Carbon Monoxide Oxidation under Transient Conditions: A Fourier-Transform Infrared Transmission Spectroscopy Study

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In contrast to the apparent simplicity of the overall reaction, oxidation of CO over Pt/A2O3 is known to present complex behavior. Self-sustained oscillations, hysteresis loops in conversion, and enormous rate enhancements under forced feed concentration cycling have been observed. In this study the dynamic behavior of the IR-active surface CO species was followed with a fast-scan Fourier-Transform Infrared (FTIR) during transient response and periodic operation. Depending on the conditions, up to four linearly adsorbed CO bands at 2123, 2092, 2073, and 2061 cm\(^{-1}\), and a bridge-bonded CO band at 1850 cm\(^{-1}\) were observed. The time-averaged and transient intensities of the bands were found to be significantly different during periodic operation as compared to steady state. Linearly adsorbed CO on metallic platinum (2073 cm\(^{-1}\)) was found to have the fastest response to changes in the gas-phase concentration. It was also observed that CO adsorbed on platinum oxide is very stable and does not take part in the reaction to any appreciable extent. CO, production rates during periodic operation were found to correlate extremely well with the integrated total absorbance of the 2092-cm\(^{-1}\) band, assigned to CO linearly adsorbed on a platinum atom sharing an oxygen with a neighbor. Based on the experimental observations a detailed mechanism of CO oxidation on platinum is proposed. The model can successfully explain the enormous rate enhancements observed during periodic operation.

I. INTRODUCTION

Oxidation of CO over supported platinum exhibits a number of complex behavior patterns under a variety of reaction conditions. Self-sustained oscillations of reaction rate under steady feed stream concentrations were initially observed by Hugo and Jakubith (1). The interest in this phenomenon grew rapidly and the subject was reviewed by Schmitz (2) and by Slinko (3). Hysteresis loops, where more than one steady state are observed depending on the history of the reactor's environment in terms of temperature or inlet concentration of CO, are well documented (4, 5). Cutlip (6) found that the (time average) rate of reaction under isothermal conditions could be enhanced dramatically (more than an order of magnitude compared to the equivalent steady state) by periodically switching the feed between CO and O\(_2\). This work by Cutlip has been extended to shorter switching periods by Barshad and Gulari (7), where the switching times were short enough to be comparable to the surface processes. An extensive mapping of this phenomenon, with respect to the parameters associated with periodic operation, was also presented.

This complex behavior stands in sharp contrast with the apparent simplicity of the reaction if the gas-phase species alone are considered. Efforts to model this reaction, by accounting for surface reaction with bimolecular Langmuir–Hinshelwood (LH) rate expression, have resulted in limited success. Rate expressions that are based on the assumption that both CO and O\(_2\) adsorption processes are in equilibrium can hardly predict the steady-state rate of reaction over a limited range of pressures and concentrations. Herz and Marin (8) developed a model which describes the experimental behavior of CO oxidation without invoking the competitive equilibrium ad-
Infrared spectroscopy is one of the few techniques that can be used for in situ experiments at atmospheric pressure. Especially attractive, in this case, is the fact that CO adsorbed on Pt/Al2O3 has intense absorption bands in the IR spectra. The availability of a large amount of IR data for this system is also helpful in interpreting the results.

The purpose of this study was to investigate the transients of surface CO species in all the IR absorption bands. The experiments were designed to follow the rate of adsorption on reduced and oxidized platinum and to explore the behavior of surface species under periodic operation where significant rate enhancement is observed. Specifically, the answers to the following questions were sought:

1. Can transients in any of the surface species be correlated with the transients in CO2 production (dynamic and time average)?
2. What is the dynamic behavior of surface CO species under reactive and nonreactive conditions?
3. What is the role of platinum and platinum oxide in the reaction?
4. To what extent can rate enhancements be attributed to temperature excursions on the catalyst surface?

II. EXPERIMENTAL

a. Catalyst and Reagents

A 6.2 wt% Pt/Al2O3 was prepared by impregnating high-purity alumina (BDH) with aqueous H2PtCl6 solution. The catalyst was then dried in air for 2 h and calcined in air at 773 K for 4 h. The catalyst powder was pressed into pellets by a 25.4-mm die using 80 mg per pellet. The resulting pellet thickness was 0.25 mm. Dispersion was found to be 16% using CO and O2 chemisorption at room temperature. Before using, the catalyst was pretreated in situ by flowing O2 and then H2 for 2 h at atmospheric pressure and 503 K.

The gases used were 99.99% pure N2 (Air Products), 99.99% pure O2 (Matheson), and 99.6% pure CO containing 0.3% N2, traces of Ar and CO2, and 20 ppm of Fe (CO)5. Iron carbonyl was removed by decomposing it at 700 K. The results were found to be identical with or without the carbonyl trap.

b. Apparatus

Details of the flow measurement and control system are given elsewhere (9). The system is capable of switching the feed to the single-pellet reactor between different streams with different compositions of CO, O2, and N2 without changing the total volumetric flow rate, thus keeping the residence time constant to ±2%.

The catalyst pellet was mounted in a liquid IR cell (Harrick) with 25.4-mm NaCl windows and an optical path length of 0.9 mm. This short path length eliminated the IR signal from gas-phase CO. The cell was heated by a heating tape and the temperature was controlled to ±0.5 K.

c. Procedure

The majority of the experimental work presented here was performed with the sample at 413 K, and a total pressure of 104.2 kPa. The flow rate through the sample cell was 85 cm3/min, which along with a cell volume of 1 cm3 resulted in a residence time of <1 sec. Since the shortest cycle time used in this study was 10 sec, the shape of the transients is not significantly distorted by the filtering action of the cell.

Two different kinds of experiments are presented in this paper. The first is the transient response of surface species to a step change in gas-phase composition of the feed. The second kind is periodic operation.
where the reactor inlet was switched between 15 vol% \( \text{O}_2 \) in \( \text{N}_2 \) and 10 vol% \( \text{CO} \) in \( \text{N}_2 \). There are two parameters associated with this type of operation that are worth defining: (i) time period (TP), as in any other cyclic process, is the time it takes the process to repeat itself; and (ii) duty fraction (DF) is the fraction of the time period that \( \text{CO} \) is in the feed stream. The results that we present in this paper correspond to a duty fraction of 0.2 (for reasons that will be discussed later). The time-averaged concentrations were used as a reference for periodic operation.

All the IR spectra were taken with a fast-scan Digilab FTS-20 Fourier-transform IR spectrometer capable of taking up to seven spectra/second with a resolution of 8 cm\(^{-1}\). For most of the data presented here the actual time resolution was 0.6 sec since an interactive data acquisition program was used.

Time-averaged spectra were also taken in both periodic operation and steady-state experiments. In those cases a higher resolution of 4 cm\(^{-1}\) was used and speed was of no interest. Once repetitive steady operation was achieved, successive spectra were averaged over 10 time periods to determine the time-averaged surface coverage, with high signal-to-noise ratio.

III. RESULTS

The main features of our steady state and transient spectra are the four bands shown in Fig. 1. These four bands exist with different intensities under all of our operating conditions. The first is an intense band at 2120 cm\(^{-1}\), the frequency of which varied between 2123 and 2119 cm\(^{-1}\). This band, according to traditional assignment, is due to carbon monoxide adsorbed on supported platinum oxide (10). The second is the 2092-cm\(^{-1}\) band that sometimes looked like a shoulder on the 2120- or the 2073-cm\(^{-1}\) bands, but in other cases was distinct and clear with some structure consisting of peaks at 2090 and 2094 cm\(^{-1}\). This band is assigned to CO adsorbed on a platinum atom sharing an oxygen with a coordination number of about +1 (10). The third, and the last in this group of bands, due to linearly adsorbed CO, is the 2073-cm\(^{-1}\) band, assigned to CO adsorbed on reduced platinum crystallites (10). This band was also strong and distinct and was located between 2073 and 2080 cm\(^{-1}\) under reactive conditions. The fourth band located at 1850 cm\(^{-1}\) is due to bridge-bonded CO. This band was relatively weak, 0.01–0.02 absorbance units compared to 30 to 100 absorbance units for the 2073-cm\(^{-1}\) band, and did not change its frequency. A fifth band at \(~2060\) cm\(^{-1}\) was observable at times as a distinct band during CO adsorption transients on reduced Pt and as a shoulder during periodic operation. This band is assigned to CO linearly adsorbed on Pt atms with low coordination numbers.

a. Effect of Hydrogen on the CO Spectrum

Figure 2 shows the CO adsorption spectrum after first exposing the catalyst to the reaction mixture for 24 h and then switching the feed to 15% \( \text{H}_2 \) in \( \text{N}_2 \) at 413 K for 30 min. The important points to note are that the intensity of the 2120-cm\(^{-1}\) band is very small, the 2073-cm\(^{-1}\) band is shifted down in frequency to 2063 cm\(^{-1}\), there are low-frequency shoulders at 2031 and 1980 cm\(^{-1}\), and that the total integrated intensity...
Fig. 2. IR spectrum of adsorbed CO obtained after reducing a broken-in catalyst with hydrogen for 30 min.

is only about one-third of that shown in Fig. 1.

b. CO Adsorption on Reduced Catalyst

Figures 3a and b present the dynamics of CO adsorption on reduced platinum. After aging and reducing the catalyst the cell was purged with nitrogen, and at time zero the feed was switched to 10% CO in N₂ and successive spectra averaged over 1 sec each were taken. We see that from time zero to 17 sec the frequency of the main peak is constant at 2076 cm⁻¹. After 7 sec a low-frequency shoulder at approximately 2044 cm⁻¹ becomes visible. The main peak is due to CO linearly adsorbed on Pt⁰, and the wide shoulder is probably due to adsorption on low-coordination sites. The changes in the 1850-cm⁻¹ bridge-bonded CO band were much slower and, because of lower S/N, were not analyzed. Following the increases in the height of the 2076-cm⁻¹ band revealed that there were two time constants, a short one of ~3 sec and a much longer one of ~30 sec. Exposure to CO for 15 min produces dramatic changes in the band shapes: the peak absorbance is double that of \( t = 17 \) sec, the peak frequency shifts down to 2073 cm⁻¹, and the low-frequency side is very asymmetric.

Oxidation of CO adsorbed on to the catalyst by first purging the gas-phase CO and

Fig. 3. (a) Time-dependent CO adsorption spectra on the reduced catalyst. Only some of the representative individual spectra are shown. (b) Peak absorbance at 2076 cm⁻¹ measured as a function of time. Also shown is the time-dependent absorbance of the shoulder at 2044 cm⁻¹. Absorbances shown in this figure were obtained from individual spectra, some of which are shown in (a).
then switching the feed to 10% O₂ in N₂ showed no unusual transients. The intensity of the 2073-cm⁻¹ band decreased uniformly without showing any shifts in frequency.

Figure 4 shows the dynamics of CO adsorption onto partially oxidized catalyst. The catalyst was pretreated with oxygen for 30 min and then the gas-phase O₂ was flushed with N₂ before introducing 10% CO in N₂. The frequency of the band assigned to CO adsorbed on platinum oxide stays constant at 2122 cm⁻¹ whereas the frequency of the more intense band at 2087 cm⁻¹ slowly shifts down to 2076 cm⁻¹ after 20 sec and all the way down to 2073 cm⁻¹ after 10 min.

c. Periodic Operation Results

All the periodic operation experiments and the equivalent steady-state experiments were carried out with the same time-average concentration of both CO and O₂. In order to keep the number of variables to a minimum CO (10% CO in N₂) was fed into the reactor 20% of the time (duty fraction of 0.2) while oxygen was flowing in for the rest of the time. The period of cycling was varied from 10 to 50 sec. The equivalent steady-state feed concentrations corresponding to this cyclic feed strategy are 2% CO, 12% O₂, and 86% N₂.

The reactor reaches steady cyclic operation fairly quickly, a fact that was verified by comparing spectra averaged over 5 periods and spaced 15–20 min apart. When the difference between two such spectra diminished to the noise level (0.002 absorbance units) it was considered to be steady periodic operation.

Figure 5 shows the time-averaged spectra obtained by adding and averaging 400 to 800 successive scans spanning exactly a whole number of time periods. The spectra in Fig. 5 can be divided, qualitatively, into two groups. Steady state, 10-, and 20-sec time periods show high absorbance at 2077 cm⁻¹ and relatively low absorbance at 2123 cm⁻¹. TP = 30-, 40-, and 50-sec spectra have higher absorbances at 2123 cm⁻¹, a new band at 2092 cm⁻¹, and much lower absorbance at 2073 cm⁻¹.

Proceeding on the assumption that the spectra in Fig. 5a are the result of superposition of several individual peaks with Gaussian lineshapes, we have deconvoluted the spectra to quantitate the contribution of each surface CO species. The results of the deconvolution are summarized in Table 1. Important points to note are that the total integrated absorbance is approximately constant, the half-widths of the 2123- and 2073-cm⁻¹ bands are relatively constant whereas the half-width of the 2092-cm⁻¹ band increases fivefold. Simultaneous with these measurements the time-averaged rate of CO₂ concentration in the outlet was measured with an external IR detector. The correlation between the time-averaged spectra and the CO₂ production rate is shown in Fig. 5b where the changes from the steady state are plotted. The most important observation to be made in Fig. 5b
is that the 2123- and 2092-cm\(^{-1}\) bands have positive correlation and the 2073-cm\(^{-1}\) band has negative correlation with the changes in the CO\(_2\) concentration.

While the time-averaged spectra during periodic operation are helpful in determining what changes are taking place on the catalyst surface they do not have the time resolution to answer questions about the reaction intermediates. In order to address the question of the species responsible for the increased CO\(_2\) production 0.6-sec time resolution IR spectra was taken during periodic operation. The data was analyzed in two ways, by simultaneously following the absorbance at the fixed wavenumbers of 2123, 2092, 2073, and 1850 cm\(^{-1}\) with a bandwidth of 8 wavenumbers, and by deconvoluting the individual spectra as a sum of Gaussians. Figure 6a shows the results of the first type of analysis. Figures 6b and c show individual spectra taken at the certain points shown in Fig. 6a. Important points to note in Fig. 6a are: the absorbances at 1850 and 2123 cm\(^{-1}\) change very little with the changes in the gas-phase composition, 2073- and 2092-cm\(^{-1}\) absorbances change significantly during one cycle, and that there is a 20-sec induction time (the distance A in the figure) after oxygen is turned on before any significant changes are seen in the absorbances. This induction time was found to be a strong function of temperature.

Table 2 gives the results of the Gaussian deconvolution by nonlinear least-squares analysis. Overall the quality of the fits were very good (correlation coefficients \(\geq 0.9999\) or an average deviation of less than 0.5% between the fitted and the experimental curve). In this analysis inclusion of a fourth
TABLE 1
Deconvolution of Time-Averaged IR Absorption Spectra of CO Obtained during Periodic Operation into Individual Peaks

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<td>2120</td>
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<td>4354</td>
<td>4321</td>
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Percentage contribution by each band

- 2123 cm⁻¹: 13.4, 16.2, 15.5, 29.5, 30.5
- 2092 cm⁻¹: 11.3, 11.2, 10.7, 31.0, 32.8
- 2073 cm⁻¹: 75.3, 72.6, 73.8, 39.5, 36.7
- Gaussian with a peak frequency of 2061 cm⁻¹ was found to be necessary. This peak can be identified with either isolated CO molecules or CO adsorbed on low-coordination sites. In a complete cycle, for most of the oxygen portion of the period (length A), the intensities of the 2123- and 2073-cm⁻¹ bands are high and there is no 2092-cm⁻¹ band. Only one spectrum is given for this region because all of the individual spectra were identical. During this time the CO₂ production was below the detection limit of the spectrometer.

Small amounts of CO₂ are produced all the time for either CO or oxygen in the gas phase. After the induction period A, the intensity of the 2073-cm⁻¹ band starts decreasing sharply. The intensity of the 2092-cm⁻¹ band increases dramatically and a surge in CO₂ production occurs at point e in Fig. 6a. This surge coincides with the maximum in the integrated area of the 2092-cm⁻¹ band. After the CO pulse is on, the integrated absorbance of the 2092-cm⁻¹ band continues increasing, reaching a maximum roughly halfway through the CO pulse (point j in Fig. 6a). At this point the 2092-cm⁻¹ band has the maximum integrated absorbance and a large surge of gas-phase CO₂ is again detected. In comparison the 2073-cm⁻¹ band absorbance is almost zero and starts increasing after the 2092-cm⁻¹ band starts decreasing. This decrease is accompanied by a sharp drop in the gas-phase CO₂ concentration. From the deconvolution results we also observe that, in contrast to transients of the type shown in Fig. 3, the absorbance of the 2061-cm⁻¹ band increases before the 2073-cm⁻¹ band.

Figure 7 shows the behavior of gas-phase CO₂ and CO concentration in the immediate vicinity of the catalyst surface during periodic operation under similar conditions but with a monolithic reactor designed to detect fast gas-phase transients (II). Again there is a lag time after oxygen is intro-

TABLE 2
Results of Gaussian Peak Deconvolution of Selected Individual Spectra during Periodic Operation

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<th>Peak height</th>
<th>Half-width</th>
<th>Integrated area</th>
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Fig. 6. (a) Plot of time-dependent changes in the peak absorbances of the IR bands during periodic operation with a period of 40 sec and a CO duty fraction of 0.2. The continuous curves shown were obtained by joining individual data points (not shown for clarity) separated by 0.6 sec. Also shown are the CO and O₂ portions of the period. Lowercase letters indicate the locations of individual spectra which were analyzed in detail. (—) 2073 cm⁻¹, (—) 2123 cm⁻¹, and (—) 2092 cm⁻¹. (b) Some of the individual spectra taken during periodic operation. The lowercase letters refer to the corresponding location in (a). (c) Some of the individual spectra taken during periodic operation. The lowercase letters refer to the corresponding location in (a).
duced and there are two peaks in the CO₂ concentration per period.

IV. DISCUSSION

a. CO Adsorption on Reduced Platinum

One of the central questions regarding adsorption CO on platinum group metals has been the question of patch-like adsorption (island formation) or random uniform adsorption. Unfortunately, there is no direct way of determining whether this type of adsorption occurs on polycrystalline catalyst particles, and we must rely on indirect evidence. Crossley and King (12) demonstrated that the frequency shifts observed in the stretching frequency of linearly adsorbed CO on single-crystal platinum surfaces are entirely due to adsorbate-adsorbate coupling interactions. Transient adsorption results given in Fig. 3a show that the main adsorption band peak frequency is stable for more than an order of magnitude in absorbance (or surface coverage). This can be taken as an indication that the environment for individual CO molecules adsorbed onto the surface does not change while the total surface coverage increases. One possible reason for the observed behavior is island-like adsorption. In this type of adsorption most of the CO molecules will be in the inside of the island, thus their stretching frequency will not change as the island size or the number of islands increase. A second possibility, chromatographic adsorption, has been pointed out by Bell and co-workers for palladium (13). While we cannot completely disprove chromatographic adsorption possibility there is strong evidence against it. If chromatographic adsorption is the mode of adsorption the absorbance at the peak should increase linearly with time for a square concentration front advancing through the pellet. Figure 3b shows the absorbance as a function of time at two frequencies. It is clear that linear increase is not the case. The curve for 2076 cm⁻¹ has two characteristic times, a short one of 3 sec, and a much longer one of about 80 sec.

A simple calculation using the analytical solution of Dudukovic (14) for a pellet shows that, for our case, the concentration of CO in the middle of the pellet reaches its value on the outside of the pellet in less than 1 sec. Yet even after almost 100 sec the peak absorbance is only half of the maximum reached after 10 min. A final point to consider is the fact that at 413 K there is a reasonable amount of desorption of CO preventing complete chromatographic adsorption. Based on the above evidence we tend to believe in island-like adsorption under the conditions of our experiments. Similar conclusions have been reached by Haaland and Williams (15), and Gonzales et al. (16). The change in the characteristic time shown in Fig. 3b is not surprising because, as suggested by Nishiyama and Wise (17), the activation energy for CO desorption is coverage dependent. In contrast to Fig. 3a the peak frequency shifts downward significantly when the adsorbed CO is reacted with hydrogen, as shown in Fig. 2, or during nonreactive thermal desorption. These findings are again in agreement with the results of Haaland and Williams (15).

b. Periodic Operation and Rate Enhancements

One of the more interesting recent findings about catalytic oxidation of CO over supported platinum has been the enormous rate enhancements obtained by periodic feed switching. Cutlip (6) explained the increased rate as being due to increased surface coverage by oxygen. Critics have also tended to attribute the increase to mass and heat transfer effects during concentration cycling. Our main aim in this study was to find out the reasons for the dramatic rate enhancements and, if possible, the surface species responsible for it. Despite the very large number of publications on the subject, the exact mechanism of CO oxidation and the surface species taking part in the rate-determining step are not known. Eladheri and Tsotis (18) observed that the IR absorbance at 2073 cm⁻¹ oscillated out of
phase with the gas-phase CO₂ concentration. Haaland and Williams (15) found no direct correlation between the CO₂ production rate and the intensity of any of the CO bands they were observing (2073 and 1850 cm⁻¹). They concluded that a yet undetected surface species was responsible for CO₂ production.

We believe that the CO absorption spectra obtained during periodic operation provides some possible answers to the question of surface species responsible for CO₂ production. If, in Fig. 5a, we compare the steady-state spectrum with the periodic operation spectra with TP ≥ 30 sec, we see two dramatic differences: (i) the 2120-cm⁻¹ peak is higher during periodic operation and the 2092-cm⁻¹ peak is very clearly present during periodic operation but absent during steady state, and (ii) the relative intensity of the 2073-cm⁻¹ band is lower. Overall, however, the total integrated absorbances are the same within error limits (±7%). In Fig. 5b we have plotted the integrated intensities of the four CO bands given in Table 2 along with the time-averaged CO₂ concentration in the outlet (which is proportional to the time-average rate of reaction). We see that the outlet concentration of CO₂ shows a slow increase as the time period is increased from 10 to 20 sec and then a sharp increase in going from TP = 20 sec to TP = 30 sec (the precise time period for observing this sudden jump is 25 sec). At 30 sec, the time-averaged CO₂ concentration is exactly three times the steady-state value. If one of the surface CO species is responsible for the increased rate, then its surface coverage should also change by a parallel amount. Looking at the integrated absorbances of the four CO stretch bands we see that changes in the integrated absorbances of the 2092- and 2123-cm⁻¹ bands correlate with the changes in the CO₂ concentration quite well. For the bands at 2073 and 1850 cm⁻¹ we have negative correlation, in good agreement with Eldaheri and Tsotis (18).

If we make the somewhat questionable assumptions that there is no IR-inactive CO species on the catalyst surface, and that the extinction coefficients for all the linearly adsorbed CO species are roughly the same, the total absorbance data given in Table 2 leads to the conclusion that surface coverage by CO does not change when going from steady state to equivalent periodic operation. Thus the increase must be due to a change in the surface concentration of the active species.

Perhaps the most clear-cut conclusion one can draw from the results of time-averaged IR spectra is that the increased rates of reaction during periodic operation are due to changes occurring on the catalyst surface and not due to heat and mass transfer effects. Based on Fig. 5b it is very difficult to distinguish which CO species is the active one. If the increase in the rate of reaction is due to an increase in the active surface CO species then the CO species absorbing at 2123 and 2092 cm⁻¹ are the candidates. As seen in Fig. 5b, the increases in the areas of these bands, particularly the 2092-cm⁻¹ band, closely parallel the changes in the CO₂ concentration. A somewhat less plausible argument would be to say that increased rates of reaction would lead to reduced surface concentration of the active CO species (2073 cm⁻¹).

If we look at Fig. 6a and Table 2 we see that the peak width, absorbance at the peak frequency, and the total integrated absorbance of the 2123-cm⁻¹ band are all constant during one complete cycle. Thus it is clear that the CO adsorbed on platinum oxide is not taking part in the reaction and we are left with three candidates for the active species: CO adsorbed on a platinum atom sharing an adsorbed oxygen with a neighbor (2092 cm⁻¹), CO adsorbed on metallic platinum (2073 and 2061 cm⁻¹), and an IR-inactive CO species that cannot be detected. Since there is no literature evidence for the existence of significant amounts of IR-inactive CO on Pt we will ignore this possibility. All along the time period marked by A in Fig. 6a the spectra show no change, as seen
from the individual spectra given in Fig. 6b, and very little CO₂ is produced. Yet during this time the integrated absorbance due to CO adsorbed on metallic platinum (2061 and 2073-cm⁻¹ peaks) is quite high, accounting for almost two-thirds of the total absorbance as given in Table 2. Thus it is clear that high levels of surface CO adsorbed on metallic Pt do not result in high reaction rates.

During one period two large surges in CO₂ concentration in the gas phase are seen. The peak of the first surge is at point e, and the larger second surge is between points i and j in Fig. 6a. If we look at the individual spectra or Table 2 we see that these are precisely the points at which the integrated absorbance of the 2092-cm⁻¹ band is high and the integrated absorbance of the 2073- and 2061-cm⁻¹ bands are low. Particularly at point j, CO adsorbed on partially oxidized platinum has the highest absorbance. At point e it is clear that CO adsorbed on metallic platinum is the source of CO for both the CO₂ produced, and also the CO adsorbed on partially oxidized platinum. On the other hand at points i and j it is equally clear the CO adsorbed on partially oxidized platinum comes from gas-phase CO because there is very little CO adsorbed on metallic platinum. If we assume that the same mechanism is responsible for the formation of CO₂ at all four points we reach the conclusion that at points i and j the observed CO₂ is produced from CO adsorbed on partially oxidized platinum which is the only active species on the surface. Supporting evidence for this is again available from our see-through reactor results shown in Fig. 7. The surge in the gas-phase CO₂ concentration during the O₂ on portion of the period is significantly lower than the surge during the CO on portion of the period in excellent agreement with the integrated absorbances given in Table 2. The level of gas-phase CO₂ is also higher between points e–h than between points a–c again in agreement with the integrated absorbance of the 2092-cm⁻¹ band given in Table 2. This very strong positive correlation between the area of the 2092-cm⁻¹ band and the CO₂ production rate during periodic operation establishes the surface species responsible for this band as the primary candidate for the reactive intermediate. On the other hand there is no regular correlation with the integrated absorbance of the 2073-cm⁻¹ band.

A final interesting point brought out very clearly by the results in Fig. 6 is the asymmetry of the reaction with respect to gas-phase oxygen and CO. There is an induction time of 19 sec (at 413K) from the time oxygen feed is on to the surge of CO₂. In contrast, only 3 sec pass between the time CO feed is on and the large surge of CO₂ seen in the gas phase. We have observed the same asymmetry with palladium (19). In the case of palladium, it is known that CO islands are formed when oxygen is adsorbed on a Pd(111) surface with high CO coverage (φ = 0.5 or higher) whereas the opposite experiment leads to the formation of islands of intimately mixed and reactive CO and oxygen (20). It is possible that on Pt the 2092-cm⁻¹ band could be due to a similar surface structure.

Based on the above results, we propose the following model for CO oxidation during periodic operation:
INFRARED SPECTROSCOPY OF CO OXIDATION

(1) \( \text{O}_2 + 2(\text{Pt})_n \rightleftharpoons 2(\text{Pt})_n\text{O}^* \) 
(relatively slow)

(2) \( \text{O}_2 + 2\text{Pt} \rightleftharpoons 2\text{PtO} \)

(3) \( \text{CO} + (\text{Pt})_n\text{O}^* \rightleftharpoons \text{CO}^*(\text{Pt})_n\text{O}^* \)
(fast)

(4) \( \text{CO}^*(\text{Pt})_n\text{O}^* \rightleftharpoons (\text{Pt})_n + \text{CO}_2 \)
(fast)

(5) \( \text{CO} + \text{Pt} \rightleftharpoons \text{PtCO}^* \)

(6) \( \text{CO} + 2\text{Pt} \rightleftharpoons \text{Pt}_2\text{CO}^* \)

(7) \( \text{CO} + \text{PtO} \rightleftharpoons (\text{PtO})\text{CO}^* \)

(8) \( (\text{PtO})\text{CO}^* \rightleftharpoons \text{Pt} + \text{CO}_2 \)
(very slow)

(9) \( \text{PtCO}^* + (\text{Pt})_n\text{O}^* \rightleftharpoons \text{CO}^*(\text{Pt})_{n+1}\text{O}^* \)

(10) \( \text{CO}^*(\text{Pt})_{n+1}\text{O}^* \rightleftharpoons (\text{Pt})_{n+1} + \text{CO}_2 \)
(fast)

Where \( n \geq 2 \), and the asterisk denotes surface species. The mechanism for the formation of the active species is schematically shown in Fig. 8.

According to this model the reactive oxygens are those that are shared by at least two platinum atoms. As seen in Fig. 6, CO adsorbed on platinum oxide which is easily formed under moderate conditions (21) is inactive in the reaction. A similar observation was made by Ilerz (22) at higher temperatures. The reaction between the surface oxygen and carbon monoxide occurs when a surface CO diffuses to the oxygen site (during the oxygen on portion of the period) or when a gas-phase CO adsorbs on one of the platinum atoms sharing the oxygen. This model satisfies essentially all the necessary requirements:

(i) Adsorption of oxygen during the oxygen on portion of the period is slow because of the need for a multiatom site. Since adsorption is slow the concentration of the reactive complex is relatively low. Reactive intermediates are formed by the surface diffusion of CO to the active oxygen site.

(ii) During the CO on portion of the cycle the concentration of the reactive intermediate is much higher due to the fact that CO can adsorb on both metallic and oxygen-sharing Pt sites. In addition, CO molecules adsorbed on metallic Pt can diffuse to the active oxygen sites.

(iii) At steady state most of the catalyst surface will be covered with CO adsorbed on metallic Pt, leaving very few clusters of metallic platinum needed to form active oxygen adsorption sites. Since there is plenty of surface CO the rate of reaction at steady state will be determined by the availability of the active oxygen sites. The concentration of the reactive intermediate containing both CO and oxygen will be very low due to the rapid rate of decomposition and the slow rate of formation.

(iv) This model also explains why we were not able to detect significant amounts of the 2092-cm\(^{-1}\) species during an oxygen titration transient of the CO-pretreated catalyst. Since the rate will be limited by step (1) in the mechanism given above, significant amounts of the reactive intermediate cannot accumulate on the surface.

According to the above model the time-averaged rates of reaction during periodic operation are much higher than the equivalent steady-state rates or the maximum steady-state rates because during periodic operation the surface is never completely covered by adsorbed CO. Exposure to oxygen only, for a large portion of the period, consumes much of the surface CO and leaves behind a large number of adsorbed reactive oxygen sites which react very rapidly during the CO portion of the period.

Another observation we have made using

![Fig. 8. Schematic diagram showing the structure of the proposed reactive intermediate responsible for CO\(_2\) production and the two possible mechanisms leading to its formation during periodic operation.](image-url)
our see-through reactor (23) provides additional support for the above model: during reactive step testing of the CO-pretreated catalyst with oxygen, some of the adsorbed CO is seen to desorb and readsorb. This process leads to the formation of multatom centers for oxygen to adsorb on and always precedes the surge in the CO$_2$ production rate. The induction period seen with oxygen can also be decreased or eliminated completely by purging the reactor with an inert gas for extended periods of time and thus desorbing some of the CO from the surface.

Finally, we would like to address the issue of temperature excursions during steady state and periodic operation. We monitored the surface temperature of the pellet using an IR thermometer with a spatial resolution of ca. 0.125 in. and thermal resolution of 1 K. No temperature excursions of more than ±2 K were detectable, and there was no correlation with the changes in the gas-phase concentrations. While not ruling out instantaneous hot spots that can be measured with imbedded thermocouples (23), we conclude that even if under some operating conditions temperature excursions are possible they are not the reason for the increased reaction rates during periodic operation.

IV. CONCLUSIONS

The experimental data presented above provide evidence for the following important conclusions:

1. CO adsorbed on platinum oxide is very stable, nonreactive, and does not diffuse on the catalyst surface. Platinum oxide covered with CO does not get reduced at an appreciable rate.

2. Under reactive (with oxygen) and non-reactive conditions the frequency of CO adsorbed linearly on metallic platinum stays constant, providing indirect evidence for adsorption in the form of "islands."

3. The integrated area of the 2092-cm$^{-1}$ band, assigned to CO linearly adsorbed on platinum atoms sharing an adsorbed oxygen with their neighbors, correlates very well with the rate of CO$_2$ production during periodic operation. According to the available evidence this species is the reactive intermediate on the catalyst surface.

4. CO adsorbed linearly on metallic platinum serves as a source of adsorbed CO when there is no gas-phase CO but is not the active surface species.

5. Periodic operation leads to significant changes in the surface concentrations of the various adsorbed CO species on the surface. During periodic operation the time-averaged concentration of the reactive intermediate is much higher than steady state leading to dramatically increased rates of reaction.

Based on the experimental evidence a detailed mechanism, which is able to explain all the experimental observations made in this study, is proposed.

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