature between 298 and 450 K after which the substrate was heated to 773 K while monitoring the CO peak. The observed peak shape is equivalent to that reported earlier (9, 12). The area under the CO peak is proportional to the amount of CO(a). In order to compare these data in which CO was detected with results given below in which CO_2 was detected, the mass spectral data were adjusted for relative sensitivities. The results at various temperatures are shown in Fig. 1. The coverage θ_{CO} was defined as the area of the CO peak relative to the maximum area which was obtained by flashing from room temperature. The maximum value is independent of p_{CO} as shown in Fig. 1. These data are in general agreement with those reported in the literature (8, 10, 11).

III.2. CO Adsorption with a CO/O₂/Pd System: Flash Desorption

A steady-state flowing CO/O₂/Pd system was established at 450 K and then the substrate was heated while monitoring the CO peak. Afterward the system was returned to the same steady state condition and the CO_2 peak was recorded during a second flash desorption experiment.

Figure 2 shows CO and CO_2 transients generated by flash desorption originating from several 450 K steady states (i.e., at 450 K, steady CO, O_2 , and CO_2 pressures were achieved and then the system was

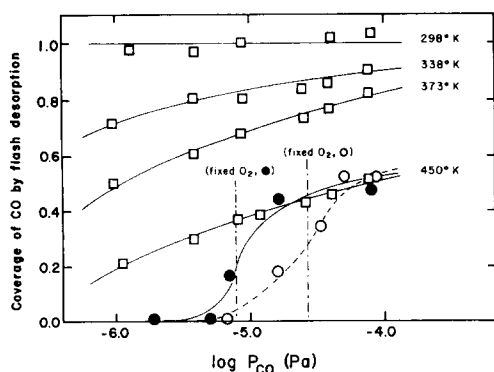


FIG. 1. CO adsorption isotherm determined by flash desorption in the presence and absence of oxygen. (\square), Without oxygen at the various temperatures shown; (\bullet), with 7.74×10^{-6} Pa of oxygen at 450 K; (\circ), with 2.67×10^{-5} Pa of oxygen at 450 K.

flushed). The decrease of background CO pressure after the peak is due to the reaction $\text{CO}(\text{g}) + \text{O}(\text{a}) \rightarrow \text{CO}_2$ (23, 25). The desorption of CO is nearly complete around 673 K, and the arrows in Fig. 2 show the position of this temperature. The CO_2 peak consists of two parts. The first part begins at relatively low temperatures and ends around 673 K. It is attributed to interactions between $\text{CO}(\text{g})$ and $\text{O}(\text{a})$ and between $\text{CO}(\text{a})$ and $\text{O}(\text{a})$ (23, 25, 26). The CO_2 formed at higher temperatures is attributed solely to interaction between $\text{CO}(\text{g})$ and $\text{O}(\text{a})$ (23, 25). Therefore, the decrease in CO background noted in Fig. 2 should equal the increase in CO_2 background. The dashed lines of Fig. 2 are arbitrarily drawn as a point-by-point reference line for constructing a mirror image of the CO_2 production curve.

To obtain a measure of the $\text{CO}(\text{a})$ at the instant when the flash desorption began, it is necessary to account properly for three kinds of processes which influence the observed CO spectrum: (i) desorption of CO, (ii) reactions of adsorbed CO, and (iii) reactions of gas phase CO. Let us first suppose, for the sake of discussion, that reactions of $\text{CO}(\text{g})$ to produce CO_2 do not occur during heating. Then, since

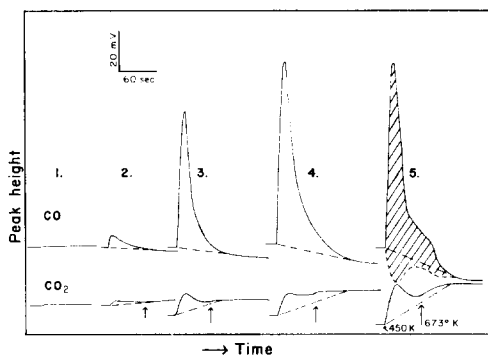


FIG. 2. Flash desorption peaks of CO and CO_2 induced by heating the substrate from a kinetic steady state at 450 K to a final temperature of 773 K. The steady-state pressures (in pascals) of CO, O_2 , and CO_2 for each pair of peaks are as follows in the form $\{p_{\text{CO}}, p_{\text{O}_2}, p_{\text{CO}_2}\}$: (1) 1.83×10^{-6} , 7.6×10^{-6} , 3.46×10^{-6} ; (2) 6.94×10^{-6} , 8.0×10^{-6} , 1.45×10^{-5} ; (3) 2.67×10^{-5} , 7.65×10^{-6} , 1.01×10^{-5} ; (4) 8.67×10^{-5} , 7.74×10^{-6} , 8.0×10^{-6} ; (5) 4.93×10^{-5} , 2.67×10^{-5} , 1.05×10^{-5} .

neither CO nor CO_2 remains adsorbed on Pd at these temperatures (23), the amount of adsorbed CO would be given by the sum of the CO peak and the CO_2 peak in Fig. 2. Now let us remove the restriction stated above. Reactions of $\text{CO}(\text{g})$ to produce CO_2 will increase the CO_2 peak and reduce the CO peak by equal amounts, so that the sum of these two (the cross-hatched area of curve 5 in Fig. 2) will still give correctly the amount of initially adsorbed CO. Parenthetically, the above argument applies to mass spectrometer signals which have been adjusted for relative sensitivities.

From Fig. 2 we note that when p_{CO} is smaller than p_{O_2} , the areas of the CO and CO_2 peaks are very small; thus, $\text{CO}(\text{a})$ is very small. For $p_{\text{CO}} > p_{\text{O}_2}$, both CO and CO_2 peaks increase with p_{CO} ; however, the area of the CO peak is much larger than that of CO_2 . The amounts of $\text{CO}(\text{a})$ determined as described above under a fixed p_{O_2} and various p_{CO} are plotted as open and closed circles in Fig. 1. As shown, θ_{CO} is very small for $p_{\text{CO}} < p_{\text{O}_2}$, increases sharply around $p_{\text{CO}} = p_{\text{O}_2}$, and approaches

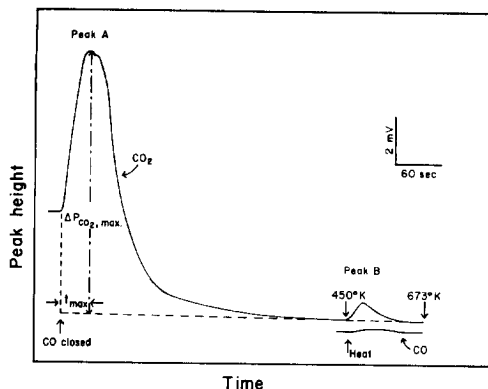


FIG. 3. Peak A, a typical transient in CO_2 formation induced by a pressure jump in CO at 450 K. The CO, O_2 and CO_2 pressures just before the CO valve was closed are 8.7×10^{-5} , 1.4×10^{-5} , and 7.8×10^{-6} Pa, respectively. Peak B, the CO_2 and CO peaks observed upon heating the substrate following completion of a CO_2 transient experiment, i.e., after reaching a steady state.

the value measured for the CO/Pd system when $p_{\text{CO}} > p_{\text{O}_2}$. Note the marked difference between the CO/Pd and the CO/ O_2 /Pd system when $p_{\text{CO}} < p_{\text{O}_2}$.

III.3. CO Adsorption with a CO/ O_2 /Pd System: Pressure Jump Method

It has been shown in a previous paper (26) that, at relatively low temperatures and during the course of the steady-state CO oxidation reaction, the amount of CO(a) can be determined by analyzing the transient CO_2 formation which occurs following a pressure jump in carbon monoxide. We have applied this method at 450 K and find the results reported below.

After establishing a steady-state flowing CO/ O_2 /Pd system, the CO valve was rapidly closed to induce a transient spectrum; the CO partial pressure dropped very rapidly while the formation rate of CO_2 increased slowly, went through a maximum, and finally decreased to a new steady value as shown in Fig. 3. The steady state achieved after the CO_2 transient was dictated by the background pressures of CO and O_2 . If, instead of closing the

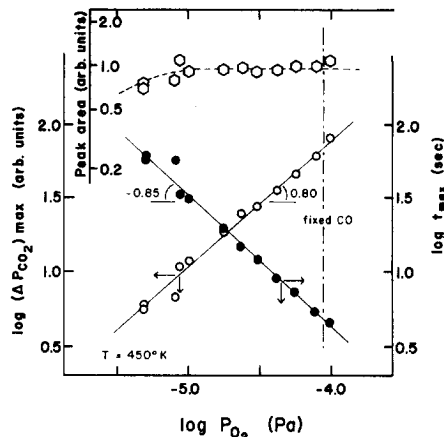


FIG. 4. Variations with O_2 pressure of the maximum peak height, $(\Delta p_{\text{CO}_2})_{\text{max}}$, the time, t_{max} , and the CO_2 peak area at 450 K. The CO pressure was fixed at 8.7×10^{-5} Pa. The (\bullet) , t_{max} ; (\circ) , $(\Delta p_{\text{CO}_2})_{\text{max}}$; (\square) , CO_2 peak area.

CO valve, the substrate was heated from the initial 450 K steady state, a significant amount of CO, but only a small amount of CO_2 , was desorbed when $p_{\text{CO}} \geq p_{\text{O}_2}$ (see Fig. 2). Thus, in the pressure jump experiments, the large pulse of CO_2 which appears after the CO valve was closed cannot arise from desorption of previously formed $\text{CO}_2(\text{a})$ and must be formed by the reaction of CO(a). From this we note the following: If at 450 K almost all the CO(a) is desorbed as CO_2 , rather than as CO, then the amount of CO(a) can be determined from the transient CO_2 peak area, peak A of Fig. 3.

In order to confirm this point, the dependence of the CO_2 peak area on p_{O_2} was examined at a fixed steady-state CO pressure (8.7×10^{-5} Pa). The results, shown in Fig. 4, are in agreement with those reported previously at lower temperatures (26). The magnitude and shape of the CO_2 peak are very sensitive to the flowing oxygen pressure. The maximum peak height, $(\Delta p_{\text{CO}_2})_{\text{max}}$, i.e., the difference between the maximum peak height and the final CO_2 background as drawn for peak A of Fig. 3, shows an order of 0.8 with

respect to p_{O_2} , whereas the time required to reach the maximum after the CO value was closed, t_{max} , depends on oxygen pressure with an order of -0.85 . For $p_{CO} \geq p_{O_2}$, the area under the CO_2 peak enclosed by dashed lines of Fig. 3 was constant independent of p_{O_2} except when $p_{O_2} \ll p_{CO}$.

When p_{O_2} was very small, there were considerable opportunities for making significant errors in computing the amount of CO(a), since the very broad peak became difficult to distinguish from the CO_2 background and since CO(a) was not entirely eliminated from the surface after the transient CO_2 peak appeared to reach the final steady state. The slight decreases in the peak area noted in Fig. 4 when $p_{O_2} \ll p_{CO}$ are attributed to these two effects.

The incomplete elimination of CO(a) merits further discussion. After the transient CO_2 peak appeared to reach the final steady state the substrate was heated to about 673 K, monitoring CO_2 and CO peaks. A typical result, shown as peak B in Fig. 3, indicates no measurable CO desorption, but a small amount of CO_2 is produced. Apparently, even after CO_2 appeared to reach a steady state, a small amount of adsorbed CO was still present. Upon heating, this CO(a) was desorbed as CO_2 through a Langmuir-Hinshelwood reaction, $CO(a) + O(a) \rightarrow CO_2$ (26). When p_{O_2} was larger than about 5.3×10^{-6} Pa, the area of peak B was insignificant compared to peak A. Thus, under these conditions, the elimination of CO(a) from the surface was complete prior to the formation of peak B. On the other hand, when p_{O_2} was smaller than 5.3×10^{-6} Pa, the CO_2 area of peak B became significant.

If at 450 K, a significant amount of CO(a) was desorbed as CO rather than CO_2 at least two things should occur: (i) the CO mass spectrum should show some structure due to CO desorption and (ii) the area of peak A of Fig. 3 should

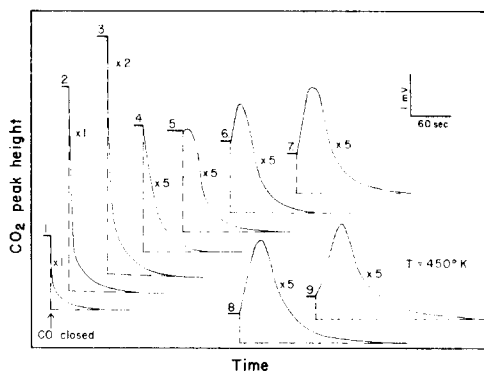


FIG. 5. Transient CO_2 formation observed under various CO pressures at a fixed p_{O_2} . Origins are arbitrarily shifted in time and height for better viewing. The oxygen pressure during the steady-state was 2.7×10^{-6} Pa. The CO pressure (in pascals) for each curve is: (1) 3.92×10^{-6} , (2) 7.70×10^{-6} , (3) 1.58×10^{-5} , (4) 2.24×10^{-5} , (5) 2.66×10^{-5} , (6) 3.70×10^{-5} , (7) 9.27×10^{-5} , (8) 1.61×10^{-4} , (9) 2.90×10^{-4} .

decrease with decreasing oxygen pressure. Neither is observed experimentally; there is no detectable structure in the CO decay, and the area of peak A is independent of p_{O_2} when it exceeds about 6×10^{-6} Pa. Thus the amount of CO(a) can be determined, even at temperatures as high as 450 K, by analysis of the areas of the CO_2 transients.

A series of experiments at a fixed O_2 pressure and various CO pressures was analyzed to ascertain how CO(a) varied with CO pressure according to the pressure jump method. The results are displayed in Fig. 5 with origins arbitrarily shifted for easier viewing. When $p_{CO} < p_{O_2}$, the CO_2 partial pressure decreased immediately after the CO flow was terminated. When p_{CO} approached p_{O_2} , the CO_2 decay curve showed a small shoulder which is indicative of a small amount of CO(a). When p_{CO} exceeded p_{O_2} , the CO_2 peaked and the peak area increased with increasing p_{CO} . The areas of these peaks, after correction for mass spectrometer sensitivities, are plotted in Fig. 6. The coverage is defined as the corrected area of the CO_2 peak

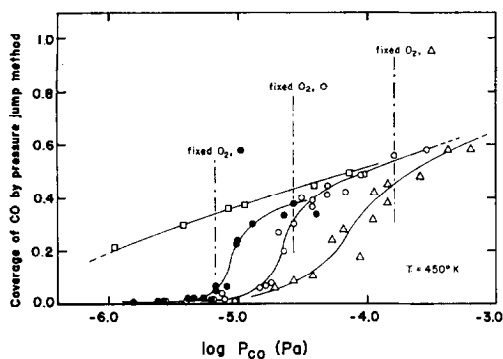


Fig. 6. Isotherms for CO adsorption as determined by the pressure jump method in the course of the CO oxidation reaction at 450 K. The fixed O_2 pressures are: (●), 6.7×10^{-6} Pa; (○), 2.69×10^{-5} Pa; and (Δ), 1.60×10^{-4} Pa. These curves are to be compared to the CO adsorption isotherm determined in the absence of oxygen (□) by the flash desorption method.

relative to the area of the CO desorption peak obtained by heating from room temperature (see Fig. 1). As Fig. 6 illustrates, for $p_{CO} > p_{O_2}$, θ_{CO} is almost identical with that observed in the CO/Pd system. The isotherm shown for the CO/Pd system was obtained by flash desorption as discussed earlier in this paper. For $p_{O_2} = 6.7 \times 10^{-6}$ and 2.7×10^{-5} Pa, note that CO(a) is very small when $p_{CO} < p_{O_2}$ and rises abruptly near $p_{CO} = p_{O_2}$ to the CO/Pd system result. At a higher O_2 pressure, 1.6×10^{-4} Pa, the increase in θ_{CO} begins much earlier with respect to the fixed O_2 pressure, and the region of increase is spread over a much broader range of CO pressures.

IV. DISCUSSION

Comparing Figs. 1 and 6 we note that the flash desorption and pressure jump methods yield results in excellent accord. When $p_{CO} > p_{O_2}$, CO(a) is relatively large and nearly equal to the amount adsorbed in the CO/Pd system. Over the region studied here, the CO coverage ranges from about 0.4 to 0.6 of that found by flash desorption from room temperature. Near

$p_{CO} = p_{O_2}$ we find, by both methods, a sharp decline in θ_{CO} to values near zero which persist as p_{CO} decreases to even lower values. As Figs. 1 and 6 both illustrate, the isotherms for the CO/ O_2 /Pd system under working conditions differ significantly from those for the CO/Pd system. Qualitatively, when CO(a) is large, the oxidation reaction occurs slowly and is inhibited by CO pressure. Contrariwise, when CO(a) is low, the reaction occurs readily and the rate increases with CO pressure. According to the isotherms then, when p_{O_2} is below 2.7×10^{-5} Pa and at $T = 450$ K, the CO inhibition effect will be observed in kinetic measurements only when $p_{CO} > p_{O_2}$. When the O_2 pressure increases to 1.6×10^{-4} Pa or greater, the CO inhibition effect will be noted even for p_{CO} significantly less than p_{O_2} . These predictions are in good agreement with the kinetic data reported earlier (23).

Under conditions of large CO(a), the rate of CO_2 formation is limited by O_2 adsorption (23) and should be proportional to p_{O_2} , and the available surface area for O_2 adsorption. The latter is determined by θ_{CO} , since previous data (23) on the CO/ O_2 /Pd system show that when $p_{CO} > p_{O_2}$, the amount of O(a) is much smaller than that of CO(a). The available surface area for oxygen adsorption should decrease as θ_{CO} increases. By plotting logarithms of the available surface area versus $\log p_{CO}$, we have a graph whose slope gives the magnitude of the negative order, i.e., CO inhibition effect. At very low O(a), the number of unoccupied single sites is proportional to $1 - \theta_{CO}$. Since it takes two sites to adsorb one oxygen molecule, the available surface area should be proportional to $(1 - \theta_{CO})^2$, as a first approximation (28).

Figure 7 shows such a log-log plot of $(1 - \theta_{CO})^2$ versus p_{CO} at a fixed O_2 pressure and at 450 K. Coverages from Fig. 6 were used to calculate the quantity

$(1 - \theta_{\text{CO}})^2$. Curve 1 presents $(1 - \theta_{\text{CO}})^2$ calculated from the CO isotherm for the CO/Pd system and corresponds to the limiting value for very small pressures of oxygen. For $p_{\text{O}_2} = 6.7 \times 10^{-6}$ and 2.7×10^{-5} Pa, the plots shows a sharp decrease around $p_{\text{CO}} = p_{\text{O}_2}$ and a straight line when $p_{\text{CO}} > p_{\text{O}_2}$. At a higher O₂ pressure, 1.6×10^{-4} Pa, the straight line appears even when $p_{\text{CO}} < p_{\text{O}_2}$. The slopes of these straight lines vary from -0.26 to -0.62 with increases in O₂ pressure in the range 10^{-6} – 10^{-3} Pa. These predictions from Fig. 7 are in general agreement with kinetic results reported previously (23), in which the magnitude of the negative order changed from -0.46 to -0.78 over the same pressure range. However, the predicted order is a little smaller than that obtained from the kinetic results. This difference may be due to inadequacies in representing the available surface area as $(1 - \theta_{\text{CO}})^2$ (28).

V. SUMMARY

The amount of carbon monoxide adsorbed on palladium during the course of CO oxidation reaction at 450 K was determined by two methods, a flash desorption technique and a pressure jump method. The results obtained by these methods agree quite satisfactorily. The pressure of O₂ and CO were generally in the range 10^{-6} – 10^{-3} Pa.

For the CO/O₂/Pd system at 450 K, CO(a) is large and nearly equals that obtained for the CO/Pd system, when $p_{\text{CO}} > p_{\text{O}_2}$. The CO/O₂/Pd isotherm falls sharply below the CO/Pd isotherm when $p_{\text{CO}} \approx p_{\text{O}_2}$ and CO(a) becomes very small for $p_{\text{CO}} < p_{\text{O}_2}$. As the O₂ pressure increases there is, however, less sharpness in the change from low to high CO(a). These results are in good agreement with the predictions from kinetic work reported previously.

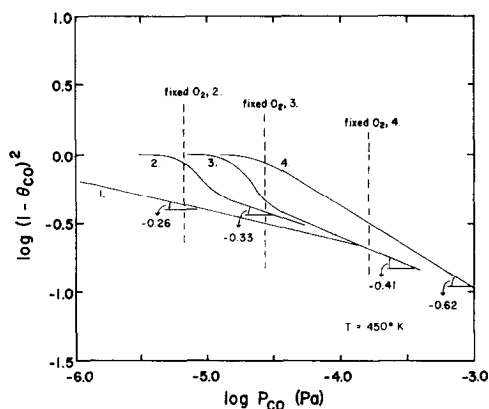


FIG. 7. Variations with CO pressure of available surface area for oxygen adsorption, $(1 - \theta_{\text{CO}})^2$, at 450 K. (1) Without oxygen; (2), with 6.7×10^{-6} Pa of oxygen; (3), with 2.7×10^{-5} Pa of oxygen; (4), with 1.6×10^{-4} Pa of oxygen; The slope of the linear portion of each curve is indicated.

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REFERENCES

1. Ford, R. R., *Advan. Catal.* **21**, 51 (1970).
2. Eischens, R. P., Francis, S. A., and Pliskin, W. A., *J. Phys. Chem.* **60**, 194 (1956).
3. Eischens, R. P., and Pliskin, W. A., *Advan. Catal.* **10**, 1 (1958).
4. Nash, C. P., and DeSieno, R. P., *J. Phys. Chem.* **69**, 2139 (1965).
5. Garland, C. W., Lord, R. C., and Troiano, P. F., *J. Phys. Chem.* **69**, 1188, 1195 (1965).
6. Baddour, R. F., Modell, M., and Hensser, V. K., *J. Phys. Chem.* **72**, 3621 (1968).
7. Palazov, A., Chang, C. C., and Kokes, R. J., *J. Catal.* **36**, 338 (1975).
8. Ertl, G., and Koch, J., in "Adsorption-Desorption Phenomena" (F. Ricca, Ed.), p. 345. Academic Press, New York, 1972; *Z. Phys. Chem. N.F.* **69**, 323 (1970).
9. Ertl, G., and Koch, J., in "Proceedings Vth International Congress on Catalysis" (J. W. Hightower, Ed.), p. 67. North-Holland-Elsevier, New York, 1973.
10. Conrad, H., Ertl, G., Koch, J., and Latta, E. E., *Surface Sci.* **43**, 462 (1974).
11. Tracy, J. C., and Palmberg, P. W., *Surface Sci.* **14**, 274 (1969); *J. Chem. Phys.* **51**, 4852 (1969).

12. Close, J. S., and White, J. M., *J. Catal.* **36**, 185 (1975).
13. Lambert, R. M., *Surface Sci.* **49**, 325 (1975).
14. Ertl, G., and Rau, P., *Surface Sci.* **15**, 443 (1969).
15. Ertl, G., *Surface Sci.* **47**, 86 (1975).
16. Kawasaki, K., and Sugita, T., *Surface Sci.* **6**, 395 (1967).
17. Kawasaki, K., Sugita, T., and Ebisawa, S., *J. Chem. Phys.* **44**, 2313 (1966).
18. Daghli, A. G., and Eley, D. D., in "Proceedings International Congress on Catalysis, 2nd Paris (1960)," Vol. 2, p. 1615, 1961.
19. Modell, M., Sc.D. thesis. Massachusetts Institute of Technology, Cambridge, Mass., 1964.
20. Schwab, G. M., and Gossner, K., *Z. Phys. Chem. (Frankfurt)* **16**, 39 (1958).
21. Tajbl, D. G., Simons, J. B., and Carberry, J. J., *Ind. Eng. Chem. Fundam.* **5**, 171 (1966).
22. Goldsmith, R. L., Ph.D. thesis. Massachusetts Institute of Technology, Cambridge, Mass., 1966.
23. Matsushima, T., Almy, D. B., Foyt, D. C., Close, J. S., and White, J. M., *J. Catal.*, **29**, 277 (1975).
24. Ertl, G., and Neumann, M., *Z. Phys. Chem. N.F.* **90**, 127 (1974).
25. Matsushima, T., and White, J. M., *J. Catal.*, **29**, 265 (1975).
26. Matsushima, T., and White, J. M., *J. Catal.*, in press.
27. Bonzel, H. P., and Ku, R., *Surface Sci.* **33**, 91 (1972).
28. Hayward, D. O., and Trapnell, B. M. W., "Chemisorption," p. 92. Butterworths, Washington, D. C., 1964.