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Infrared Spectral Studies of Reactions of Carbon Monoxide and Oxygen on Pt/SiO_2[1]

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The reaction of oxygen gas with CO adsorbed on two samples of Pt/SiO_2 with different particle sizes has been followed by direct monitoring of the infrared absorption near 2075 cm^{-1}. In contrast to earlier reports the rate of CO_2 formation did not show a simple second-order dependence on CO coverage and this discrepancy is explained by improved spectrometer performance. During the course of reaction the peak frequency of the residual CO molecules remained almost constant indicating the maintenance of high local CO coverage throughout. This is interpretable in terms of island formation on individual particles with reaction only at the interface between islands. Evacuation halted oxidation even though the sample as a whole still contained both adsorbed oxygen and adsorbed CO. Reaction between them became impossible probably because individual particles contained only one adsorbed species. An accelerated rate was observed when oxygen was readmitted to a partially reacted system. Over a limited range the fall in θ_{CO} was linear with ln(time) pointing to a steadily rising activation energy. Reaction of CO with an initially oxygen covered surface exhibited similar behavior whilst the presence of both gases led to maximal CO coverages below 100°C even when oxygen was in excess. The origin of the increase in activation energy is believed to be the intrinsic inter- and intraparticulate heterogeneity of supported platinum.

INTRODUCTION

In recent years experiments using well-defined surfaces have provided detailed information on catalysis of carbon monoxide oxidation by the platinum group metals (*1*). The situation is best understood for palladium where the work of Ertl and coworkers (*2, 3*) has demonstrated that the reaction proceeds by a Langmuir–Hinshelwood step between an adsorbed carbon monoxide molecule and an oxygen atom rather than by an Eley–Rideal process as previously supposed. However, since the adsorbed species form a variety of mixed and separate surface phases depending on individual and total coverages no unique kinetic expression is possible and observed activation energies are coverage dependent. Even so, under conditions such that carbon monoxide coverage is high there can be a quite remarkable rate correspondence between low-pressure results and those of "practical catalysis" using pressures many orders of magnitude greater (*1, 4*).

Initial attempts to model CO oxidation over supported platinum generally assumed adsorption/desorption equilibrium for carbon monoxide and for oxygen as *molecules* with a slow reaction between them as the rate-determining step (*5, 7*). However, whilst the fit was often relatively good (*5, 6*) the optimized parameters tended to show unreasonable temperature dependencies (*6, 7*). Furthermore, that basic scheme cannot adequately account for near discontinuities in rate as the carbon monoxide pressure is increased (*8*) or the observation of certain types of rate oscillations (*9*). Recently Herz and Marin (*8*) showed that better results can be obtained with a model which conforms more closely to the situation for well-defined crystal planes and incorporates a variation in the activation energy for carbon monoxide desorption with coverage. According to Sheintuch and

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Schmitz (*9*) rate oscillations under gradientless conditions are also best explained by a variation of either activation and/or desorption energy with coverage.

In this work we have used infrared spectroscopy to follow the disappearance of adsorbed carbon monoxide from platinum particles due to reaction with gas-phase oxygen thus repeating and extending a much earlier study due to Heyne and Tompkins (*10*). Our measurements with improved techniques fail to confirm their claim that the reaction rate is second order in adsorbed carbon monoxide. Rather, our results point to a variation in activation energy with overall coverage (as postulated in the above-mentioned works) and provide an estimate for the magnitude of the effect.

EXPERIMENTAL

Two samples of supported Pt were used. One was of the conventional type for infrared studies and similar to that used by Heyne and Tompkins (*10*). It consisted of 5 wt% Pt on aerosil-type silica (Cabosil HS5). Conventional H_2 chemisorption studies (*11*) gave the percentage Pt exposed as surface atoms to be 18% indicating the approximate particle size to be 6 nm. The second sample was that designated 63-SiO_2-Ion X-S by Uchiyama *et al.* (*12*) and comprised 0.5 wt% Pt on wide-pore silica gel (Davison Grade 62). The percentage Pt exposed was 63.5% and the average Pt particle size 1.6 nm.

Samples of each were finely ground and pressed into 3.2-cm-diameter pellets weighing approximately 25 mg cm^{-2} using a pressure of approximately 30 MPa. Two near-identical pieces 18 × 8 mm were cut from each pellet and one each placed in the small aluminum holders of the identical reference and sample beam cells. The *in situ* cylindrical cells were constructed of Pyrex glass 16 cm in length with a central internal diameter of 22 mm flaring to 30 mm at the ends. The narrower section was wound with heating wire and insulated. The temperature could be maintained constant to ±1°C in the range 40 to 360°C using a proportional controller operating off a platinum resistance sensor adjacent to the windings. Pellet temperatures were recorded by iron–constantan thermocouples located in an internal thermowell which positioned the sample holder. Potassium bromide windows were sealed to the ends of the tube by O-rings tightened by heavy aluminum caps which served to dissipate heat.

Infrared spectra were recorded with a Perkin–Elmer model 580 ratio-recording spectrometer operating with a spectral slitwidth of 3.5 cm^{-1} which was sufficiently small to avoid bandshape distortion given the minimum half-width of 25 cm^{-1} for the CO band under study. Peak frequencies were accurate to ±1 cm^{-1}. Use of paired pieces of the same pellet in reference and sample beams produced a baseline flat to ±0.05 in absorbance over the region 2200–1800 cm^{-1} despite sloping baselines due to scattering and the presence of background silica peaks exceeding 0.5 in absorbance for the individual pellets. Due to the large particle size of the silica support, samples of the 0.5% Pt/wide-pore silica exhibited more scattering than did samples of 5% Pt/Cabosil and this coupled with a threefold smaller number of surface Pt atoms per unit weight available for adsorption resulted in a much poorer signal-to-noise ratio. In consequence measurements with the 0.5% Pt material were restricted to checks to confirm the generality of the findings with the 5% Pt samples.

During the course of kinetic runs with 5% Pt samples absorbances could be measured with a precision of ±0.005 in absorbance. However, absolute values varied by up to ±4% depending on the positioning of the movable spectrometer with respect to the fixed cells and in consequence to the exact portions of the slightly nonuniform pellets that were traversed by the 12 × 2-mm focused beam of the spectrometer. This placed a limit on the accuracy with which measured rates could be determined and compared for separate experiments even with the same pellet.

Prior to reaction each pellet was reduced several times with about 50 Torr (1 Torr = 133.3 Pa) of prepurified hydrogen at 350°C with evacuation at 350°C to 10^{-4} Torr between each reduction. The reference cell was then evacuated, isolated, and left at room temperature. The sample beam pellet was cycled alternately in a few Torr of CO then O_2 gas. The final step consisted of introduction of CO gas to the oxygen-covered surface and allowing the CO infrared absorption band to build up to the required absorbance value. The cell was then evacuated for 10 min and a known pressure of oxygen gas was introduced. The rate of removal of adsorbed CO was followed by either repeatedly scanning the spectral region from 2140 to 2000 cm^{-1} at set intervals or by fixing the instrument at the wavelength of the absorption band and monitoring band intensity as a function of time. The former procedure was more accurate since it permitted exact correction for baseline drift and the slight changes in peak frequency with absorbance but the latter allowed the following of reactions with half-lives as short as a few seconds.

Initial O_2 pressures lay within the range 0.5 to 3 Torr as measured accurately by a capacitance manometer (M.K.S. Instruments) and consumption of oxygen during the course of reaction reduced that partial pressure by 15% at most and generally by less than 5%. As mentioned by Heyne and Tompkins (*10*) absolute values for rates of CO removal in this system are very sensitive to the exact procedure by which the initial CO layer is created. In most of our work each reaction between adsorbed CO and O_2 gas was driven to completion between successive experiments by raising the temperature to 120°C followed by evacuation of excess O_2 and product CO_2 for a fixed period prior to building up of adsorbed CO at the next reaction temperature. Experiments conducted with different procedures resulted in somewhat different absolute rates but nevertheless similar overall conclusions regarding kinetic behavior, activation energies, etc.

RESULTS

Figure 1 shows some of the spectra obtained during a typical kinetic run at 52°C for the reaction between oxygen gas and carbon monoxide adsorbed on a pellet of the 5% Pt/SiO_2 material. The initial spectrum showed the narrow slightly asymmetric band ($\Delta\bar{\nu}_{1/2}$ = 28 cm^{-1}) evident at 2078 cm^{-1} and characteristic of linearly adsorbed CO (*13*). (A weak broad peak of absorbance <0.06 and half-width ≃70 cm^{-1} attributable to bridged CO molecules (*13*) was also present near 1840 cm^{-1}.) Subsequent spectra illustrate that reaction of the adsorbed CO with 1 Torr (133 Pa) of O_2 gas was initially fast with 50% removal within 3 min but slowed rapidly so that about 7% of the starting CO layer was still present after 85 min. The spectral characteristics of the CO band then remaining (peak $\bar{\nu}$ = 2075 cm^{-1}, $\Delta\bar{\nu}_{1/2}$ = 42 cm^{-1}) differed only slightly from the initial values. Similar behavior was observed during the oxidation of CO adsorbed on the 0.5% Pt/SiO_2 sample ex-

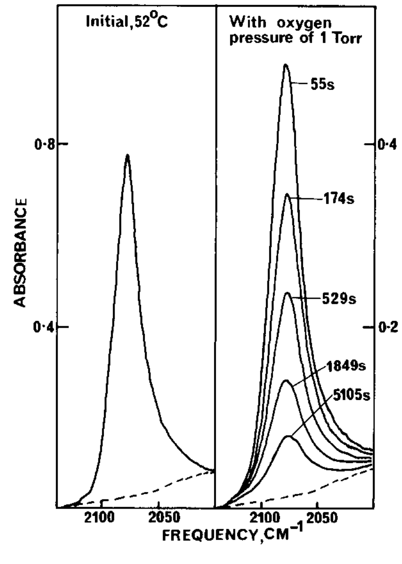

FIG. 1. Typical spectra illustrating course of reaction between adsorbed CO and O_2 gas; 5% Pt/SiO_2, 1 Torr O_2 gas, 52°C.

cept that the peak frequency was near 2072 cm^{-1} for high absorbances decreasing to 2070 cm^{-1} with near-complete removal.

The change in half-width prevented the direct use of absorbances as a measure of concentration and a procedure described elsewhere (14) was used to convert absorbances to CO surface coverages defined by

$$\theta_{CO} = \frac{\text{CO molecules absorbed}}{\text{surface Pt atoms as measured by hydrogen chemisorption}}.$$

Figure 2 shows first- and second-order plots for the change in θ_{CO} with time. In contradistinction to the results of Heyne and Tompkins (10) the second-order plot was not linear thus ruling out their claim for the relationship $-d\theta_{CO}/dt = k_2\theta_{CO}^2$. A first-order relationship $-d\theta_{CO}/dt = k_1\theta_{CO}$ or the simple Langmuir–Hinshelwood situation $-d\theta_{CO}/dt = k_{LH}\theta_{CO}\theta_{O_2}$ are also incompatible. The very rapid falloff in rate points to a dependence of activation energy on θ_{CO}. If the variation is linear due to either intrinsic heterogeneity or interaction on a homogeneous surface then the situation is formally similar to the Elovich equation for adsorption (15). In the present case this leads to

$$-d\theta_{CO}/dt = k \exp[-(E_0 - \alpha\theta_{CO})/RT], \quad (1)$$

where E_0 is the activation energy for $\theta_{CO} = 0$, α is the difference between the highest and lowest values for the activation energy, and k is the rate constant for the homogeneous model and (RT/α) times that constant for the heterogeneous model. The assumptions and limitations of Eq. (1) are as outlined by Aharoni and Tompkins (15) for the Elovich case. The value of α must be sufficiently large that the variation of rate with coverage is primarily determined by the exponential in $\alpha\theta/RT$ so that the form of the kinetic expression in surface concentrations has become both immaterial and unobtainable. The assumption is least valid at low θ_{CO}.

Integration of Eq. (1) from an initial $\theta_{CO}{}^0$ over a period of time t then gives

$$\theta_{CO} = E_0/\alpha + (RT/\alpha)\ln(RT/k\alpha) - (RT/\alpha)\ln(t + t_0), \quad (2)$$

where

$$t_0 = (RT/k\alpha)\exp[E_0 - \alpha\theta_{CO}{}^0)/RT].$$

Thus if t_0 is sufficiently small then plots of θ_{CO} versus ln(time) should be linear with slope equal to $(-RT/\alpha)$. Figure 3 shows a test of this equation for a set of experiments

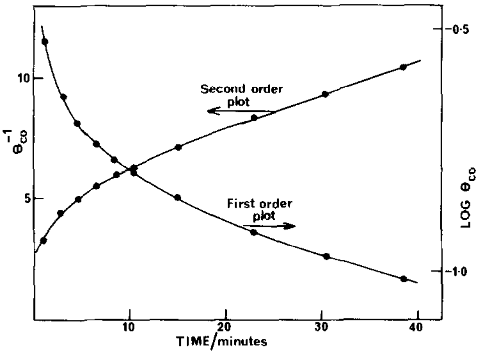

FIG. 2. First- and second-order plots for disappearance of adsorbed CO with time (condition as per Fig. 1).

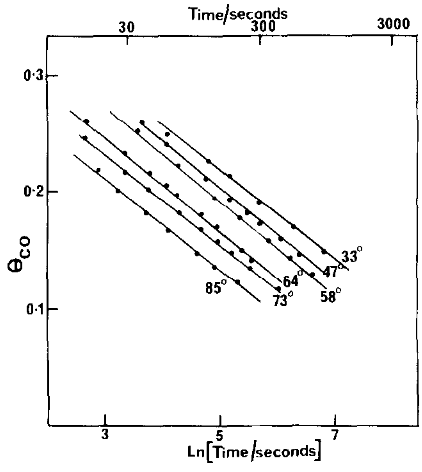

FIG. 3. Carbon monoxide coverage versus ln(time) plots for reactions with 1 Torr of O_2 gas at different temperatures; 5% Pt/SiO_2, $\theta_{CO}{}^0 = 0.30 \pm 0.02$.

differing only in reaction temperature. The plots are fairly linear (with $\alpha \simeq 50$ kJ mol^{-1}) in contrast to the decided curvature exhibited in Fig. 2 over the same range of CO coverages. An Arrhenius plot constructed from the data of Fig. 3 at $\theta_{\text{CO}} = 0.2$, calculating rates as

$$\text{rate} = -\frac{d\theta_{\text{CO}}}{dt} = -\frac{1}{t}\frac{d\theta_{\text{CO}}}{d\ln t} \qquad (3)$$

yielded a value of 48 kJ mol^{-1} for the apparent activation energy at that coverage.

As can be seen from Fig. 4 experiments with starting carbon monoxide coverages close to the maximum obtainable did not conform exactly to Eq. (2) over the full range. The most reasonable explanation is that the relationship between E_a and θ_{CO} is not exactly linear as supposed earlier. Figure 5 shows the relationships required to give exact agreement between experiment (plotted points) and calculation (solid lines) in Fig. 4. The calculations were performed stepwise using the unintegrated equation $-d\theta_{\text{CO}}/dt = k\exp[-E_a(\theta_{\text{CO}})/RT]$ arriving at the function $E_a(\theta_{\text{CO}})$ in a trial-and-error fashion. In so doing it was assumed that the value $E_a = 48$ kJ mol^{-1} at $\theta_{\text{CO}} = 0.2$ found for the 0.5% Pt sample also applied for the 0.5% Pt sample. Since this could not be verified better than within the experimental error of ± 6 kJ mol^{-1} any attempt to imply similarities or differences between the two samples on the basis of Fig. 5 must be approached with caution.

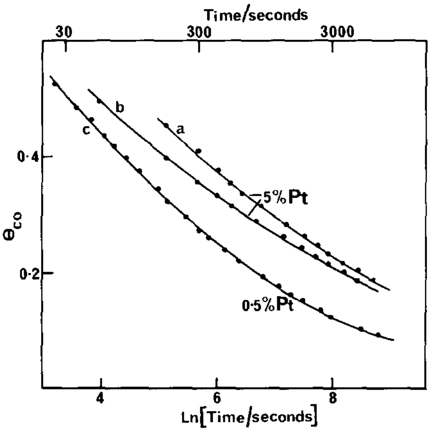

FIG. 4. Carbon monoxide coverage as a function of ln(time) for the following conditions: (a) 5% Pt/SiO_2, 35°C, O_2 pressure = 1.0 Torr, $\theta_{\text{CO}}{}^0 \simeq 0.65$; (b) 5% Pt/SiO_2, 37°C, O_2 pressure = 2.1 Torr, $\theta_{\text{CO}}{}^0 \simeq 0.65$; (c) 0.5% Pt/SiO_2, 39°C, O_2 pressure = 1.0 Torr, $\theta_{\text{CO}}{}^0 \simeq 0.65$. Plotted points correspond to data, solid lines to calculations (assuming the variation of activation energy with residual coverage given in Fig. 5).

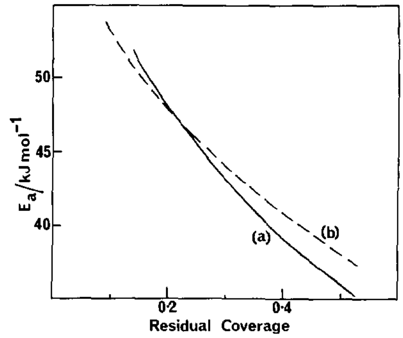

FIG. 5. Relationship between activation energy and residual coverage required to produce calculated lines of Fig. 4. (a) 5% Pt/SiO_2; (b) 0.5% Pt/SiO_2.

The relationship of rates (calculated via Eq. (3)) to some system variables is shown in Table 1. The reproducibility was about 20% due to difficulties in exactly reproducing the complete experimental conditions. The overall conclusions are: (i) CO removal showed a small positive-order dependence on oxygen pressure at high CO coverages; (ii) reaction rates on the 0.5% Pt sample were similar to that on the 5% Pt sample; (iii) there was a strong inverse relationship between rate and starting CO coverage. The latter difference spanned a factor of 40 in going from $\theta_{\text{CO}}{}^0 = 0.60$ to $\theta_{\text{CO}}{}^0 = 0.34$.

The same effect was apparent during the course of individual experiments during which the oxygen gas phase was first removed and later replaced. Figure 6 shows the absorbance versus time behavior for one such experiment, whilst in Figure 7 data for a similar experiment have been replotted in the form of ln(rate) versus θ_{CO} so as to eliminate the time variable. Rates on recommencement clearly exceeded those expected by extrapolation of the pre-

TABLE 1

Effect of Initial CO Coverage ($\theta_{CO}{}^0$) and O_2 Pressure on Rate of CO Removal

Sample	Temperature (°C)	$\theta_{CO}{}^0$	O_2 pressure (Torr)	$10^4\,[-d\theta_{CO}/dt]^a$ when	
				$\theta_{CO} = 0.2$	$\theta_{CO} = 0.1$
5% Pt	37	0.35	1.0	6.9	0.45
	37	0.44	1.0	1.0	0.1
	39	0.45	1.0	1.5	0.17
	42	0.53	1.0	0.61	0.065
	37	0.65	1.0	0.21	0.032
	35	0.65	1.0	0.14	0.020
	37	0.65	2.1	0.18	0.026
5% Pt	37	0.34	1.0	—	0.8
	37	0.33	2.0	—	0.7
	42	0.42	0.5	1.8	0.26
	42	0.42	1.0	1.9	0.23
	42	0.42	2.7	2.4	0.26
0.5% Pt	40	0.37	1.0	7.2	0.35
	39	0.45	1.0	1.4	0.14
	39	0.65	1.0	0.9	0.09

[a] Units are s^{-1}.

vious stage of reaction to the same coverage. Figure 6 also shows that reaction of adsorbed CO did proceed for some time after oxygen removal was commenced (pressure was reduced by a factor of 100 in less than 20 s).

A limited set of experiments was carried out for reaction between gas-phase CO and a surface covered with residual oxygen following complete oxidation of adsorbed CO at 120°C. This reverse reaction yielded CO_2 gas and adsorbed CO in a 1 : 1 ratio (*10, 16*) and as can be seen from the plots of Fig. 8 the buildup in the CO coverage with time also deviated slightly from Eq. (2) in such a way as to indicate a variation in activation energy across the surface similar to that of Fig. 5.

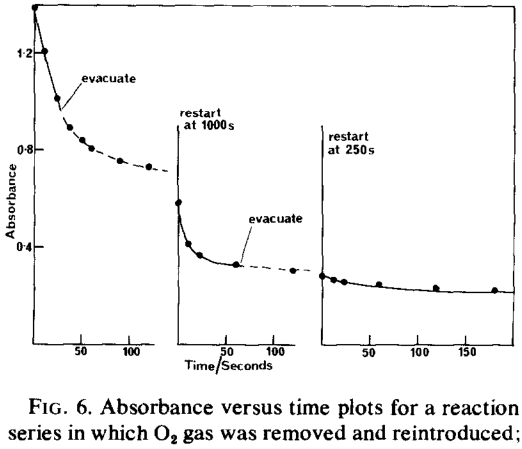

FIG. 6. Absorbance versus time plots for a reaction series in which O_2 gas was removed and reintroduced; 5% Pt/SiO_2, 47°C, O_2 pressure ≃ 1 Torr, $\theta_{CO}{}^0 \simeq 0.64$.

Comparison of Figs. 4 and 8 showed that the rate of change of CO coverage in the former instance was greater at high CO coverages but lower at low coverages and led to the possible expectation that when both gases were present the CO coverage would settle at an intermediate value. Experiments of this type using a gas mixture with a 1 : 3 CO : O_2 ratio and intermediate starting coverages are given in Fig. 9. At starting temperatures of 89°C and below the CO coverages increased steeply to the maximum obtainable in the absence of oxygen at which point catalysis of the oxidation of gas-phase carbon monoxide was very slow. On the other hand with starting temperatures of 119°C and above catalysis was readily measurable as a pressure decrease

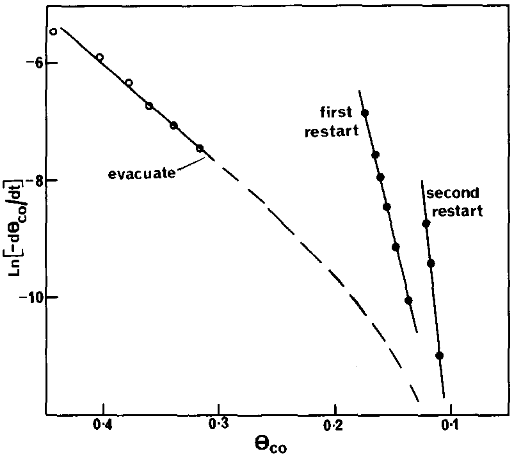

FIG. 7. $\ln(-d\theta_{CO}/dt)$ as a function of CO coverage for an experiment of the type shown in Fig. 6.; 5% Pt/SiO_2, 51°C, O_2 pressure $\simeq$ 1 Torr, $\theta_{CO}{}^0 \simeq 0.66$.

in the system and eventually by a rapid decline in CO coverage. In the experiment in which the temperature was increased from its starting value of 89°C, the CO coverage slowly increased and catalysis was small until the temperature reached 111°C when the onset of reaction was apparent both as a pressure drop and a fall in CO coverage as in the experiment started at 119°C. These experiments showed that any bare sites produced by either of the *net* reactions

$$CO(ads) + \tfrac{1}{2}O_2(gas) \rightarrow CO_2(gas)$$

or

$$CO(gas) + O(ads) \rightarrow CO_2(gas)$$

were filled by CO molecules in preference to O_2 and this effectively prevented the continuance of either reaction. Only when the rate of the first reaction or of CO desorption rose above a critical value did rapid catalysis occur.

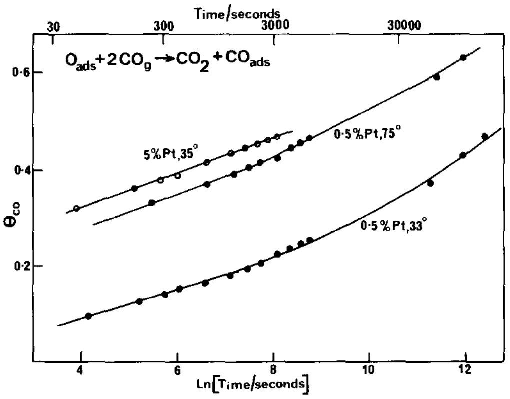

FIG. 8. Carbon monoxide coverage versus ln(time) plots for reaction of 2.3 Torr of CO gas with oxygen-covered Pt/SiO_2 surfaces.

DISCUSSION

The present results for the reaction of oxygen gas with CO molecules adsorbed on Pt/SiO_2 agree fairly closely with those of Heyne and Tompkins (*10*) with respect to apparent activation energy, initial rates, and dependence on oxygen pressure. However, we fail to confirm their claim of a second-order dependence of rate on θ_{CO} and thus for a mechanism unique to this system. In fact recent work with single-crystal Pt planes shows that reaction proceeds by a Langmuir-Hinshelwood step between adsorbed CO and adsorbed oxygen atoms and in the later discussion we will try to explain all our results on that basis. Differences in spectrometer performance are probably the cause of the discrepancy between the findings of Heyne and Tompkins (*10*) and our own as to kinetics. They used a spectrometer with a large spectral slitwidth (23 cm^{-1} compared to the 3.5 cm^{-1} available to us)

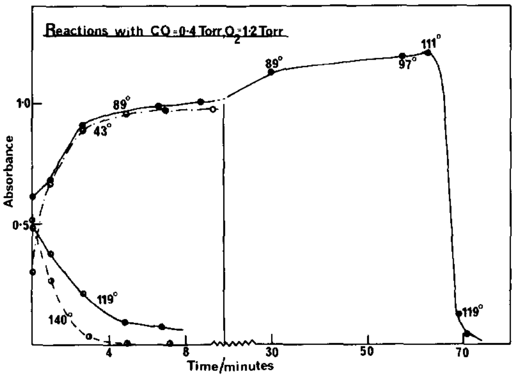

FIG. 9. Absorbance of CO band near 2075 cm^{-1} as a function of time for reactions of partially CO covered 5% Pt/SiO_2 surfaces with 1 : 3 CO/O_2 gas mixtures at different temperatures.

and scanned at a relatively rapid rate (in excess of 100 cm^{-1}/min). The effect of both these factors is to introduce proportionately greater errors in the scanning of the narrower bands with high absorbances (*17*, *18*) but in the absence of knowledge as to the time constant used no quantitative estimates as to errors are possible. An exponential relationship as in Eq. (1) may be experimentally indistinguishable from second-order kinetics over a limited range (in this case near where $\theta_{CO} = RT/\alpha \simeq 0.07$). Systematic errors present in spectral measurements at high absorbances probably led Heyne and Tompkins (*10*) to observe apparent conformity over a more extended range.

Spectrometer performance may also be a factor in one other major difference. They stated that during the course of the oxidation the peak frequency of the remaining adsorbed CO molecules fell from 2089 to 2030 cm^{-1}, whereas in our work it remained almost constant at 2076 ± 3 cm^{-1} (for the 5% Pt/SiO_2). A similar constancy in frequency has been reported for the oxidation of CO on Pt(111) and Ir films by reflection absorption infrared measurements (*19*, *20*). By contrast it is well known that the adsorption of CO on Pt/SiO_2 in the absence of oxygen produces a band at 2040 cm^{-1} at low coverages which shifts steadily toward 2070 cm^{-1} with increasing coverages primarily as a result of dipole–dipole interactions (*21*). Thus high and constant frequencies during the course of CO oxidation as found here and in the studies noted above imply that residual CO molecules retained *locally* high coverages throughout.

The experiment corresponding to Fig. 6 confirmed Heyne and Tompkin's observation that if the gas-phase oxygen was pumped out during the course of a run then oxidation of adsorbed CO came to halt within some tens of seconds and there was no subsequent change in CO band intensity (even over many hours). This was so even though the sample as a whole certainly still contained both adsorbed CO and adsorbed oxygen. Heyne and Tompkins (*10*) regarded this as absolute evidence against the currently favored Langmuir–Hinshelwood scheme. In fact what is really implied is that either individual metal particles contained both adsorbed species which did not react for some reason or that the reaction had proceeded in such a way that at any given time individual particles retained either oxygen or carbon monoxide but not both so that further reaction became impossible without an intervening desorption/readsorption step.

The former explanation faces the following hurdles. Individual carbon monoxide molecules adsorbed on bulk crystal faces are believed to be highly mobile (the observation of sharp LEED patterns at subambient temperature is generally taken as evidence for that) and thus on a small particle should be able to sample all vacant sites. The LEED measurements for Pd(111) also show that when both adsorbed oxygen atoms and carbon monoxide are present and intermingled at high total coverages then CO_2 formation commences at temperatures as low as 260 K (*3*). Thus it seems that the only way in which both species might coexist on the same particle would be in the form of separate patches in which attractive lateral interactions within the CO patch prevented the migration of edge molecules to immobile oxygen atoms. This would also maintain high local CO coverages as required by the spectroscopic results.

Certainly there is good evidence for island formation. Crossley and King (*22*) inferred the presence of patches containing on average 15 molecules from their reflection-infrared results for adsorption of CO on Pt(111) and (110). LEED measurements (*3*) show for Pd(111) that separate domains of CO and O atoms are favored under some conditions. However, even then CO_2 formation still took place below 350 K at rates approaching some hundredths of a monolayer per second. By contrast Reinalda and Ponec (*20*) reported that exposure of Ir films containing low coverages of CO to oxygen gas at 300 K induced formation of islands of CO that did not react with nearby oxygen until the temperature was raised. Thus the existence of nonreacting separate patches of CO molecules and oxygen atoms on the same platinum particle cannot be ruled out. Whilst the surface diffusion lengths could barely exceed 10 atom diameters the existence of rows of edge atoms and other forms of heterogeneity may impose restrictions which serve to confine molecules to particular areas.

In our view the reaction of oxygen gas with CO absorbed on Pt/SiO_2 proceeds in the following way under the conditions of our experiments. The initially near complete CO layer inhibits oxygen adsorption but nonetheless gaps exist as a result of momentary CO desorption or at vacant edge or corner atoms. Dissociative adsorption of an oxygen molecule at such sites leads to rapid formation of two CO_2 molecules and the creation of more adsorption sites. Thus reaction proceeds at the perimeter of an expanding area containing only oxygen and into the CO-covered region. On a truly uniform surface an acceleration in rate might be expected until half the surface was cleared. However, small particles exhibit heterogeneity [the observed half-width of $\geq 28\ \text{cm}^{-1}$ for the CO absorption band is clear evidence of this since on single-crystal planes it seldom exceeds 10 cm^{-1} (*22*)]. In consequence reaction spreads more rapidly in some directions than others leaving molecules on less reactive sites behind and giving rise to steadily increasing activation energy. For the same reason of heterogeneity one does not expect the process to start and proceed in phase on each particle. Therefore in the middle stages of oxidation over the pellet as a whole, reaction may be near complete on some particles, in progress at various stages on others, and perhaps yet to commence on a few. Local high coverage is thus being maintained as required by the spectroscopic results and furthermore since the residual CO molecules are in smaller patches with greater edge effects and on the least uniform sites one expects some increase in half-width as observed.

If the oxygen gas phase is now removed reaction will proceed across particles containing both adsorbed species until either the species in stoichiometric deficit is totally consumed or patches of residual CO molecules become too widely separated from oxygen atoms to react further. Experiments such as those of Fig. 6 provide some support for this idea since CO removal did continue for up to 100 s after evacuation was commenced. Once reaction becomes insignificant then one can reasonably expect some redistribution of CO molecules on individual particles back to vacant more reactive sites and from the more highly populated to less populated particles as well. Thus on average residual CO molecules may be both more reactive and more likely to have adjacent vacant sites for oxygen adsorption and the observed more rapid reaction on oxygen readmission is to be expected.

The same effect would explain the strong dependence of rate on starting CO coverage if the reverse reaction between adsorbed oxygen and gas-phase CO exhibited similar behavior. Spectra support this view since during this reaction the CO absorption band first appeared at $\geq 2070\ \text{cm}^{-1}$ thus indicating locally high coverage from the inception of reaction. Similar behavior has been observed with Ir films at low pressure (*20*) but not with Pt(111) where CO molecule adsorption consequent upon oxygen atom removal is random (*19*). However, in the latter work oxygen coverages were quite low (probably $O/Pt = 0.25$), whereas ratios up to $O/Pt = 0.95$ have been reported (*23*) for pressures in the Torr range as used here.

The data of Fig. 5 provide support for modeling studies (*8*, *9*) which suppose coverage-dependent activation energies. However, the origin of this variation with supported platinum particles is clearly not a direct relationship between CO coverage and activation energy since otherwise the reverse reaction O(adsorbed) + CO(gas) would *accelerate* rather than slow as the CO coverage built up. Rather the cause must be intrinsic heterogeneity as stated earlier and two forms may be identified. One arises from the difference between particles (i.e., an interparticulate effect) and the second is associated with the spread in activity across the surface of an individual particle (an intraparticulate effect). It can be seen from Figs. 4 and 8 that the CO(adsorbed) + O_2(gas) reaction was faster on the 0.5% Pt/SiO_2 sample (with its smaller Pt particle size) than on the 5% Pt/SiO_2 sample, whereas the reverse was true for the O(adsorbed) + CO(gas) reaction. Presumably this is a consequence of the different effects of the above heterogeneity on the reactivity of adsorbed oxygen and carbon monoxide.

Our results have some bearing on steady-state catalysis. The data of Fig. 9 using mixtures show that at moderate temperatures with near-stoichiometric mixtures catalysis occurs in the presence of a near-complete layer of CO as is well known with Pd/SiO_2 (*24*). The effect of intraparticulate heterogeneity will then be minimal (although it is possible that individual Pt particles may make disproportionately large contributions to the overall rate). Steady-state turnover frequencies show little dependence on particle size under such conditions (*25*, *26*). However, complications can ensue if the CO pressure is reduced below the point where the supply of CO to the surface is insufficient to keep up with the reaction. As shown by the calculations of Herz and Marin (*8*) a discontinuity in rate is then predicted as the entire surface changes over from being predominantly CO covered to partial coverage by oxygen alone. However if substantial interparticulate heterogeneity did exist as favored by our work the CO/O_2 pressure ratio required to induce changeover would differ from particle to particle and a situation in which some were CO covered and others oxygen covered could be envisaged.

Finally it is pointed out that the existence of intrinsic heterogeneity poses some problems in modeling since the use of equations such as

$$\text{rate} = kf(\theta_i, \theta_j) \exp[-E_0 - \alpha\theta_{i,j}]$$

which suppose direct relationships between activation energy and coverage are justified only under special conditions. Rather the instantaneous rate should be obtained by the summation over many nonequivalent patches each exhibiting its own internal activation energy distribution. As with the Elovich equation (*15*) this can give rise to equations of the above form in some circumstances but in general the spread in activation energies needs to be large (tens of kJ mol^{-1}).

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