

The Origin of Apparent Deactivation during the Oxidation of Carbon Monoxide over Silica-Supported Platinum at Moderate Temperatures

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A case of apparent deactivation of a Pt/SiO₂ catalyst for the oxidation of a carbon monoxide during long periods on stream at 450 K has been studied using a combined infrared cell/flow reactor. When the catalyst was precovered by carbon monoxide, stable rates and high carbon monoxide coverages were observed from the commencement of reaction. However, direct exposure of reduced catalyst to carbon monoxide/oxygen mixtures resulted in much higher initial rates and a significantly lower initial carbon monoxide coverage. The activity subsequently declined and the coverage increased reaching the steady values characteristic of catalysts precovered by carbon monoxide after 24 h. It is believed that direct exposure to mixtures creates a ratio of oxygen coverage to carbon monoxide coverage which is much higher than the equilibrium one. The adsorbed CO forms patches and the oxygen adatoms exhibit a wide spread of activity. The catalytic rate is slow within CO patches and faster at the edges where oxygen adatoms are located. The apparent deactivation is caused by loss of the latter sites as the oxygen adatoms initially laid down are gradually consumed and replaced by adsorbed CO. © 1986 Academic Press, Inc.

INTRODUCTION

Some years ago we studied the oxidation of carbon monoxide over the series of well-characterized silica-supported platinum catalysts prepared by Burwell *et al.* (1) and reported (2) that under stoichiometric conditions turnover frequencies at 450 K depended only marginally on Pt particle size. We also found that the activity of each catalyst declined slowly with time. However, initial activity could be recovered by treatment in flowing helium alone at reaction temperature. These effects could not be duplicated by Herskowitz *et al.* (3), perhaps due to a different experimental procedure (4), but have since been substantiated by Sarkany and Gonzalez (5). As yet the origin of the observed activity changes has not been established. Here we wish to report the results of experiments in which carbon monoxide coverage has been monitored by infrared spectroscopy simultaneously with the activity decline. They enable the offer-

ing of a much improved interpretation for the latter.

A great deal is, of course, now known about the mechanism of carbon monoxide over platinum (6). While most of the detailed information comes from studies using well-defined surfaces at low pressure (7) much of this is believed transferable to conditions of practical catalysis (6). Indeed, the kinetic models developed recently by Creighton *et al.* (8) for reaction on polycrystalline surfaces at low pressures and by Herz and Marin (9) for Pt/Al₂O₃ at much higher pressures are very similar. Both incorporate a dependence of the heat of adsorption of carbon monoxide on coverage and are consistent with the existence of the multiplicities, hysteresis, and oscillations that have been observed experimentally when the carbon monoxide/oxygen ratio is varied (8-12). Recently, Elhaderi and Tsois (12) have shown using infrared spectroscopy that carbon monoxide coverage oscillates out of phase with rate during reaction over Pt/Al₂O₃. Similarly, Haaland and Williams (13) reported that carbon

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monoxide coverage correlates inversely with rate under conditions where hysteresis is observed under steady-state conditions in the same system. They also note spectral evidence for the formation of islands of CO as we have done (14). It appears that the time scale of the process studied here is also related to nonrandom site occupancy and site heterogeneity.

EXPERIMENTAL

A Pt/SiO₂ catalyst particularly suitable for infrared spectroscopy was made by ion exchange of an Aerosil-type silica (Cabosil HS5, surface area 320 m² g⁻¹, Cabot Corp.) with a platinum amine complex according to the procedure of Dorling *et al.* (15). It contained 0.96 wt% Pt and the dispersion (percentage atoms exposed) was 92% as measured by the standard chemisorption technique using H₂ at 0°C (16). The support consisted of near uniform nonporous spheres with mean diameter of 7 nm. The apparent average radius for the pores between the packed spheres was 9 nm based on N₂ adsorption/desorption measurements. Most activity measurements were made with a single pressed disk of this material of diameter 18 mm and weight 26.4 mg. It was contained within an infrared cell/flow reactor, identical to that described by Hicks *et al.* (17), and placed in the sample beam of a Perkin-Elmer 580 spectrometer. The combination of a thin disk, very small Pt particles, and small SiO₂ particles gave high transmission for a catalyst sample (50% at 2100 cm⁻¹) and a baseline virtually devoid of slope (apart from weak SiO₂ overtone modes) over the spectral region of interest. Spectra could be recorded with a repeatability of ±0.005 absorbance units using a spectral slit width of 3.7 cm⁻¹.

The infrared cell/flow reactor was connected via 1/16 in. o.d. diameter tubing to, on the inlet side, a gas supply system and, on the outlet side, to a gas chromatograph. The general arrangement has been described earlier (18) but two small volume

switching valves (Carle Inst.) were incorporated to allow rapid switches between three separate gas streams. Even at flow rates as low as 20 cm³ min⁻¹ the dead space of tubing and reactor was sufficiently small that compositional changes were complete within the cell in a few seconds. Activity testing was carried out using a single cylinder of test gas (C.I.G. Ltd.) containing 2.09% CO and 1.03% O₂ in helium. It was passed through a cooled silica gel trap upstream of the switching valve although experiments without this trap in place gave the same results. A similar gas mixture containing 1.74% CO alone in helium was used in experiments requiring prior exposure to CO.

The catalyst disk was pressed from material prerduced at 350°C and further reduced in dilute H₂/He in the flow cell itself at 300°C (close to the maximum feasible for the Kal-rez O-rings used to seal the windows). Following this reduction the sample was cooled to reaction temperature in helium. The helium was stated to contain a maximum of 1 ppm O₂ as supplied and further purified by passage through a 4A molecular sieve column cooled to 77 K.

Conversion of CO was calculated from the relative areas of CO and CO₂ peaks in chromatograms of the exit gas as determined by a Hewlett-Packard 3390A integrator. Conversions were kept below 20% and converted to turnover frequencies per surface Pt atom making the differential reactor approximation and knowing the inlet gas composition and overall flow rate (as determined by a Brooks mass flowmeter).

RESULTS

Initial experiments were aimed to see if the changes in activity with time noted previously (2) could be duplicated with rather different catalyst form and reactor geometry used here. Following reduction at 573 K the catalyst was cooled to 450 K in helium and a switch to the test gas made. The subsequent changes in turnover frequency and

peak absorbance of the band due to linearly adsorbed carbon monoxide with times on stream of 2 min to 22 h are shown in semi-logarithmic form in Fig. 1. Some of the spectra are shown in Fig. 2. Both the evolution of activity with time and actual turnover frequencies at any one time are very similar to our earlier findings (2) for a set of five of the Pt/SiO₂ preparations of Burwell *et al.* (1). It is also clear from the spectroscopic data that the activity decrease is associated with an *increase* in the absorbance of the band due to linearly adsorbed CO. There is, however, little change in peak frequency or half-width. The latter is quite small (14 cm⁻¹) and quite comparable to that for adsorption on individual crystal planes (19–22). The relationship between activity and absorbance is fairly close to simple inverse but also reasonably consistent with that expected for a simple Langmuir–Hinshelwood model, i.e.,

$$\text{Turnover frequency (T.F.)} = k_R \theta_O \theta_{CO} \quad (1)$$

At the temperatures used both oxygen and carbon monoxide are strongly held so that after the initial adsorption phase one expects all sites to be covered and $\theta_O \approx 1 - \theta_{CO}$. Assuming $\theta_{CO} = bA$ where A is the absorbance and b is proportional to the extinction coefficient and substituting

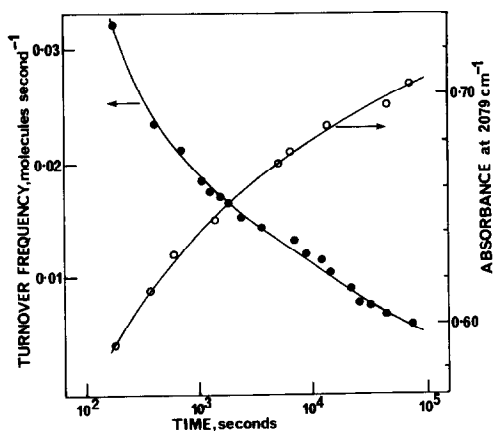


FIG. 1. Turnover frequency and peak intensity of band due to adsorbed CO as a function of time on stream at 450 K.

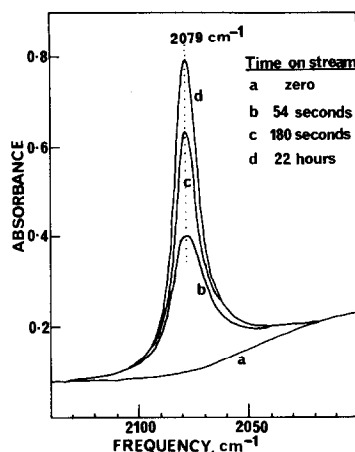


FIG. 2. Infrared spectra corresponding to data of Fig. 1.

$$\text{T.F.} = k_R b A (1 - b A)$$

or

$$\text{T.F./}A = k_R b - k_R b^2 A \quad (2)$$

As can be seen from Fig. 3 there is a fairly good correlation between T.F./ A and A as this equation predicts.

Since high CO coverages reduce activity one might expect that prior coverage by CO would lower initial activity. To test this a reactivated sample was first exposed to 1.74% CO in helium. Spectra showed a more rapid development of the CO absorp-

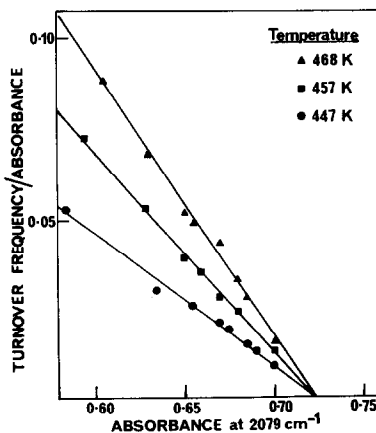


FIG. 3. Test of relationship between turnover frequency/absorbance and absorbance during reaction at temperatures of 468, 457, and 447 K.

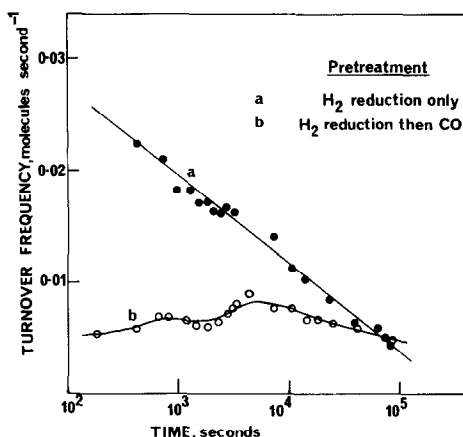


FIG. 4. Effect of prior coverage by CO on the turnover frequency versus time profile at 450 K.

tion band than in Fig. 2. After an hour a direct switch was made from CO in helium to the CO + O₂ mixture. Subsequent activity measurements are shown in Fig. 4 in comparison to a standard run starting from a reactivated catalyst. Clearly, prior coverage by CO results in a constant activity equivalent to the standard run after a day on stream.

However, this behavior was observed only if the switch from the CO stream to the CO + O₂ stream was direct. Intervening treatment in flowing helium resulted in some CO desorption and partial restoration of initially higher activity and a decline in activity thereafter. The actual course of desorption at 450 K following step changes from CO, or from the CO + O₂ test mixture, to helium is shown in Figs. 5a and b. Initial removal of CO was slightly faster in the latter case due to some reaction with gas-phase oxygen before all the latter was swept from the cell. Thereafter, the behavior was similar in the two cases with 90% removal in 20 min. Reactions recommenced subsequent to this point showed activity versus time profiles indistinguishable from the standard runs of Figs. 1a and 4b. Thus, deactivation/reactivation cycles could be repeated many times without the need for H₂ reduction or even temperature changes.

Some of the actual spectra on which the

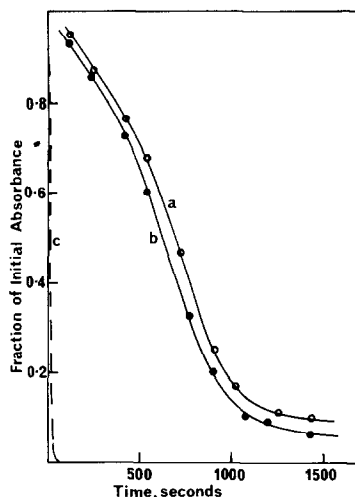


FIG. 5. Disappearance of absorption band of adsorbed CO following (a) switch from 1.74% CO in He to He alone; (b) switch from 2.09% CO and 1.03% O₂ in helium to He alone; (c) switch from 2.09% CO and 1.03% O₂ in He to 1% O₂ in He.

desorption curve of Fig. 5 is based are shown in Fig. 6. They exhibit a decline in peak frequency with decreasing coverage in contrast to the negligible frequency change which accompanies increases in absorbance during the course of reaction (Fig. 2). As argued by Haaland and Williams (13) and ourselves (14) a constant frequency im-

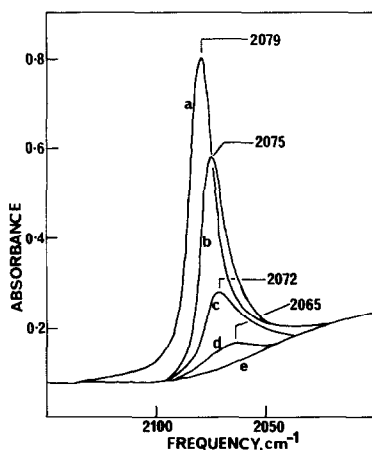


FIG. 6. Infrared spectra corresponding to data of Fig. 5a. Spectra (a) and (e) are the starting spectrum and the background, respectively, while (b), (c), and (d) correspond to desorption times of 6, 13, and 20 min, respectively.

plies that the adsorbed CO forms patches of reasonable size while decreasing frequency results from the disruption of dipole-dipole coupling within the patches as vacant sites are created.

Curve (c) of Fig. 5 shows the disappearance of adsorbed CO following a step change from the CO + O₂ test gas to O₂ (1% in He). All CO was reacted off in less than 10 s which was not much longer than the flushing time for the cell itself. By collecting the CO₂ evolved in experiments of this type in the sample loop cooled to 77 K and then determining the quantity with the chromatograph the maximum surface coverage under reaction conditions could be calculated. The value was 0.93 CO molecules per surface Pt atom. The corresponding value calculated from the maximum absorbance alone using an equation we have validated (23) at rather lower coverages was 1.1.

A few experiments were carried out to test the effect of prior exposure to O₂ at 450 K on subsequent activity. The initial analysis after a minute or two showed an activity slightly above that of the standard experiment of Fig. 1 but the subsequent deactivation profile was identical in the two cases. In our earlier work (2) we showed that O₂ treatment at 620 K lowered the entire curve by 40%.

DISCUSSION

The spectroscopic measurements show that the gradual decline in activity observed by Sarkany and Gonzalez (5) and ourselves (2) during carbon monoxide oxidation over Pt/SiO₂ is associated with an increase in carbon monoxide coverage. It does not seem likely that the inhibition of rate results purely from a change in the packing of molecules on a surface covered by CO alone. In the first place, LEED measurements (6, 7) indicate that CO mobility on Pt is relatively high at the temperatures used here. It is therefore unrealistic to imagine that rearrangements could take hours on particles

containing at most a few hundred adsorption sites. Second, the spectra measured during desorption show changes in peak frequency when the number of vacant sites is changed whereas the peak frequency remains constant during deactivation. Hence, it seems more likely that the observed increase in CO coverage results from replacement of adsorbed oxygen adatoms by CO rather than by rearrangement of CO molecules on sites. In other words, initial exposure creates a ratio of CO coverage to oxygen adatom coverage which has high activity and the subsequent slow changes in rate and coverage reflect the approach to the ultimate steady state. This would not be unexpected. According to Creighton *et al.* (8) the initial sticking probability of carbon monoxide on polycrystalline platinum is slightly greater than that of oxygen. Under our conditions the carbon monoxide pressure is twice that of oxygen but this factor is compensated by oxygen dissociation. Hence, on initial exposure of the reduced sample to the reaction mixture coverage by CO molecules should be only slightly greater than that by oxygen adatoms. The spectra show a rapid rise in CO coverage in CO coverage in the initial minute (to 70% of the subsequent maximum). Presumably, at this point the remaining sites are mostly occupied by oxygen adatoms. Thereafter, vacant sites will be filled preferentially by carbon monoxide since its site requirement is smaller. The system can be expected to progress to higher CO coverages as observed.

Recently, Klein and Schmidt (24) have described a general model to explain the time scale of processes of this type. Their model assumes that the adsorption site requirements for the competing species are the same, which is not the case here, but it can be used to estimate the minimum likely speed for such a process in our system. When one reactant does not desorb, as with oxygen here, Klein and Schmidt's model predicts that the time constant for the final approach to equilibrium should be given by

$$\tau \approx \frac{1 + f}{k_{-\text{CO}} + (1 - f)k_{\text{R}}}, \quad (3)$$

where f is the ratio of the adsorption rate of O₂ to that for CO, $k_{-\text{CO}}$ is the desorption rate constant for CO, and k_{R} is the Langmuir–Hinshelwood rate constant for the reaction between adsorbed CO and adsorbed oxygen atoms expressed in fractional coverage terms.

In the present case one expects $f < 0.5$ for the reasons given earlier and limits can be set on $k_{-\text{CO}}$ and k_{R} in the following way. The apparent value of $k_{-\text{CO}}$ indicated by the data of Fig. 5a is about 10^{-3} s^{-1} . This is certainly a lower limit since the calculations of Herz *et al.* (25) and Gorte (26) indicate that desorption from porous materials is almost inevitably mass-transfer limited in situations like ours. If the basis of Eq. (2) is correct than k_{R} can be calculated from slopes and intercepts of Fig. 3. At 450 K the value is $k_{\text{R}} \approx 0.2 \text{ s}^{-1}$.

Substituting these estimates into (3) gives $\tau \leq 15 \text{ s}$ and one predicts that the final approach to equilibrium should be exponential with a halftime of less than 15 s. Experimentally, the system does not relax exponentially and the halftime is certainly greater than 1000 s. The probable cause of the great difference is that the oxygen adatoms created during initial adsorption have a broad spread of activities and are removed at different rates. The recent work of Gland *et al.* (27) with Pt (321) surfaces clearly shows that oxygen adsorbed on rougher step sites are less reactive than those located on smooth terrace sites. Small particles are certain to contain a wide spread of site energies.

The change in CO absorbance with time can therefore be attributed to gradual removal of oxygen species of low reactivity and their replacement by adsorbed CO molecules. The way in which this changeover is able to reduce the catalytic rate is probably partially related to the nonrandom arrangement of adsorbed species initially created. As argued by Haaland and Williams (13)

and ourselves (14) the absence of a significant change in peak frequency with absorbance during the apparent deactivation (Fig. 2) indicates that the bulk of the CO molecules are present in patches of sufficient size to allow a relatively constant degree of dipole–dipole coupling. (By contrast the spectra of Fig. 5 measured during desorption show a substantial change in frequency due to the disruption of coupling by the creation of vacant sites.) Thus, it seems that oxygen adatoms created on initial contact are not randomly intermingled with CO molecules but located at the periphery of CO-covered patches. Within such patches catalysis of a reaction of a gas-phase molecule requires creation of a vacant site by CO desorption (or a previous reaction event) followed by oxygen adsorption and dissociation. Carbon monoxide readsorption is well known to severely inhibit the latter at high CO coverages as in the patches (6). The process is likely to be easier at the edges of CO-covered patches which is where the unreactive oxygens are located. As they are slowly removed the number of edge sites will decrease and one expects the catalytic rate to decline toward the value characteristic of a complete layer of CO. If the surface is equilibrated with CO prior to reaction then this rate will apply from the start of reaction as in Fig. 4.

We have considered several alternative explanations for the activity loss. In particular it was previously suggested (2) that the formation of oxidized sites might be involved. While that possibility cannot be ruled out we believe that the present explanation can account better for the three salient experimental observations, namely, the correlation between apparent deactivation and CO coverage, complete reactivation in helium alone, and the production of low and stable catalytic rates following prior exposure to CO.

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