JOURNAL OF CATALYSIS **110**, 319–329 (1988)

CO Oxidation on Pt/SiO_2 and Pd/SiO_2 Catalysts: Rapid FTIR Transient Studies

YAO-EN LI, DIRK BOECKER,[1] AND RICHARD D. GONZALEZ[2]

Department of Chemical Engineering, University of Illinois, Box 4348, Chicago, Illinois 60680

Received July 14, 1987; revised October 6, 1987

Transient studies on the oxidation of CO have been performed over Pd/SiO_2 and Pt/SiO_2 catalysts using a rapid scan FTIR coupled to a quadrupole mass spectrometer. When a 5% CO(He) mixture was replaced by 5% O_2(He) at 80°C, an induction period of about 110 s was observed before the oxidation reaction was initiated. The length of this induction period was observed to decrease sharply with increasing temperature. When a 5% O_2(He) mixture was replaced by 5% CO(He), the induction periods were almost zero and independent of temperature. The data are explained in terms of a CO–O_2 reaction model consisting of CO islands with highly reactive boundaries. The reaction occurs preferentially at the periphery of these islands of reactivity.

INTRODUCTION

The oxidation of CO over noble metal catalysts has been one of the most frequently studied and is also perhaps the best understood catalytic reaction. The reaction is a problem which has attracted both the industrial and the academic sector and has fascinated catalytic researchers for many years. It is of immense importance in the control of emissions from automotive exhaust gases, environmental clean up, and a variety of industrial applications of significant economic importance. A number of excellent reviews have recently appeared in the literature which deal with the reaction on both well-defined crystal surfaces (*1*, *2*) and supported noble metal catalysts (*3*). Of particular interest in the case of supported Pt is the occurrence of multiple steady states (*4*), the presence of self-sustained oscillations (*3*) and references therein), the existence of CO islands of reactivity (*5*, *6*), and induced metal and adlayer phase transitions (*1*). The importance of considering intraparticle diffusion in the case of porous catalysts has been pointed out by Hegedus *et al.* (*7*). More recently Herz and Marin (*4*) have shown quite convincingly that multiple steady states can arise as a result of coupling between nonequilibrium absorption and surface kinetics.

The formation of CO islands and centers of reactivity have also been suggested as possible mechanisms which can lead to self-sustained oscillations. This possibility is nicely illustrated in a recent *in situ* FTIR study by Boecker and Wicke (*6*) and by Boecker (*8*) on Pd/TiO_2. The catalytic reaction cycle which incorporates both an autocatalytic and an inhibition step can be summarized as follows: Initially the surface is covered by oxygen in a (2 × 2) adsorbate layer configuration. Small isolated patches of CO give rise to a single wide CO infrared band centered at 1900 cm^{-1}. This vibration is due to CO adsorbed in a bridge-bonded configuration with each CO coordinated to about three surface Pd atoms. This assignment is due to the IRAS work of Bradshaw and Hoffman (*9*) and Hoffman *et al.* (*10*). As the CO islands grow in size, the reaction rate increases to a maximum. Because the

---

[1] Present address: Department of Physical Chemistry, Scholsse Platz 4, University of Muenster, 4400 Muenster, West Germany.

[2] To whom correspondence should be addressed.

0021-9517/88 $3.00

reaction occurs at the perimeter of these CO islands, the reaction rate decreases as the CO islands increase in size and decrease in number. By forming these CO islands an increasing number of surface sites are lost to the reaction due the inability of oxygen to adsorb inside an organized CO surface structure. Concomitant with this increase in CO island size, a second sharp absorption band centered at 1980 cm^{-1} is observed in the infrared spectrum of CO. This band has been assigned by Bradshaw and Hoffman to CO coordinated to two Pd surface atoms (*9*). This surface species can be related to the adsorbed CO present inside the CO domains and can be seen when the adsorbate phase changes occur during CO island formation. A further increase in CO island size leads to a compression of surface oxygen into a more dense ($\sqrt{3} \times \sqrt{3}$) adlayer structure. Because this surface oxygen which has undergone a phase transition of sorts has been shown to be considerably more reactive than oxygen adsorbed in a (2×2) oxygen adlayer configuration (*1*, *2*), the reaction rate again increases, thus completing the reaction cycle. It appears, therefore, that surface phase transformations can lead to self-sustained oscillations. It should be emphasized that this model makes the assumption that adsorbate phases on supported Pd particles can be related to those observed on well-defined single-crystal surfaces studied under UHV conditions (*1*, *2*). This assumption, although not perhaps completely justified, is nevertheless attractive. Recent CO oxidation studies performed by Goodman and Peden (*11*) on well-defined single-crystal surfaces show that CO oxidation rates extrapolate nicely to those obtained on supported noble metal catalysts. Oh *et al.* (*12*) have also shown that the pressure gap between UHV and ambient pressure can be successfully bridged for the catalytic oxidation of CO over Rh(111) and Rh/Al_2O_3. These studies may add considerable validity to the assumptions made by Boecker and Wicke (*6*). This would be particularly true for the case of relatively large Pd particles having a well-defined crystallographic morphology.

Taking these results into consideration, we felt that a rapid transient FTIR study which separates the autocatalytic from the inhibition step might shed further light on the subject. The inhibition step can be studied by starting with a monolayer of oxygen and reacting it with CO in the transient mode. For the autocatalytic step, the sequence can be reversed; i.e., a monolayer of CO is reacted with O_2 and the transient response is again studied.

EXPERIMENTAL

Infrared cell reactor. In order to meet the requirements of rapid *in situ* transient measurements, an infrared cell reactor should, as a minimum, conform to the following: (i) the residence time in the infrared cell reactor should be less than the time required to scan the spectrum; (ii) the reactant gases should preferably be forced through the sample disk with little or no leakage around the edges; (iii) the outlet from the infrared cell reactor should be properly interfaced with a quadruple mass spectrometer or another suitable analytical measuring device for analyzing the gas phase; and (iv) the cell should be constructed to handle adequate heating schedules. Nagai *et al.* (*13*) have recently described an infrared cell reactor which meets these requirements. Briefly, the cell dimensions are such that the net reactor-cell volume is 1.5 ml at a flow rate of 100 ml/min. With this cell, residence times of 1.0 s can be achieved. In this study, four coadded interferograms per second were used. Thus, a residence time which was close to that required for transient response studies was obtained.

Flow system. A block diagram of the associated components used in the flow system is outlined in Fig. 1. The reactor was placed in the samples chamber of an FTIR (FTS40, Digilab) spectrometer. The gas phase composition in the reactor was monitored by a quadrupole mass spectrometer

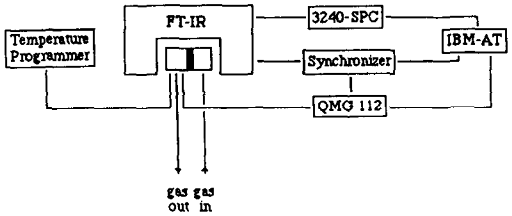

FIG. 1. Reactor system diagram.

(QMG 112, Balzers). A synchronizer was designed in our laboratory to coordinate the scanning of the FTIR and the QMG. The infrared data were processed in a 3240-SPC data station (Digilab) and could be transferred to a personal computer (IBM-AT). The mass spectral data were collected and analyzed in the IBM-AT. The temperature of the reactor was controlled by a temperature programmer (Valley Forge Instruments Inc., Model PC 6011). The temperature gradient between the inside and the outside of the reactor was observed to change from 10 to 50°C depending upon the reactor temperature. All the temperatures reported in the experiments were gas phase temperatures measured inside the reactor.

Materials. The silica-supported Pt and Pd catalysts were prepared from solutions containing the appropriate weight of $H_2PtCl_6 \cdot 6H_2O$ or $PdCl_2 \cdot 3H_2O$ (Strem Chemical). The solutions were added to a predetermined weight of Cab-O-Sil (grade M-5, average pore diameter 14 nm, surface area of 200 m^2/g, Cabot Corp., Boston, MA), using a rotovapor in a dropwise manner. The concentration of the metal precursors in the solution used for impregnation was adjusted to give a nominal metal loading of 1% by weight of Pt or Pd. The resulting catalysts were dried at room temperature under vacuum. For use in the spectroscopic reactor, the sample disks were prepared by pressing the ground catalysts (50 to 80 mesh) into self-supporting disks 1.25 cm in diameter with an optical density of approximately 80 mg/cm^2.

It was found convenient to use O_2 and CO premixed with He to give the following compositions: 5% CO in He and 5% O_2 in He. All gases were research grade or better and were purchased from the Linox Co. (Chicago, IL). The concentration of O_2 in the He carrier gas was reduced to less than 0.2 ppm through the use of a molecular sieve maintained at −78°C, an oxygen purifier (Supelco Co.), and an MnO trap activated in H_2 at 673 K.

Gas flow rates were controlled by using Tylan (Model FC260) electronic flow controllers. The flow controllers were calibrated by the manufacturer using gas mixtures which were identical to those used in this study. The calibration was rechecked in our laboratory by means of a bubble flow meter and a gas chromatograph.

Chemisorption measurements were performed by using the dynamic pulse method (*14*). Metal dispersions were calculated on the basis of a CO to exposed Pt absorption stoichiometry of 0.89 (*5*, *16*) and a CO to exposed Pd stoichiometry ratio of 1.0 (*17*). These adsorption ratios have been moderately well established and result in Pt and Pd dispersions of 22.4 and 14.7%, respectively.

Procedure. Prior to a transient study, the freshly pressed sample disks were reduced according to the following schedule: The catalyst was exposed to flowing He (100 ml/min) at 50°C. The temperature was then increased at a linear rate of 10°C/min to 150°C in flowing He and maintained at 150°C for 0.5 h. The He flow was switched to H_2 (100 ml/min) at 150°C and the temperature was then increased at 10°C/min to 455°C. The catalyst was reduced in flowing H_2 for 3 h at 455°C followed by treatment in flowing He for 0.5 h at the same temperature. The temperature was then reduced to 50°C in flowing He.

The procedure used for the transient studies was as follows: treatment in flowing He at 50°C (100 ml/min) for 0.5 h. The gas flow was then switched to 5% CO in He (100 ml/min) for 0.5 h. At this point the transient was initiated by switching to 5% O_2 in He. The infrared spectra and the mass spectrometer response were recorded continuously during the transient response study. Data points consisted of four coadded interferograms at a scan rate of 0.25 s/scan. Each data point, therefore, represents an elapsed time of 1 s. Following the conclusion of the transient response study (about 10 min), the O_2 flow over the catalyst was continued for an additional 40 min at the same reaction temperature. The gas flow was then switched to 5% CO in He (100 ml/min) and the reverse transient was studied in the same manner. Approximately five transient studies were performed at each reaction temperature.

Following the conclusion of the transient study at a given temperature, the gas flow was changed to pure He and the temperature was increased in flowing He at a linear rate of 10°C/min to the next reaction temperature. Identical procedures were used at each of the reaction temperatures studied.

RESULTS

Infrared spectra. Three infrared bands assigned to CO chemisorbed on Pd/SiO_2 were observed. The absorption band centered at 2070 cm^{-1} was assigned to CO linearly coordinated to a single Pd surface atom. The strong absorption band centered at 1978 cm^{-1} was assigned to CO coordinated to two Pd surface atoms while the absorption band centered at 1932 cm^{-1} was attributed to triply coordinated CO. These assignments are based on the single-crystal studies of Bradshaw and Hoffman (*9*). However, assignments based on CO adsorption on different Pd crystallographic planes have also appeared in the recent literature (*18*). A single CO absorption band centered at 2090 cm^{-1} was observed on Pt/SiO_2. This absorption band was attributed to CO linearly adsorbed on single Pt surface atoms.

Unfortunately, the frequencies of the CO(g) absorbance band and the surface CO absorbance band overlap and result in a convoluted peak. To separate these two bands, the following method was used (*19*): It was observed that the ratios of the intensities of the P-branch to the maximum intensity of the R-branch remained nearly constant over a range of CO(g) pressures and temperatures. The convoluted peak was considered as resulting from the additive intensities of the surface CO absorbance and the CO(g) absorbance. By measuring the intensities of the CO(g) R-branch and the convoluted peak, the contribution of the gas P-branch was eliminated through

$$I(\nu) = A(\nu) - B(\nu) * (r/p),$$

where $I(\nu)$ is the corrected absorbance of the surface CO, $A(\nu)$ is the absorbance of the convoluted adsorbed and gas phase CO, $B(\nu)$ is the absorbance of the R-branch gas phase CO, and the r/p term is the result of the calibrated ratio of the R- and P-branch gas phase CO in the absence of adsorbed species.

This mathematical manipulation makes two assumptions: one, that the effects of the gas and surface CO are additive, and two, that the surface CO peak frequency shift caused by the convolution is negligible, since the location of this peak determines the value of the constant r/p ratio. This method was applied to all spectral data.

In addition to the infrared bands assigned to the CO chemisorbed species, the rate of evolution of CO_2 was followed by monitoring the R-branch of gas phase CO_2 centered at 2361 cm^{-1} throughout the transient study. This provides a qualitative independent check of the mass spectral response data.

The CO–O_2 transient response. The transient response FTIR signal obtained when O_2 was added to a monolayer of CO chemisorbed on Pd/SiO_2 at the lowest temperature of this study (80°C) is shown in Fig. 2A. The corresponding mass spectral data are shown in Fig. 2B. Gas phase CO_2 was observed following an induction period of 120 s after O_2 entered the reactor. The induction period was taken as the time elapsed between O_2 entry into the reactor

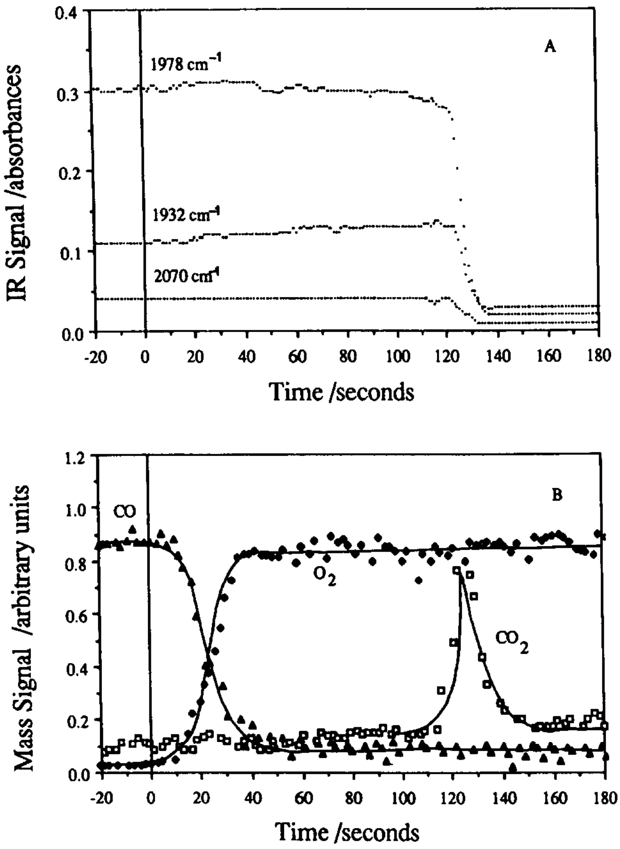

FIG. 2. (A) FTIR transient response for O_2 reacted with a monolayer of CO at 80°C on Pd/SiO$_2$. (B) Mass spectra response (5% O_2 in He with a flow rate of 100 ml/min).

and the time at which the evolution of gas phase CO_2 was first observed. Induction periods were corrected for the dead space volume corresponding to the stainless-steel tubing located upstream of the reactor by means of a dead space time calibration. There were no differences in the reactivity of the three different CO species chemisorbed on the Pd/SiO$_2$ surface as observed by the rapid decrease in the absorbance of all three infrared bands following the initial appearance of CO_2 in the gas phase. The time interval between successive data points was 1 s. Significant tailing was observed on the rate of evolution of CO_2 resulting in an unsymmetrical mass spectra signal response. The position of the maximum absorbance of gas phase CO_2 observed in the FTIR coincided with the maximum rate of CO_2 evolution observed in the mass spectral data. The frequencies of all three infrared bands were invariant throughout the duration of the transient, suggesting that the environment immediately surrounding adsorbed CO does not change significantly with CO surface coverage. Similar data corresponding to the highest reaction temperature studied are shown in Figs. 3A and 3B. Of interest is the sharp decrease in the induction time required to observe the initial evolution of gas phase CO_2 from the catalyst. The evolution of CO_2 was initially observed following an induction time of about 1 s, the maximum rate occurring at about 12 s. This suggests that the dissociative adsorption of O_2 required to initiate the reaction is strongly inhibited by adsorbed CO at lower tempera-

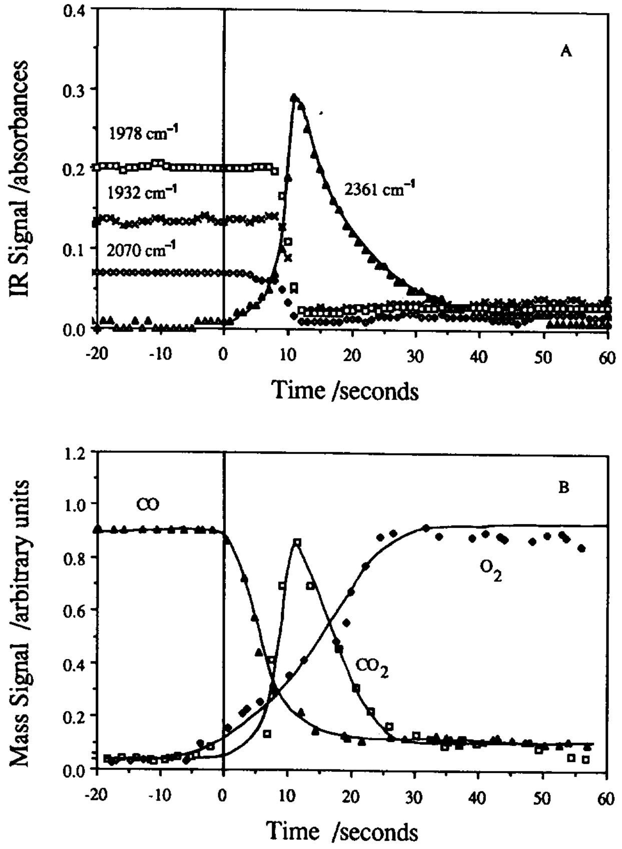

FIG. 3. (A) FTIR transient response for O_2 reacted with a monolayer of CO at 200°C on Pd/SiO_2. (B) Mass spectra response (5% O_2 in He with a flow rate of 100 ml/min).

tures. At higher temperatures, the adsorption of CO and O_2 becomes more competitive, resulting in considerably lower induction times. The induction times are summarized in Table 1. These represent the time average of five transient studies taken at each temperature.

The results of the CO–O_2 transient study on Pt/SiO_2 were very similar to those observed for Pd/SiO_2. For this reason we do not show the transient response here. As in the case of Pd/SiO_2 there was no shift in the position of the CO stretching vibration at 2090 cm^{-1} with CO surface coverage during the duration of the transient. The induction times observed for Pt/SiO_2 were nearly identical to those observed for Pd/SiO_2 (Table 1).

The O_2–CO transient response. The FTIR transient response signal obtained when CO was contacted with an oxygen-covered Pd/SiO_2 catalyst at 80°C is shown in Fig. 4A and the corresponding mass spectra response data are shown in Fig. 4B.

TABLE 1

Induction Time versus Temperature

Pd/SiO_2		Pt/SiO_2	
Temperature (°C)	Induction time (s)	Temperature (°C)	Induction time (s)
200	1 ± 0.1	195	4 ± 0.2
168	9 ± 0.5	162	12 ± 1.6
132	25 ± 1.7	132	27 ± 2.3
114	38 ± 0.5	117	29 ± 1.9
80	98 ± 0.4	80	109 ± 8.6

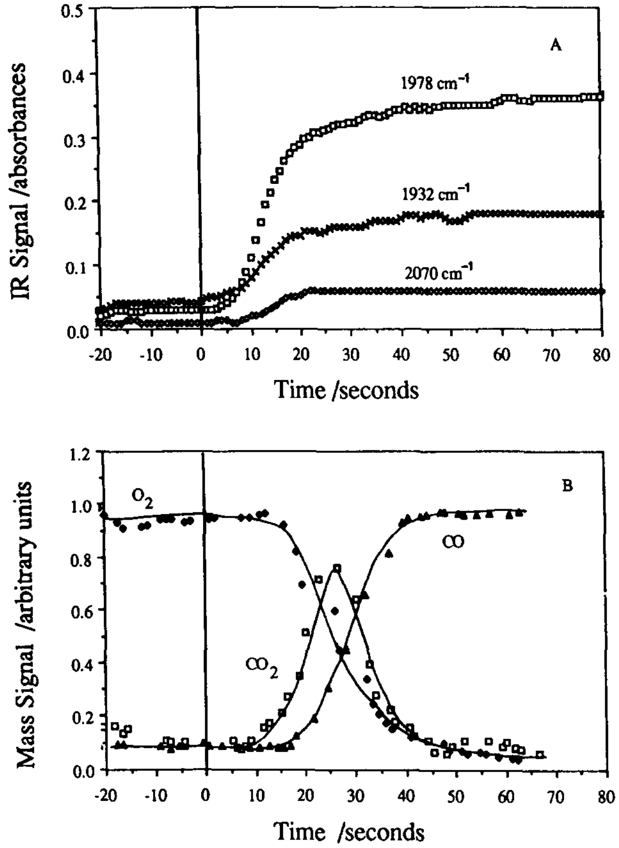

FIG. 4. (A) FTIR transient response for CO reacted with a monolayer of oxygen at 80°C on Pd/SiO_2. (B) Mass spectra response (5% O_2 in He with a flow rate of 100 ml/min).

In sharp contrast to the $CO–O_2$ transient, the induction time required for the initiation of the reaction was essentially zero. The evolution of CO_2 was observed immediately following exposure of the O_2 covered monolayer to gas phase CO. The maximum in the rate of evolution of CO_2 occurred after about 10 s. Identical results were obtained at 200°C. The increase in the absorbance of the infrared bands assigned to the three different CO chemisorbed species was observed to increase at the same rate. As in the case of the $CO–O_2$ transients, the position of these bands did not change with CO surface coverage.

The shape of the mass spectrometer response signal for CO_2 evolution was significantly different from that observed for the $CO–O_2$ transient response study (compare Figs. 2 and 4). In the case of the $O_2–CO$ transient study the mass spectral response signal was nearly symmetrical while for the $CO–O_2$ transient significant tailing occurred. These results suggest that the adsorption of CO on Pd/SiO_2 is not inhibited by chemisorbed oxygen. Additionally the symmetry of the mass spectral response signal suggests that the reaction of CO with surface oxygen is very fast and that the slow step is gas phase transport of CO to the surface. Chemisorbed CO was not detected on the Pd/SiO_2 surface until the reaction was essentially complete.

$O_2–CO$ transient studies observed over Pt/SiO_2 were identical to those obtained on Pd/SiO_2. No induction time was observed and the shape of the CO_2 production peak was symmetric with respect to time.

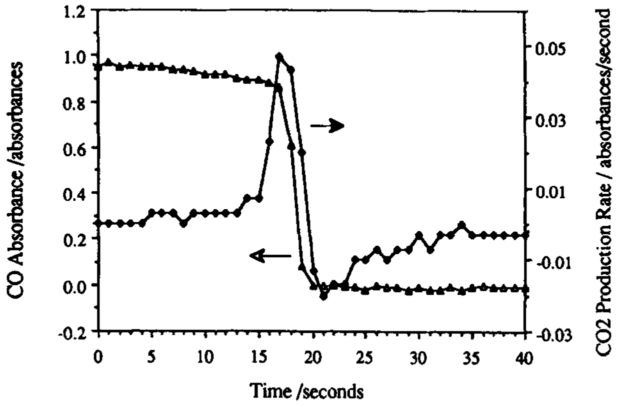

FIG. 5. Transient response of CO coverage and the rate of CO_2 formation on Pt/SiO_2, O_2 reacted with a monolayer of CO at 195°C (5% O_2 in He with a flow rate of 100 ml/min).

The maximum rate of reaction. In order to determine the CO surface coverage corresponding to the maximum reaction rate, the transient response signals for the rate of CO_2 production and the CO surface coverage on Pt/SiO_2 were plotted in Fig. 5. The CO surface coverage was calculated on the assumption that the extinction coefficient for adsorbed CO was not a function of surface coverage. There is good evidence from the published literature that this is a reasonably good assumption ((*20*) and reference therein). Because relatively few mass spectral data points were obtained for the formation of CO_2, the change in the absorbance of the R-branch of CO_2 (2361 cm^{-1}) was used as an indication of the rate of production of CO_2. The results of the plot show that the maximum rate occurred for a CO surface coverage of about 85%.

DISCUSSION

The catalytic oxidation of CO over supported noble metal catalysts displays a typical behavior regarding the pressure dependence of CO. Studies of this reaction over Pt (*6*, *15*), Ir (*21*), Rh (*22*), and Pd catalysts (*17*) supported on SiO_2 are qualitatively similar in that turnover frequencies plotted against the partial pressure of CO show three characteristic kinetic regions: At low CO/O_2 partial pressure ratios, the surface coverage of oxygen is at its maximum. Because the sticking coefficients for CO on noble metals are not a function of oxygen surface coverage, the reaction rate is controlled by the rate of CO adsorption. Following inhibition of the reaction by CO, the surface is almost completely covered by CO. In this region, the reaction rate is controlled by the CO desorption rate and by the dissociative sticking coefficient of oxygen, which is strongly dependent on the surface coverage of CO (*23*). Kinetically (*1*), in this region, the rate can be expressed by

$$r = k\theta_{CO}\theta_O = k'S(O_2)P_{O_2},$$

where θ_{CO} and θ_O represent the surface covered by CO and oxygen, respectively, and $S(O_2)$ is the sticking coefficient for the dissociative adsorption of oxygen on the supported metal. It is important to note that the sum of θ_{CO} and θ_O does not necessarily add up to 1 (*24*). The monolayer surface coverage has been shown to depend quite critically on the composition of the adlayer. The roll-over region between low and high P_{CO}/P_{O_2} partial pressure ratios is characterized by rapidly changing CO and oxygen surface coverages. In this region, the apparent activation energy for the reaction changes from 0 to about 100 kJ/mole and the reaction rate orders in CO and O_2 change from about +1 and −1 and +1, respectively. Surface coverages of CO in both of these regions have been substantiated by numerous *in situ* infrared studies (*8, 15, 21*). The position of the roll-over point is strongly dependent upon temperature (*21*). When the temperature is increased, the rate of oxygen adsorption becomes competitive with the rate of CO desorption. For this reason, higher P_{CO}/P_{O_2} ratios are required to maintain a steady-state concentration of CO on the surface. The higher rate of CO desorption facilitates the dissociative adsorption of oxygen, which requires dual sites. The adsorption of oxygen has been shown to be first order in the partial pressure of oxygen (*12*). Presumably the precursor to chemisorbed oxygen atoms on the surface is sufficiently mobile so that it can migrate until it is able to find suitable dual sites so that it can dissociate.

The results of this present transient study are in agreement with this concept. At low temperatures and at monolayer coverages of CO, the dissociative adsorption of oxygen is a difficult step, and, most likely, it is rate determining. This is consistent with the relatively long induction times required for the initiation of the surface reaction which can be observed by the incipient evolution of the product CO_2 molecules from the surface of the catalyst (Table 1). At higher temperatures, the desorption of CO promotes the dissociative adsorption of oxygen. This results in much shorter induction times. For the temperature range used in this study, induction times were always less than 1 s for the oxygen-saturated surface exposed to gas phase CO. The relatively long induction time observed for the CO–O_2 transient study at 80°C on both Pd/SiO$_2$ and Pt/SiO$_2$ was in sharp contrast to similar transient response studies obtained on Rh/SiO$_2$ (*25*). On Rh/SiO$_2$, the induction time at low temperatures was about 7 s. This is probably due to the much higher dissociative sticking coefficient for oxygen on Rh (*23*).

The invariance in the position of the infrared absorption bands for both Pt/SiO$_2$ and Pd/SiO$_2$ during the entire transient study shows that the surface CO remains strongly dipole coupled. This suggests that adsorbed CO retains an island configuration throughout the course of the transient reaction. If the CO and oxygen adlayer were completely mixed, the frequency of adsorbed CO would have decreased with increasing oxygen surface coverage. This was never observed. In contrast to the invariant position of all three CO absorption bands on Pd/SiO$_2$ and the single CO absorption frequency on Pt/SiO$_2$, a temperature-programmed desorption study performed in the absence of oxygen showed that the position of the CO infrared stretching frequency decreased monotonically with decreasing CO surface coverage. For this reason we suggest that the CO–oxygen surface reaction occurs at the periphery of the CO islands. This is in agreement with similar results reported by Boecker and Wicke (*6*), Boecker (*8*), and Haaland and Williams (*5*). The shape of the CO_2 mass spectral response signal reinforces this argument. Initially, the reaction occurs at the periphery of the monolayer of CO and is slow due to the relatively low interfacial surface area surrounding the large CO adlayer. As the reaction advances, the larger CO islands break up into smaller islands. This results in a sharp increase in the interfacial surface area with a corresponding large increase in the reaction rate. As the surface becomes depleted in CO, the reaction rate tails off and gradually decreases to zero. This CO island reaction model is reinforced by the observation that the maximum CO oxidation rate over Pt/SiO$_2$ is observed when the CO surface coverage is about 85%. For the case of a completely mixed adlayer Langmuir–Hinshelwood kinetics would predict a maximum in the reaction rate when the surface coverages of both oxygen and CO are nearly equal. Because this is not observed, we feel that separate CO and oxygen phases coexist under the conditions of the transient study.

The reactivity of all three adsorbed CO

species on Pd/SiO_2 was nearly equal. This result is in disagreement with the oscillatory reaction study of Boecker (*8*) in which the CO adsorbed species giving rise to a bridge-bonded configuration with an infrared band centered at 1978 cm^{-1} was shown to oscillate in preference to the CO species giving rise to the absorbance band centered at 1932 cm^{-1}. We can only conclude that in the case of the transient study all three reaction sites were at, or close to, equilibrium and that a rapid interconversion of adsorbed CO molecules between these sites was possible.

The reverse transient in which CO is reacted with a monolayer of oxygen is in agreement with the concept that the adsorption of CO onto an oxygen-covered surface is fast and is probably not rate controlling. The near perfect symmetry of the mass spectral response signal for the evolution of CO_2 from the catalyst surface suggests that the surface reaction is fast and is limited by the constant flux of CO, which diffuses to the surface from the gas phase.

Although the experimental evidence strongly suggests the presence of CO islands of reactivity for the catalytic oxidation of CO over Pt/SiO_2 and Pd/SiO_2, it would be premature to conclude that the buildup and collapse of CO islands of reactivity are responsible for sustaining oscillatory behavior. There are a large number of reactions which exhibit oscillatory behavior and do not sustain segregated phases on the surface. In a recent study involving CO oxidation on Rh/SiO_2 (*25*), we concluded that the CO–oxygen adlayer is probably mixed. However, large self-sustained oscillations were observed. This is also likely for the case of the H_2–O_2, CO–NO, NH_3–O_2, C_2H_4–O_2, CH_3OH–O_2, NO–O_2, and C_6H_{12}–O_2 reactions ((*3*) and references therein) which also exhibit strong self-sustained oscillations. The solution of the relevant heat and mass balance equations (*26–28*) suggests that the occurrence of self-sustained oscillations is strongly dependent on the kinetic parameters which determine the reaction rates. The occurrence of CO islands on Pt and Pd is in all likelihood a consequence of the adsorption of CO.

CONCLUSIONS

The following important conclusions emerge from this study:

(i) The dissociative adsorption of oxygen on Pt/SiO_2 and Pd/SiO_2 catalysts which are covered by CO is slow and probably rate determining.

(ii) The adsorption of CO on an oxygen monolayer is fast and probably not rate determining.

(iii) The mechanism of CO oxidation over Pd/SiO_2 and Pt/SiO_2 is consistent with a model which incorporates adsorbate phase segregation on the surface.

(iv) All three chemisorbed species on Pd/SiO_2 appear to react with oxygen at about the same rate.

ACKNOWLEDGMENTS

We acknowledge support from the Petroleum Research Fund of the American Chemical Society under Grant P.R.F.14377-AC5 for this research. We also thank Mr. Lambert Lucietto of the Byron-Lambert Co., Franklin Park, Illinois, for his much needed input in overcoming numerous technical problems associated with the infrared cell-reactor design. One of us (Yao-En Li) thanks the University of Illinois for a University Fellowship. Finally, we are grateful to the U.S. Department of Energy (Grant DOE FGO2-86ER-13531), which supplied funds for the purchase of a large portion of the equipment used in this research.

REFERENCES

1. Ertl, G., and Engel, T., "The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis" (D. A. King and J. P. Woodruff, Eds.), Vol. 4, p. 73. Elsevier, Amsterdam/New York, 1982.

2. Engel, T., and Ertl, F., "Advances in Catalysis" (D. D. Eley, P. W. Selwood, and P. B. Weisz, Eds.), Vol. 28, p. 2. Academic Press, New York, 1979.

3. Razon, L. F., and Schmitz, R. A., *Rev. Sci. Eng.* **28**(1), 89 (1986).

4. Herz, L. F., and Marin, S. P., *J. Catal.* **65,** 281 (1980).

5. Haaland, D. M., and Williams, F. L., *J. Catal.* **76,** 450 (1982).

6. Boecker, D., and Wicke, E., *Ber. Bunseng. Phys. Chem.* **89,** 629 (1986).
7. Hegedus, L. L., Oh, S. H., and Baron, K., *AIChE J.* **23**(5), 632 (1977).
8. Boecker, D., Ph.D. thesis, University of Muenster, W. Germany, 1986.
9. Bradshaw, A. M., and Hoffman, F. M., *Surf. Sci.* **72,** 513 (1982).
10. Bradshaw, A. M., Ortega, A., and Hoffman, F. M., *Surf. Sci.* **119,** 79 (1982).
11. Goodman, D. W., and Peden, J., *J. Phys. Chem.* **90,** 4839 (1986).
12. Oh, S. H., Fisher, G. B., Capenter, J. E., and Goodman, D. W., *J. Catal.* **100,** 360 (1986).
13. Nagai, M., Lucietto, L., Yao-En Li, and Gonzalez, R. D., *J. Catal.* **101,** 522 (1986).
14. Sarkany, J., and Gonzalez, R. D., *J. Catal.* **76,** 75 (1982).
15. Sarkany, J., and Gonzalez, R. D., *J. Appl. Catal.* **4,** 53 (1982).
16. Sarkany, J., and Gonzalez, R. D., *J. Appl. Catal.* **5,** 85 (1983).
17. Kiss, J., and Gonzalez, R. D., "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. 2, p. 635. Dechema, Frankfurt-am-Main, 1984.
18. Rieck, J. S., and Bell, A. T., *J. Catal.* **99,** 262 (1986).
19. Regalbuto, J. H., Ph.D. thesis, University of Notre Dame, 1986.
20. Sarkany, J., and Gonzalez, R. D., *J. Appl. Spectrosc.* **36,** 320 (1982).
21. Saymeh, R., and Gonzalez, R. D., *J. Phys. Chem.* **90,** 622 (1986).
22. Kiss, J., and Gonzalez, R. D., *J. Phys. Chem.* **88**(5), 899 (1984).
23. Personal communication.
24. Sarkany, J., Bartok, M., and Gonzalez, R. D., *J. Catal.* **81,** 347 (1983).
25. Yao-En Li and Gonzalez, R. D., *J. Phys. Chem.*, in press.
26. Uppal, A., Ray, W. H., and Poore, A. B., *Chem. Eng. Sci.* **29,** 967 (1974).
27. Aris, R., *et al., Chem. Eng. Sci.* **37,** 357 (1982).
28. Epstein, I. R., *J. Phys. Chem.* **88,** 187 (1984).