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The Modification of CO Adlayers on Pt/SiO$_2$ Catalysts by Preadsorbed Oxygen: An Infrared and Pulse Microreactor Study

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Changes in the structure of CO adlayers as the result of co-adsorbed oxygen on Pt/SiO$_2$ catalysts have been studied using transmission infrared spectroscopy and pulsed microreactor studies. Preadsorbed oxygen was observed to cause a blue shift in the absorption frequency of adsorbed CO. The extent of the blue shift was observed to increase with the severity of the O$_2$ treatment. The origin of this blue shift is explained by invoking an increase in the extent of CO–CO dipole coupling. Both the infrared and microreactor studies strongly suggest that the increase in dipolar coupling occurs as the result of a compressed CO adlayer in which CO is segregated into isolated patches.

INTRODUCTION

In the study of catalytic reactions which take place at solid surfaces, it is constructive to obtain a thorough understanding of the interactive nature of the reactant species which are co-adsorbed on the catalyst surface during reaction. Even though the oxidation of CO on supported Pt has been the subject of a large number of investigations both on well-defined crystal planes (*1–3* and references therein) and on supported catalysts (*4–9*) many unanswered questions persist. In this paper, we will focus our attention on the possible existence of islands of reactivity (*5*), that is, the segregation of the reactant molecules into separate patches which contain either CO or O$_2$ molecules. The oxidation of CO at the periphery of such patches has been known for some time on well-defined Pt single crystals (*1, 2*). However, these studies have only recently been extended to include supported Pt catalysts (*5, 10*).

To probe the conditions which lead to the formation of segregated islands of CO and oxygen on silica-supported Pt catalysts, we have used a combination of infrared spectroscopy and pulse microreactor studies. Infrared spectroscopy is ideally suited for this type of study because of the wealth of information that can be obtained by probing the position of the infrared band assigned to the CO stretching vibration in the presence of co-adsorbed oxygen.

In the interpretation of the results of this study, it is important to consider briefly the two mechanisms which have been proposed to explain the relative shift in the position of the CO stretching frequency both as a function of surface coverage and of co-adsorbed oxygen. The first interpretation is that of Blyholder (*11, 12*) who extended the principals of coordination chemistry to include chemisorption of CO on supported metals. In this model, binding to the metal populates the antibonding orbitals of CO, thus weakening the carbon–metal bond and

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lowering the CO frequency. Furthermore, this model assumes that the coverage-dependent frequency shift is caused by the lowering of the antibonding population due to a competition for the electrons of the metal. This view involves the collective properties of the metal surface atoms and is, therefore, a long range effect. In the other interpretation, the electrodynamic model (*13–16*), it is assumed that each chemisorbed molecule can be represented by an oscillating point dipole. The frequency of any given dipole is shifted by its interaction with the dipoles of the other molecules, with their images, and with its own image. The theory also includes the screening of dipole images by the electronic polarizability of the adsorbate. Some authors suggest that the observed CO frequency shift as a function of surface coverage can be accounted for solely on the basis of dipolar coupling (*15*), while others conclude that these forces account for only a small fraction of the observed frequency shift.

The interaction between CO and electron acceptors such as O_2 has also been studied on Pt by infrared spectroscopy (*4, 17–19*). These results cannot be completely explained on the basis of the Blyholder back-bonding model (*11, 12*). Adsorbed oxygen can cause an increase in the CO frequency from 2070–2080 to 2120 cm^{-1} as a result of surface oxidation (Pt^{2+}) or the co-adsorption of both oxygen and CO on the same Pt surface site (*19*). However, a blue shift of 10–15 cm^{-1} in the CO frequency can also be obtained by the compression of the CO adlayer caused by oxygen adsorbed on the surface (*4, 5, 17, 20*).

In this study, we have attempted to sort out the different effects which lead to frequency shifts as a result of the co-adsorption of oxygen and CO on the surface of silica-supported Pt. The thrust of this work is to obtain a better understanding of the factors which influence island formation in the catalytic oxidation of CO.

EXPERIMENTAL

Materials

The silica-supported Pt samples (5 wt% Pt/Cab-O-Sil) used in the infrared studies were prepared by impregnation. Initially, the appropriate weight of $H_2PtCl_6 \cdot 6H_2O$ (Reanal, Budapest) was dissolved in an amount of doubly distilled water. This solution was mixed with Cab-O-Sil, grade M-5 (BDH Chemicals Ltd.), until a slurry having the consistency of a thin paste was formed. The slurry was stirred at room temperature for 1 hr and subsequently evaporated to dryness in a vacuum evaporator at 298 K. The procedure has been described in detail in a previous report (*21*).

H_2, O_2, CO, and CO_2 (Matheson Ltd.) were all research grade or better and were further purified by standard gas purification techniques.

The micropulse reactor studies were performed using a 6% Pt/Cab-O-Sil catalyst prepared in a manner similar to that described above. The Cab-O-Sil, grade M-5 was obtained from the Cabot Corporation, Boston, Massachusetts, and the gases were all research grade or better (New England Oxygen). Because gas chromatographic studies which make use of He as a carrier gas are very susceptible to O_2 poisoning, care was taken to exclude O_2 to the extent of about 0.1 ppm as measured at the catalyst sample.

Surface areas for the two catalysts studied were measured using H_2 chemisorption by the dynamic pulse method (*22*). The percentage of exposed Pt for the two catalysts studied was 25 and 22%, respectively.

Apparatus and Procedure

Infrared measurements were made using a Specord 71 ir (Zeiss Jena) double-beam spectrophotometer, fitted with a NaCl monochromator. A greaseless vacuum ir cell similar to that described in Ref. (*21*) was used with some slight modifications. The ir cell was connected to a conventional vacuum and gas handling system capable of attaining an ultimate pressure of 10^{-6} Torr (1 Torr = 133.2 N m^{-2}).

Thermal pretreatments and adsorption studies at higher temperatures were carried out in the externally heated portion of the infrared cell. Spectra were recorded at room temperature. However, the sample temperature due to heating by the infrared beam was between 310 and 320 K.

The dried catalysts were pressed into self-supporting disks at a pressure of 2000 Kp cm^{-2} (1 Kp cm^{-2} = 98.1 K N m^{-2}). They were pretreated *in situ* at 673 K.

Prior to an adsorption–desorption (reaction) experiment, a fresh catalyst was treated as follows: evacuated for 10 min at 298 K, temperature increased at a rate of 20 K min^{-1} to 373 K followed by evacuation at 373 K for 30 min, heated at 20 K min^{-1} to 673 K under vacuum followed by evacuation at 673 K for 30 min, treated in 100 Torr of O_2 at 673 K for 30 min followed by evacuation at 673 K for 30 min, reduced for 1 hr at 673 K in flowing H_2 (50 ml min^{-1}) followed by evacuation at 673 K for 1 hr. Pretreatments other than that outlined above (standard pretreatment) are described in the text.

Catalysts charged to the pulse microreactor were treated using a simple flow system in flowing He, H_2, or O_2 at 523 K. The reactions between preadsorbed CO and O_2(g) and preadsorbed oxygen and CO(g) were carried out at room temperature. The volume of the calibrated loop was 100 μl (1 μl = 1×10^{-9} m^3).

RESULTS AND DISCUSSION

The Adsorption (Reaction) of CO on a Pt Surface Pretreated with O_2: The Effect of CO Surface Coverage on the Desorption (Reaction) of CO

Following the standard pretreatment, the catalyst was exposed to 100 Torr of O_2 in the ir cell for 30 min at 298 K. The catalyst was then evacuated for 30 min and the stepwise adsorption (reaction) of CO was carried out at 298 K as the CO pressure was increased from 10^{-3} to 20 Torr (Fig. 1,A). The spectra were recorded after a 5-min adsorption (reaction) period following the admission of each dose. Only one infrared band in the spectral region between 2000 and 2100 cm^{-1} was observed, as was the case for the adsorption of CO on a bare, reduced Pt surface. The recorded CO stretching frequency increased with CO surface coverage. The frequencies for CO adsorbed on an oxygen covered surface were consistently higher by 2–5 cm^{-1} than those obtained on a reduced surface. At higher pressures (100 Torr of CO) a weak band centered between 2120 and 2130 cm^{-1} was observed. This band is easily removed by a short evacuation at room temperature and is due, in all probability, to CO adsorption on Pt^{2+} (*18*). No infrared bands were observed in the spectral region 1800–2000 cm^{-1}.

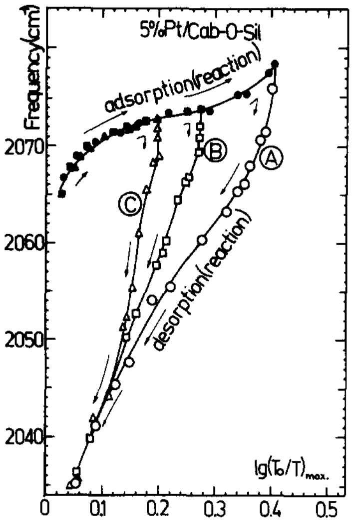

FIG. 1. Infrared frequencies for CO adsorbed on a preoxidized 6% Pt/SiO_2 catalyst as a function of absorbance. (A) θ_{CO} = 1, ○; (B) θ_{CO} = 0.67, □; (C) θ_{CO} = 0.48, △. Adsorption (reaction) at 298, filled symbols; thermal desorption (reaction) *in vacuo* at increasing temperatures, open symbols.

The desorption of CO was performed under continuous evacuation as the temperature was increased from 298 to 623 K. Prior to recording a spectrum, the sample was treated for 5–10 min at each of the following temperatures: 323, 348, 373, 423, 473, 523, 573, and 623 K. The desorption (reaction) curve corresponding to $\theta_{CO} = 1$, Fig. 1,A, was very similar to that obtained for the thermal desorption of CO from a Pt surface which had been initially reduced (*21*). This result is in line with the observation that the reaction between preadsorbed oxygen and CO(g) at 298 K has been shown to proceed quantitatively to completion according to the stoichiometric equation (*23*)

$$O(ads) + 2CO(g) = CO_2(g) + CO(ads).$$

The results of this study show the presence of an adsorption–desorption hysteresis curve in which the desorption (reaction) frequencies were markedly lower than the corresponding adsorption (reaction) frequencies at similar CO surface coverages, $\log(T_0/T)_{max}$. When desorption (and reaction) was initiated at lower surface coverages ($\theta_{CO} = 0.57$ or 0.48), the desorption branches of the hysteresis curves (Fig. 1,B, C) were quite different from those obtained for the thermal desorption of CO adsorbed on an initially reduced surface (*21*). At the onset of desorption (reaction), the CO frequency decreased by about 4 or 5 cm^{-1} without a corresponding decrease in the absorbance. Following this initial shift in frequency, both the absorbance and the frequency were observed to decrease concurrently as the desorption (reaction) branch approached the desorption curve obtained for an initial coverage of $\theta_{CO} = 1$. When CO was adsorbed on an initially reduced Pt surface, the intensity of the CO absorption band obtained during CO desorption (initiated at a CO surface coverage such that $\theta_{CO} < 1$) did not change until the frequency corresponding to the band maxima coincided with that obtained on the desorption branch of the curve (*21*).

The origin of this adsorption–desorption hysteresis has been discussed in detail in the previous paper (*21*). Briefly, it occurs as the result of the surface migration of adsorbed CO prior to thermal desorption. Due to the high sticking coefficient of CO on Pt, the adsorption of CO occurs in a random fashion. When the resultant CO adlayer is heated during thermal desorption, rearrangement of the CO surface layer occurs. This surface rearrangement results in substantial CO frequency shifts during thermal desorption. When thermal desorption is initiated at a surface coverage which is considerably less than that which corresponds to a CO monolayer, extensive rearrangement of the CO adlayer takes place prior to the onset of desorption. This surface rearrangement is concomitant with a drop in the CO stretching frequency as CO desorbs from its primary adsorption sites and readsorbs on energetically more favorable adsorption sites. In the presence of co-adsorbed oxygen, initial CO surface migration cannot occur. A mobile CO molecule will encounter an adsorbed oxygen atom and will react to form CO_2 by a Langmuir–Hinshelwood-type mechanism. As vacant surface sites are formed due to the CO–O reaction, CO surface migration can again occur. This results in a rearranged CO adlayer with a corresponding drop in the CO stretching frequency.

It is important at the outset to offer an explanation which will adequately account for the blue shift when CO is adsorbed on an oxygen treated Pt surface.

Co-adsorbed atoms and/or molecules can interact with adsorbed CO on Pt to change the ir absorption frequency. The two different points of view which are most commonly used to explain these frequency shifts are as follows: (i) oxygen acts as an electron acceptor decreasing the electron density in the metal. This, in turn, results in a decrease in the extent of d–π^* back-donation resulting in an increase in the CO stretching frequency (*11, 12, 19*); (ii) adsorbed oxygen can change the dipole coupling by forcing a compression of the CO adlayer (*13–17*).

To obtain a better understanding concerning the origin of the blue shift on the

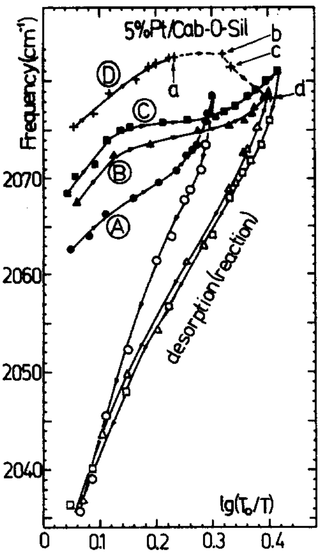

FIG. 2. The effect of different O_2 pretreatments on the frequencies of CO adsorbed (reacted) on a 6% Pt/ SiO_2 catalyst as a function of absorbance. (A) Reduced surface, ○; (B) preoxidized at 298 K, △; (C) preoxidized at 673 K, □; (D) preoxidized at 673 K followed by cooling in O_2, +. (a) 20 Torr of CO at 298 K for 30 min; (b) 20 Torr of CO at 323 K for 30 min; (c) 20 Torr of CO at 323 K for 60 min; (d) 20 Torr of CO at 373 K for 120 min.

CO stretching frequency, the effect of preadsorbed oxygen on the magnitude of the blue shift was studied in more detail.

The Effect of Different Oxygen Pretreatments on CO Adsorption (Reaction) and Desorption

After the standard pretreatment, the 5% Pt/Cab-O-Sil catalyst was treated in O_2 according to the following schedules:

(a) no further treatment, i.e., the surface remained reduced;

(b) treatment in 100 Torr of O_2 at 298 K for 30 min followed by evacuation at 298 K for 30 min;

(c) treatment in 100 Torr of O_2 at 673 K for 30 min followed by evacuation at 673 K for 30 min and cooling of the catalyst sample to 298 K *in vacuo*;

(d) treatment in 100 Torr of O_2 at 673 K for 30 min followed by cooling to 298 K in O_2 and evacuation of the sample for 30 min

The CO adsorption (reaction) was carried out as before at 298 K. The desorption (reaction) branch was obtained in a manner similar to that previously described. The results, shown in Fig. 2, clearly show that the frequency of adsorbed (reacted) CO is strongly dependent on the severity of the surface pretreatment in O_2. The effect of preadsorbed oxygen was to increase the frequency of adsorbed CO in comparison to that obtained on an untreated surface. Treatment in O_2 at 673 K instead of 298 K enhanced the blue shift by an additional 2 cm^{-1}. The largest increase was observed following oxidation at 673 K and cooling to 298 K in O_2 (blue shift of 10–12 cm^{-1}). In this case, the absorbance at the conclusion of the CO adsorption was only 0.23. Additional CO adsorption was obtained following treatment in 20 Torr of CO for 30 min (point b) or 1 hr (point c). When the temperature was increased to 373 K, the absorbance increased to 0.4 following a 1-hr exposure.

The Interaction of Preadsorbed CO with $O_2(g)$

When CO adsorbed on an initially reduced surface was reacted with $O_2(g)$ at 298 K, both the absorbance and CO frequency decreased rapidly (Fig. 3,A,B) as the O_2 gas pressure was increased from 10^{-4} to 3×10^{-2} Torr. CO bands were not observed when the pressure of O_2 exceeded 1×10^{-2} Torr. A comparison between the CO frequencies on the adsorption and reaction branches shows a red shift of about 2 cm^{-1} during reaction (Fig. 3,A,B). Following the conclusion of the reaction, the catalyst was treated in 1 Torr of O_2 for 15 min followed by evacuation at 298 K for 30 min. CO adsorbed (reacted) on the oxygen treated surface resulted in a blue shift of 5–6 cm^{-1} (Fig. 3,C,E) essentially reproducing the data shown in Fig. 2,B.

A comparison of the frequency–absorbance curves representing the reaction between preadsorbed oxygen and CO(g) (Fig. 3,E,C) and between preadsorbed CO and

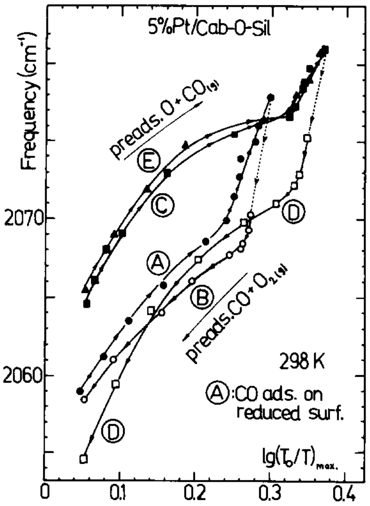

FIG. 3. Infrared frequencies for CO adsorbed on a 6% Pt/SiO_2 catalyst as a function of absorbance. (A) CO adsorption on a reduced surface, ●; (B) preadsorbed CO + $O_2(g)$, ○; (C) preadsorbed O + CO(g), ■; (D) preadsorbed CO + $O_2(g)$, □; (E) preadsorbed O + CO(g), ▲.

both cases, CO and oxygen surface coverages corresponding to the same absorbance (CO surface coverage) should be similar. However, a blue shift of approximately 10 cm^{-1} is observed when preadsorbed oxygen is reacted with CO(g). The d–π^* backbonding model assumes that the coverage-dependent frequency shift is caused by the lowering of the antibonding population due to a competition for the electrons of the metal. This view involves the collective properties of the metal surface atoms and is, therefore, a long range effect. Because oxygen surface coverages are comparable at a given CO surface coverage in both experiments, a blue shift of 10 cm^{-1} based solely on the electron antibonding population is unlikely. These results prompted us to obtain CO frequency–absorbance data by an additional method, i.e., the dissociative adsorption of CO_2, designed to also produce a partial surface coverage of oxygen.

CO_2 Adsorption on a Reduced Pt Surface at 273 K

It is well known that CO_2 is dissociatively adsorbed on Pt (*24*, *25*):

$$CO_2(g) = CO(ads) + O(ads).$$

We observed this dissociative adsorption above 473 K and followed it by observing the infrared band due to adsorbed CO (Fig. 4,A). As the CO_2 pressure in the ir cell was increased from 0.1 to 10 Torr, the absorbance of the linearly adsorbed CO increased to 0.19. No additional dissociative adsorption occurred during a 3-hr exposure to CO_2 at 473 K. Although dual vacant Pt sites are required for the dissociative adsorption of CO_2, the resulting adsorbed CO is free to migrate because of its high mobility on the Pt surface.

As the CO (and O) surface coverage was increased, the position of the CO band was observed to increase from 2034 to 2057 cm^{-1}. This curve is strikingly similar to that obtained when CO is adsorbed on a reduced Pt surface at 523 K (Fig. 4,B) and during the thermal desorption of CO at increasing temperatures (Fig. 4,C). No dissociative adsorption of CO_2 occurred on a Pt surface covered with O_2. The position of the CO stretching frequency corresponding to absorbances of 0.1, 0.15, and 0.20, respec-

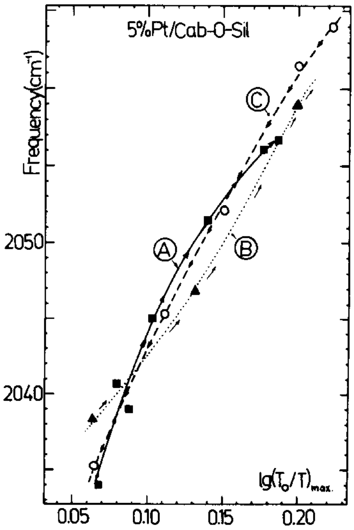

FIG. 4. The frequency of CO adsorbed on 6% Pt/ SiO_2 as a function of absorbance. (A) CO_2 adsorption at 473 K, ■; (B), CO adsorption on reduced Pt at 523 K, ▲; (C) thermal desorption of CO into a vacuum at increasing temperatures, ○.

TABLE 1

A Comparison of CO Absorption Frequencies at Comparable CO and Oxygen Surface Coverages for Different Surface Reactions

Reaction	CO absorption frequency (cm^{-1}) at A ($\log(T_0/T)_{max}$) =		
	0.10	0.15	0.20
O(ads) + 2CO(g) = CO_2(g) + CO(ads)	2070	2072	2073
CO(ads) + O_2(g) = CO_2(g) + O(ads)	2061	2063	2067
CO_2(g) = CO(ads) + O(ads)	2043	2051	2057

tively, for the three reactions studied are compared in Table 1. It is clear from these results that an electronic effect due to presence of co-adsorbed oxygen cannot satisfactorily explain these results.

The increase in the absorbance at full CO surface coverage from 0.3 on the initially reduced surface to 0.40 on the oxygen treated surface (compare Fig. 2,A,B and Fig. 3,A,C) suggests that the effect of co-adsorbed oxygen is to increase the total CO adsorption by compressing the CO adlayer. This observation can only be valid if the extinction coefficient for adsorbed CO is unchanged as a result of co-adsorbed oxygen. Some justification for this assumption is based on the experimental measurement of extinction coefficients by Heyne and Tompkins (*18*). These workers found that the extinction coefficient for CO adsorbed on Pt is unchanged by the presence of co-adsorbed oxygen. To add further validity to the argument that the CO adlayer is actually compressed due to the presence of co-adsorbed oxygen, a series of chemisorption experiments were performed.

Chemisorption Measurements in the Pulse Microreactor

Following the standard pretreatment, 100-μl pulses of CO were added to the catalyst at 298 K until saturation. Oxygen pulses (100 μl) were then added to the preadsorbed CO. The unreacted O_2 and CO_2 evolved were measured and the CO adsorbed on the catalyst was determined by material balance. Of the oxygen added in the first pulse, 25% did not react, 40% reacted to form CO_2, and 35% of the O_2 pulse was absorbed (Fig. 5,A). The addition of the second pulse resulted in no unreacted O_2. Subsequent pulses of O_2 resulted in a decrease in the surface concentration of CO and a corresponding increase in the percentage of the O_2 pulse which did not react. It is important to note that both CO and oxygen were present on the surface during reaction (Table 2).

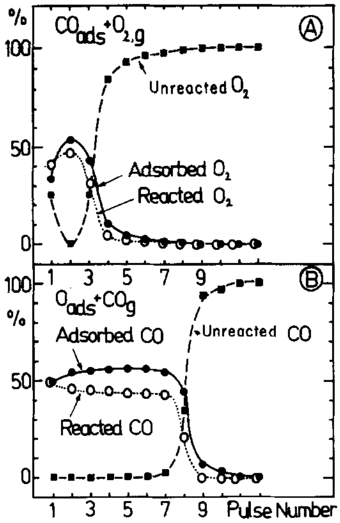

FIG. 5. (A) The addition of O_2 pulses (100 μl) to preadsorbed CO on a 5% Pt/SiO_2 catalyst at 298 K: ●, adsorbed O_2; ○, reacted O_2; ■, unreacted O_2. (B) The addition of CO pulses (100 μl) to preadsorbed oxygen on a 5% Pt/SiO_2 catalyst at 298 K: ●, adsorbed CO; ○, reacted CO; ■, unreacted CO.

Following the completion of the reaction between preadsorbed CO and O_2, the catalyst was treated in flowing O_2 (25 ml/min) for 30 min at 298 K followed by flowing He for 30 min. Pulses of CO (100 μl) were then added to the preadsorbed oxygen at 298 K. The addition of the first pulse resulted in 50% reaction and 50% adsorption on the surface:

$$O(ads) + 2CO(g) = CO_2(g) + CO(ads).$$

Six pulses of CO were added before any unreacted CO was detected by the gas chromatograph. The addition of each CO pulse resulted in about 10% more adsorp-

TABLE 2

Adsorption and Titration Measurements on a 6% Pt/SiO_2 Catalyst[a]

	Gas uptake and evolved titration products (μl)			
	CO	O_2	CO_2	H_2
1. CO adsorption on reduced Pt at 298 K	373			
2. Titration of CO in 1 by O_2 at 298 K		278	259	
3. CO added at 298 K following treatment in flowing O_2 for 10 min at 298 K	773		337	
4. H_2 adsorption on reduced Pt at 298 K				212
5. H_2 added at 298 following treatment in flowing O_2 for 10 min at 298 K				617
6. O_2 adsorption on reduced Pt at 298 K		161		
7. Titration of adsorbed oxygen in 6 by CO at 298 K	690		266	

[a] Weight of catalyst: 267 mg (reduced, dried); percentage exposed Pt: 22% (from H_2 uptake).

tion than reaction. Simultaneously, a small increase in the base line of the GC was observed. This can be understood quite easily once it is realized that adsorbed CO can react with adsorbed oxygen between pulses to form CO_2, leaving additional empty surface sites. A portion of the incoming pulse will adsorb on these vacated sites, thus leaving a smaller percentage of the pulse available for reaction.

The volume of CO adsorbed following the reaction of preadsorbed oxygen with CO(g) can be calculated from the data in Table 2, from either line 3 or 7, as

$$\mathrm{CO(ads)} = \mathrm{CO(uptake)} - \mathrm{CO_2(evolved)}.$$

The ratio of CO adsorbed following the reaction of CO with preadsorbed oxygen to that adsorbed on a reduced Pt surface is, therefore, 1.2 ± 0.1 in good agreement with the infrared result of 1.3.

These observations strongly suggest that a compression of the CO adlayer has occurred as a result of the presence of coadsorbed CO and oxygen. We also suggest that the compression of the CO adlayer results in an increase in the extent to which CO–CO dipole coupling occurs. This in turn results in a blue shift in the position of the CO stretching frequency. The net result of this increase in CO–CO dipole coupling is to induce the CO to adsorb in segregated patches or islands on the surface. A comparison of the adsorption (reaction) curve on preoxidized Pt (Fig. 2,B,C) to that on a previously reduced Pt surface (Fig. 2,A) reinforces this suggestion. On a preoxidized surface, the increase in the CO frequency with increasing CO surface coverage is much less pronounced than that observed on the reduced Pt surface. CO–CO dipole coupling is, of course, important in both cases. However, the initially higher frequency observed in the case of adsorption (reaction) on the preoxidized surface suggests that the adsorbed CO is strongly coupled even at relatively low surface coverages. The occurrence of segregated patches of CO in the presence of co-adsorbed oxygen has been observed by others. Ertl *et al.* (*26*), using LEED measurements on Pd(III), found that preadsorbed oxygen leads to a compression of the CO layer. This would lead to an increase in the extent of CO–CO dipole coupling and would, therefore, predict higher CO stretching frequencies. Using reflection–absorption ir, Shigeishi and King (*20*) observed a blue shift of 19 cm^{-1} when CO was adsorbed (reacted) on an oxidized Pt(III) surface. A similar blue shift of 10–15 cm^{-1} was obtained by Ponec *et al.* (*17*) on Pt/SiO_2 and Pt/Al_2O_3 catalysts for ^{12}CO, ^{13}CO mixtures adsorbed on oxidized surfaces. These authors interpreted their results by considering a compression of the CO adlayer. However, they could not unambiguously exclude electronic effects as a reason for the blue shift.

It is useful to consider the isolated

patches of CO as two-dimensional liquids. Because CO molecules within these two-dimensional patches have a distribution of energies, the more energetic molecules break away and are able, because of their high mobility, to react with adsorbed oxygen at the periphery of the CO islands. The results shown in Fig. 1,B,C show that during desorption (reaction) at increasing temperatures, the CO stretching frequency decreases by 4 or 5 cm^{-1} without a corresponding change in the absorbance. We interpret this to mean that CO migration away from its initial segregated island configuration is not extensive. Apparently, a mobile CO molecule encounters an oxygen atom at the periphery of its island of reactivity and reacts rapidly to form CO$_2$. It will be recalled (*21*) that in the absence of co-adsorbed oxygen extensive rearrangement of the surface layer took place prior to thermal desorption as evidenced by frequency drops of about 20 cm^{-1} prior to desorption. This result was explained by invoking the migration of adsorbed CO molecules during thermal treatment from sites of high surface coordination, on which CO–CO dipole coupling is most effective, to edges, corners, and imperfections prior to desorption.

The results of this study are, therefore, in good agreement with the recent results of Haaland and Williams (*5*), suggesting that the Pt catalyzed oxidation of CO occurs via a Langmuir–Hinshelwood mechanism at the boundary of CO islands of reactivity.

Single crystal studies (*20*) show that the reaction between preadsorbed CO and O$_2$ gas can only occur when the surface is partially covered by adsorbed CO. When the surface of Pt(III) is saturated with CO, no reaction occurs even after exposure to O$_2$ gas for 1 hr. These observations certainly rule out the possibility of an Eley–Rideal mechanism between O$_2$ gas and adsorbed CO. On supported Pt, Sárkány and Gonzalez (*22*) have observed that between 4 to 5% of the CO is reversibly adsorbed. This CO can readily be displaced by oxygen, enabling a Langmuir–Hinshelwood reaction to occur between adsorbed CO and adsorbed oxygen. These results are consistent with our pulse microreactor studies. Following the addition of the first O$_2$ pulse, the weakly adsorbed CO is displaced from the surface, enabling the adsorption of oxygen on the vacated Pt surface sites. Reaction then proceeds according to the proposed mechanism

$$\mathrm{O_2(g) + 2CO(ads) = 2O(ads) + 2CO(g)},$$

$$\mathrm{O(ads) + CO(ads) = CO_2(g)},$$

$$\mathrm{O_2(g) = 2O(ads)}.$$

This mechanism is reinforced by the relatively low conversion of CO to CO$_2$ which follows the addition of the first O$_2$ pulse (i.e., the oxygen must be adsorbed).

The results of Fig. 3 show that the frequencies of adsorbed CO are slightly lower during the reaction of preadsorbed CO with O$_2$ gas than those observed during the absorption of CO on a reduced Pt surface. Under these reactive conditions both CO and oxygen are co-adsorbed on the Pt surface. The fact that a red shift in the CO frequencies is observed rather than a blue shift is firm evidence that the d–π^* backbonding model is not a major factor in the interpretation of the spectral frequencies of CO in the presence of co-adsorbed oxygen. The similarity between the CO stretching frequencies obtained following the adsorption of CO on a reduced Pt surface and those obtained during the reaction between preadsorbed CO and O$_2$ suggests that the slight red shift obtained during the reaction branch is probably due to the relaxation of the CO–CO dipole coupling during reaction. Because the adsorption branch is obtained in the absence of preadsorbed oxygen, the compression of the CO adlayer is much less than that obtained during the adsorption (reaction) of CO in the presence of co-adsorbed oxygen (compare Figs. 2,A,B and 2,C,D). During the reaction between preadsorbed CO and O$_2$ gas, the relatively high CO frequencies suggest that the CO molecules are strongly coupled, most likely retaining an island type configuration during reaction.

There has been considerable disagreement in the literature regarding the reaction

$$2CO(g) + O(ads) = CO_2(g) + CO(ads).$$

The isotopic work of Matshushima (*3*) and the transient studies of White *et al.* (*28*) rule heavily against the occurrence of an Eley–Rideal mechanism. However, the results of this study cannot completely rule it out. It will be recalled that when the first pulse of CO was added to a preoxidized surface, 50% reacted and 50% was adsorbed. In the interval between the addition of pulses of CO, a slow Langmuir–Hinshelwood reaction occurred, as evidenced by the evolution of additional CO_2. The reactivity of subsequent pulses of CO decreases continuously following the addition of the first pulse, i.e., more CO is adsorbed than reacts. We interpret these results to mean that a small portion of the adsorbed oxygen which is very reactive reacts following the addition of the first CO pulse via an Eley–Rideal mechanism through the formation of a precursor state as recently proposed by Bennet (*29*). Subsequent reaction at lower oxygen surface coverage most likely occurs via a Langmuir–Hinshelwood mechanism between adsorbed CO and adsorbed oxygen.

We direct one final comment to the effect of oxygen treatment at higher temperatures. Recent LEED studies (*27*) of the order–disorder transition in a (2 × 2)O layer on Pt(III) and stepped Pt(s) – (10–20) (III) × (III) planes have been performed. Oxygen reactivity to CO was shown to decrease in the series O_{chem} in (2 × 2)O on Pt(III) and Pt(s) terraces > O_{chem} in 2(ID)O on steps > oxygen in surface oxides. The penetration of oxygen atoms into the metal on the steps appears to be responsible for the temperature stability of the one-dimensional oxide 2(ID)O. The oxidation of the surfaces occurs at a faster rate in the region of stepped planes (*27*). The formation of an "oxide" structure on Pt(s) takes about 1 hr at 600°K, whereas on the Pt(III) plane it takes several hours.

The Pt single crystal results can readily be extended to include supported Pt catalysts. On Pt/SiO_2, there are different exposed crystal planes, steps, edges, and imperfections. As the sample is treated in O_2, adsorbed oxygen having a different reactivity towards CO is obtained. Cant and Donaldson (*4*) observed a change in the reaction rate with surface coverage. Our results support these observations. Treatment in O_2 at 673 K followed by cooling in O_2 to room temperature results in a sharp decrease in the reactivity of the preadsorbed layer, suggesting the possible formation of a surface oxide under these conditions.

CONCLUSIONS

Several important conclusions emerge from this study, as follows:

(1) The occurrence of co-adsorbed CO and oxygen on the surface of a supported Pt catalyst does not, by itself, cause a significant blue shift in the frequency of adsorbed CO. Preadsorbed oxygen, however, forces CO to couple strongly and form segregated patches of CO in an adlayer which is significantly compressed.

(2) The reaction between preadsorbed CO and O_2 gas and between preadsorbed oxygen and CO gas occurs at the periphery of islands of reactivity.

(3) The observed blue shift in the CO stretching frequency depends on the severity of the O_2 pretreatment.

(4) The blue shift in the CO stretching frequency is primarily caused by the compression of the CO adlayer as a result of preadsorbed oxygen and not by electronic effects induced by electron acceptor admolecules.

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