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Pretreatment Effect on the Catalyst Activity and on the Enthalpy Changes during Exposure of Pd/SnO_2 and Pd Metal to CO, O_2, and CO + O_2

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The paper reports on the adsorption and the enthalpy changes observed during exposure of a Pd(2%)/SnO_2 catalyst and polycrystalline Pd powder to CO, O_2 and CO + O_2 (2:1) at different temperatures in the 300–470 K range and as a function of an oxidizing (ox) or a reducing (red) pretreatment given to the samples. A larger fraction of CO was adsorbed/reacted as compared to that of O_2 when a Pd/SnO_2(ox) sample was exposed to successive CO + O_2 (2:1) pulses. The fraction of adsorbed O_2 and the yield of CO_2 increased progressively with the rise in sample temperature. On the other hand, a negligible amount of CO and mainly O_2 was adsorbed/reacted on a Pd/SnO_2(red) sample. Even though the amount of adsorbed O_2 increased, no measurable CO_2 was formed with the rise in sample temperature. On the average, about 205, 360, 420, and 448 kJ of heat was evolved per mol of CO + O_2 adsorbed/reacted over Pd/SnO_2(red) at the respective temperatures of 300, 370, 420, and 470 K, the corresponding values in the case of the Pd/SnO_2(ox) sample being around 75, 125, 150, and 170 kJ mol^{-1}. In the case of Pd metal, the adsorption behaviour was almost independent of pretreatment and the fraction of CO or O_2 adsorbed from a CO + O_2 pulse depended on the catalyst temperature. The heat evolved per mol of CO + O_2 was found to be 171 ± 3 kJ mol^{-1} irrespective of the sample temperature. Similarly, the adsorption and the enthalpy changes during CO pulse exposures and during subsequent O_2 dozing depended on the surface species present at the time of interaction. The data provide evidence for the important role played by the lattice oxygen of support in addition to the oxygen chemisorbed at Pd sites. Whereas the CO was found to react in both the gaseous and the adsorbed forms, the oxygen participated in CO oxidation only in the adsorbed state. The thermochemical data indicate that the CO and O_2 molecules compete for metal sites and the preponderance of one of the reactions, namely $CO(g) + O(ad) \rightarrow CO_2(g)$, $CO(ad) + O(ad) \rightarrow CO_2(ad)$, or $CO(g) + O(lattice) \rightarrow CO_2(g)$ is decided by the temperature and the chemical nature of the catalyst surface at the time of interaction. The effect of H_2 pretreatment on the adsorption characteristics and also on the observed CO oxidation activity of Pd/SnO_2 is attributed to the formation of Pd–O–Sn moieties at the catalyst surface. © 1995 Academic Press, Inc.

INTRODUCTION

The catalytic properties of noble metals supported on reducible oxides, such as SnO_2, are found to depend considerably on the chosen pretreatment conditions even though contradictory results have been reported in this regard. Thus, Schryer *et al.* (1) and Drawdy *et al.* (2) observed enhancement in the CO oxidation activity when a Pt/SnO_2 catalyst was subjected to a reducing pretreatment. On the other hand, the studies performed in our laboratories have shown that an oxygen pretreated Pt/SnO_2 sample exhibited higher CO oxidation activity as compared to a corresponding reduced sample (3). A similar trend was observed using a Pd/SnO_2 catalyst (4). The activity of these catalysts is found to deteriorate with time, particularly when used for the application such as in the sealed-off CO_2 lasers where these catalysts are found useful for the reaction of CO and O formed during CO_2 dissociation under electric discharge (5). The actual cause of activity loss is, however, not yet clearly understood. The mechanistic aspects of CO oxidation on such catalysts have also evoked diverse opinions, and various postulations suggesting the importance of lattice oxygen, or that of hydroxyl groups, carbonates, or bicarbonates formed on a Pt or a Sn site have been invoked (6–11).

We therefore measured enthalpy changes during adsorption and reaction of CO or CO + O_2 over Pd metal and over a Pd/SnO_2 catalyst. The effect of a pretreatment given to the catalyst on ΔH values was also investigated in order to evaluate the role played by the oxidation states of Pd and Sn in the overall CO oxidation reaction over Pd/SnO_2 catalyst. Reaction routes involved in the CO oxidation are discussed in light of these results.

EXPERIMENTAL

Catalyst. A Pd (2 wt.%)/SnO_2 catalyst was prepared by impregnating tin oxide gel with the required amount

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TABLE 1

Metal Surface Area of Pd(2%)/SnO_2 and Pd Powder Catalysts as a Function of *in Situ* Pretreatments under H_2

H_2 pretreatment temperature	Metal surface area (±10% $m^2\ g^{-1}$ catalyst)			
	Pd/SnO_2		Pd metal	
	I from total adsorbed H_2	II from irreversibly held H_2	I from total adsorbed H_2	II from irreversibly held H_2
As prepared	3.7	3.4	9.2	1.8
440 K	2.7	2.4	7.0	0.7
475 K	1.3	1.2	6.1	0.10

of aqueous palladium dichloride solution. The tin oxide gel was prepared by precipitating hydrous tin oxide from $SnCl_4$ solution (at 275 K) using aqueous ammonia solution (3, 11, 12). The 80- to 120-mesh fraction of SnO_2 gel having N_2 adsorption BET surface area of about 160 ± 5 $m^2\ g^{-1}$ was used for preparing palladium-dispersed catalysts. The palladium was reduced to metallic form by drying the sample and then heating it in a hydrogen flow at 440 K.

For the comparative calorimetric evaluations, a palladium powder sample was prepared by direct reduction of palladium dichloride under hydrogen stream at 600 K.

Table 1 gives the metal surface area of both the Pd/SnO_2 and the Pd powder samples determined volumetrically by H_2 chemisorption method using a standard high vacuum system. The effect of *in situ* reduction at 440 and 475 K is also shown in this table. All the H_2 chemisorption measurements were done at the catalyst temperature of 373 K and at an optimised H_2 pressure of 100 Torr (1 Torr = 133 Pa) using a procedure described by Benson *et al.* (13). Before making H_2 chemisorption measurements a sample (0.5 g of Pd/SnO_2 or 0.25 g of Pd powder) was evacuated at 525 K first for 16–18 h at 10^{-3} Torr pressure and then for 3 h at 10^{-6} Torr. Whereas the columns marked I in Table 1 represent surface areas calculated from the total amount of hydrogen adsorbed (reversible + irreversible), the data in the columns marked II are calculated from the amount of irreversibly held H_2. For evaluation of the irreversibly held hydrogen, a sample exposed to 100 Torr H_2 at 373 K was evacuated at the same temperature for 30 min before using it again for the second cycle of hydrogen chemisorption (14). The data in Table 1 show that the hydrogen is weakly adsorbed over Pd powder as compared to that on Pd/SnO_2. The hydrogen reduction, however, led to drastic loss of hydrogen uptake by Pd/SnO_2, the effect being less pronounced in the case of Pd powder.

Microcalorimetry. A calvet-type heat flow microcalorimeter equipped with stainless steel gas circulation vessels (C-80 calorimeter from Setaram, France) was employed to evaluate the heat evolved during exposure of a catalyst to CO, O_2, or CO + O_2 (2 : 1) pulses at various temperatures in the range 300–500 K. A 200-mg sample (~150-μm particle size) was taken in one of the vessels whereas the reference cell was kept empty. Both of the cells were connected to a common gas manifold through fine control valves to achieve identical flow conditions. The effluent from the sample cell was analysed with an assembly of Porapak-T (0.5 m, 3 mm i.d.) and molecular sieves-5A (0.3 m, 3 mm i.d.) columns, both connected in tandem and each followed by a thermal conductivity detector maintained at room temperature. Before beginning an experiment, the catalyst was pretreated *in situ* for 1 h at 475 K either under H_2 or under O_2 flow (20 ml min^{-1}) followed by evacuation and heating under helium flow (20 ml min^{-1}) at the same temperature. The samples pretreated under hydrogen and oxygen are referred to as Pd/SnO_2(red) or Pd/SnO_2(ox) respectively in the text. Subsequent to a pretreatment, the catalyst was maintained under helium flow at required temperature and a number of adsorbate pulses were then introduced at about 15–20 min interval through an injection port provided near the entry point of the calorimeter vessel. The calorimeter response was calibrated using a standard joule calibrater.

As stated in Ref. (3), the accuracy in the measurement of heat values (Q) depended on the accuracy of gas chromatographic evaluation of gas adsorption at a particular temperature. For experiments where only a small fraction of an adsorbate was held at catalyst surface, the Q values are expressed as kJ g^{-1} palladium. The trend of the thermochemical data reported in this study was fairly reproducible during 2–3 repeated experiments even though the variation in the Q values (expressed as kJ mol^{-1} of adsorbed or reacted adsorbate) was found to be 5–10%. It

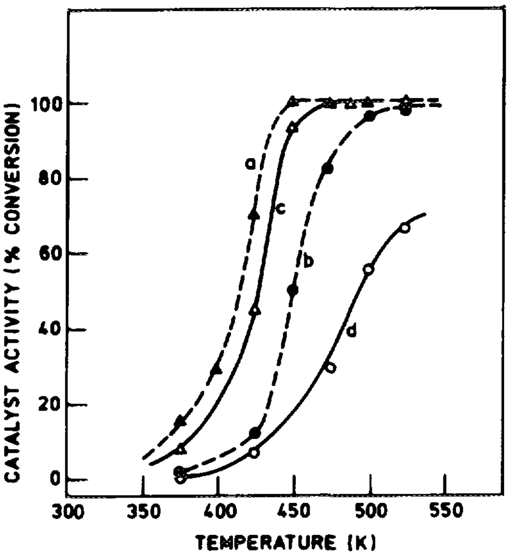

FIG. 1. CO oxidation activity of Pd(2%)/SnO_2 catalyst at different temperatures as a function of different pretreatments. Curves a,c show oxygen pretreatment at 425 and 475 K respectively, and curves b,d show reducing pretreatments at 425 and 475 K, respectively.

also needs mentioning that the Q values given in the text without + or − sign refer to the heat liberated during particular adsorption.

Catalyst activity. The CO oxidation activity was evaluated at various temperatures in the range 300–550 K using a 1 cm diameter flow-through quartz reactor. For this purpose a gas mixture containing approximately 10% CO, 5% O_2, and the rest He was reacted over 1 g Pd/SnO_2 at a flow velocity of 600 ml h^{-1} g^{-1}. The effluents were analyzed periodically using a gas chromatograph equipped with a Porapak −Q (1 m, 3 mm, i.d.) column and a FID detector coupled to a catalytic methanator. The effect of *in situ* pretreatments under hydrogen or oxygen on catalyst activity was also evaluated. For these pretreatments, a sample was heated at desired temperature under H_2 or O_2 flow (20 ml min^{-1}) followed by heating under He flow (475 K, 1 h). The catalyst maintained at required temperature was switched to CO + O_2 flow at this stage. It needs to be mentioned that subsequent to the pretreatment mentioned above, the activity measurements at various temperatures were performed with no further in between treatments.

RESULTS

Catalyst Activity

The oxygen-pretreated Pd/SnO_2 always showed higher catalyst activity at a particular temperature as compared to that of the corresponding hydrogen-pretreated sample. Curves a and b of Fig. 1 show CO oxidation activity of 2% Pd/SnO_2 catalyst subjected to pretreatments at 425 K under oxidizing and reducing atmospheres respectively. These data represent activity values obtained after 6 h reactor run time. The increase in the pretreatment temperature resulted in poorer catalyst activity in both the cases, the effect being more prominent in the case of the reduced sample. Typical data obtained for a sample pretreated at 475 K under oxidizing and reducing media are shown by curves c and d respectively in Fig. 1. The activity loss was marginally regained when a reduced sample was subjected again to an oxidizing pretreatment.

Even though the CO oxidation activity depended on

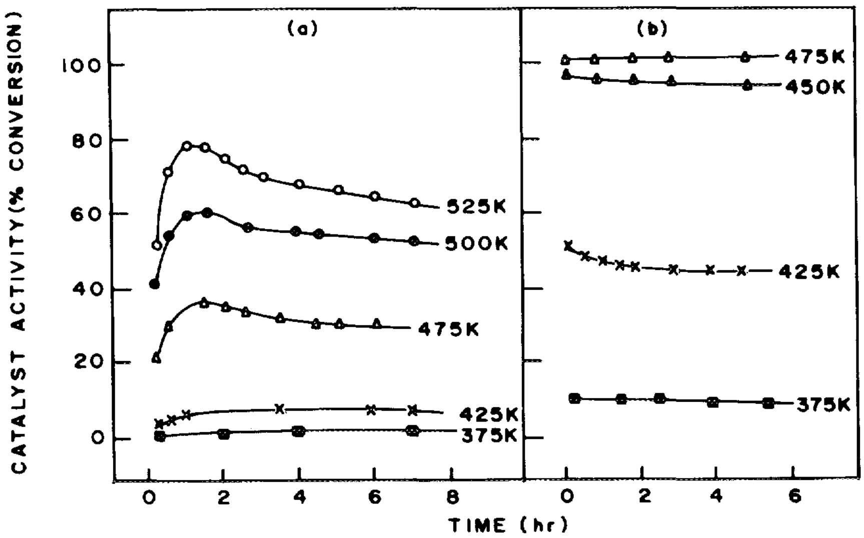

FIG. 2. Time-dependent variation of CO oxidation activity of (a) Pd(2%)/SnO_2(red) and (b) Pd(2%)/SnO_2(ox) samples at different temperatures.

TABLE 2

The Average Amount of CO Adsorbed and the Value of Heat Released per Gram of Pd Metal when 0.2 g Pd(2%)/SnO$_2$(Red) Sample Was Exposed to 4.1 μmol CO Pulses at Different Temperatures

Serial No.	Catalyst temperature (°K)	Percentage of CO adsorbed	CO$_2$ yield (%)	Heat evolved ($\Delta H \times 10^{-3}$ J)	Heat evolved (ΔH, J g^{-1} Pd)
1	300	3.6	nil	2.76	0.70
2	370	3.0	nil	5.32	1.3
3	420	3.2	nil	5.3	1.3
4	470	2.3	nil	4.5	1.1

metal content, when the samples containing different Pd content in the 1–4 wt.% range were used the pretreatment effect was similar to that shown in Fig. 1.

Figures 2a, 2b show the time-dependent CO oxidation activity of Pd(2%)/SnO$_2$ subjected to 2-h oxidizing or reducing pretreatments at 475 K as observed during the first 6–8 h of reactor run time at different temperatures. After about 2 h of reaction time, a slow but steady fall in catalyst activity was noted which persisted during investigated reaction time of ~30 h. In the case of an oxygen pretreated catalyst, the activity loss was only marginal, however.

Microcalorimetry

CO exposure. Pretreatment given to a sample had considerable effect on the fraction of the gas adsorbed and on the heat evolved when the catalyst was exposed to 8–10 successive 100-μl (~4.1 μmol) CO pulses at an interval of about 15 min. A negligible amount of CO was adsorbed over a Pd/SnO$_2$(red) sample at all the temperatures in the range 300–500 K. Correspondingly, no CO$_2$ was formed and only a small amount of heat (2–10 mJ g^{-1} of catalyst) was evolved during these exposures. Typical data obtained for CO exposures over Pd/SnO$_2$(red) are given in Table 2. In the case of an oxygen-pretreated catalyst, a fraction of CO was adsorbed/reacted to form CO$_2$ whereas the remaining amount was released in the effluent helium. The fraction of adsorbed/reacted CO reduced progressively during exposures of successive pulse injections at a particular temperature, the effect being more pronounced at lower temperature. The yield of CO$_2$ from adsorbed CO increased considerably with the rise in catalyst temperature, as shown in Fig. 3. At 300 K, only about 30–35% of adsorbed CO from the first two pulses gave rise to CO$_2$ formation whereas no CO$_2$ formed during successive CO pulse exposures (Fig. 3d). The conversion of adsorbed CO to CO$_2$ was about 60 and 92% for catalyst temperatures of 370 and 470 K, respectively

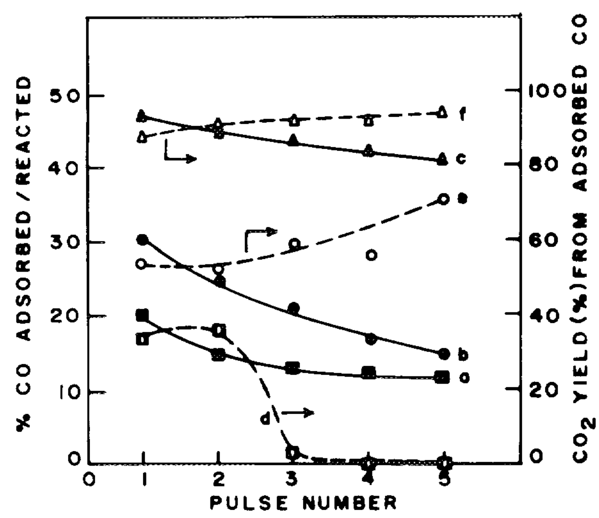

FIG. 3. Percentage of CO adsorbed/reacted (solid curves) and the yield of CO$_2$ from adsorbed CO (broken curves) when five successive 4.1 μmol CO pulses were dosed over Pd/SnO$_2$(ox) samples at different temperatures: (a,d) 300 K, (b,e) 370 K, and (c,f) 470 K.

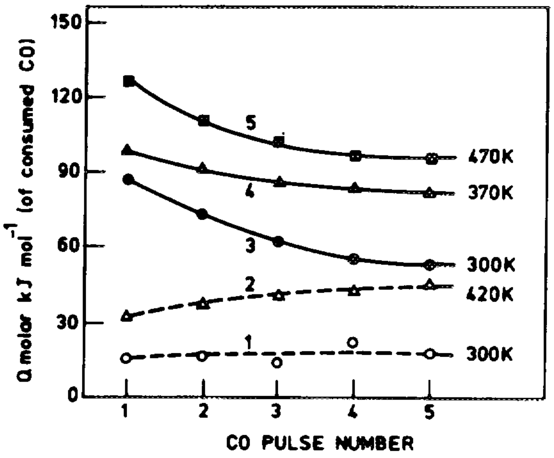

FIG. 4. Evolution of heat during exposure of successive 4.1 μmol pulse doses of CO on Pd/SnO$_2$(red) (curves 1,2) and Pd/SnO$_2$(ox) (curves 3–5) samples at different temperatures.

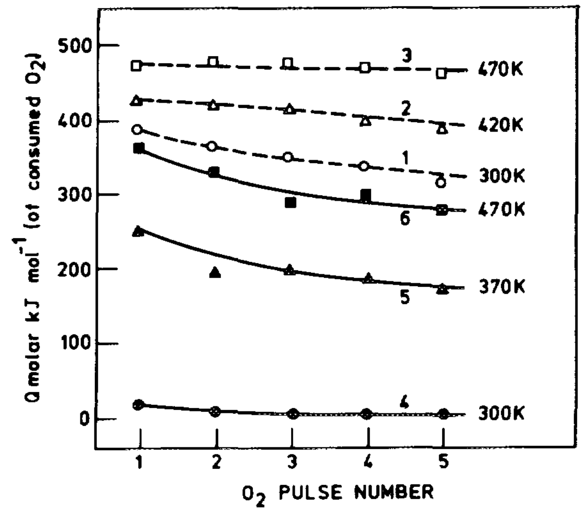

FIG. 5. Evolution of heat during exposures of successive 4.1 μmol O_2 pulse doses on Pd/SnO_2(red) (curves 1–3) and Pd/SnO_2(ox) (curves 4–6) following 10 CO pulse exposures at different temperatures.

(Figs. 3e, 3f). Also, all the successive CO pulses gave rise to an almost similar CO_2 yield, indicating participation of the lattice oxygen.

The amount of heat evolved per mole of adsorbed/reacted CO (Q molar) was much higher for the CO pulse exposures over oxygen-pretreated samples as compared to corresponding reduced samples. The Q molar values, however, increased with the rise in sample temperature in both cases. Figure 4 shows Q molar values obtained during dosing of five successive CO pulses over Pd/SnO_2(red) and Pd/SnO_2(ox) samples at a few typical temperatures. These data show that, as compared to the average Q molar values of 20 to 40 kJ mol^{-1} obtained for Pd/SnO_2(red), the corresponding values for CO exposures over Pd/SnO_2(ox) were in the range of 70 to 115 kJ mol^{-1}, depending on the catalyst temperature.

The Q molar values calculated for heat of CO_2 formation decreased marginally with the increase in sample temperature. Thus, whereas an average value of 175 ± 5 kJ mol^{-1} was obtained for CO_2 formation at 370 K, the corresponding value at 470 K was around 145 ± 5 kJ mol^{-1}. This difference could arise due to a fraction of CO_2 remaining adsorbed over the catalyst surface at lower temperatures. The room temperature adsorption of CO_2 over SnO_2 in the form of carbonate or bicarbonate species and its subsequent release in the temperature range of 300–500 K is widely reported in the literature (15, 16).

O_2 exposure following CO. Following the introduction of CO pulses as mentioned above, when the catalyst samples were exposed to a series of O_2 pulses (~4.1 μmol each) a part of the oxygen was adsorbed which increased with the catalyst temperature. Also, the reduced samples showed higher oxygen uptake as compared to the corresponding oxygen-treated samples. Similarly, the amount of heat evolved increased with the rise in temperature, the average Q molar values being around 350, 410, and 470 kJ mol^{-1} for the exposure of Pd/SnO_2(red) to O_2 pulses at 300, 420, and 470 K, respectively. In the case of Pd/SnO_2(ox) sample, comparatively smaller Q molar values were observed during oxygen pulse exposures following CO, the average values being around 8, 190, 250, and 310 kJ mol^{-1} of adsorbed/reacted O_2 at the catalyst temperatures of 300, 370, 420, and 470 K respectively. Figure 5 presents typical Q molar data for the individual O_2 pulse exposures over two samples at different temperatures.

CO + O_2 pulse exposures. Samples pretreated under hydrogen and oxygen exhibited different chemisorption behaviour when exposed to successive pulses of CO + O_2 (2 : 1). Figure 6 shows the fraction of O_2 and CO adsorbed/reacted over Pd/SnO_2(ox) at different temperatures. Whereas on the average only 3, 11, 28, and 38% of O_2 from a CO + O_2 pulse was adsorbed/reacted at 300, 370, 420, and 470 K respectively, the fraction of CO adsorbed/reacted was around 30, 45, 54, and 62% at the corresponding temperatures. An increasing amount of adsorbed/reacted CO was converted to CO_2 with the rise in sample temperature. Thus, about 25, 60, 70, and 90% of consumed CO was oxidized at catalyst temperatures of 300, 370, 420, and 470 K respectively.

In contrast, a negligible amount of CO_2 was formed when Pd/SnO_2(red) was exposed to CO + O_2 (2 : 1) pulses at all the temperatures in the 300–400 K range. In this case, a very small fraction of CO was adsorbed/reacted and, on the other hand, around 12, 40, 60, and 75% of O_2

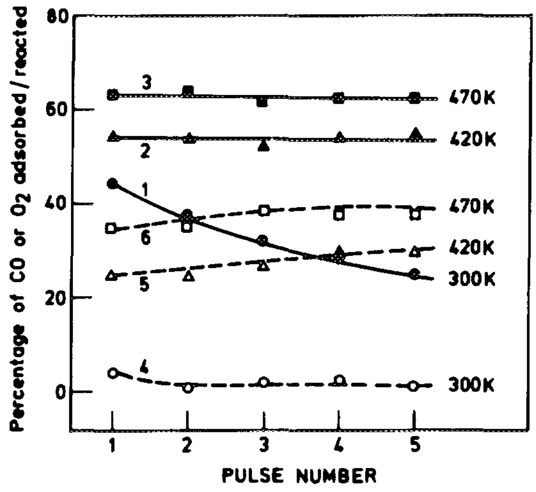

FIG. 6. Percentage of CO (curves 1–3) and O_2 (curves 4–6) adsorbed/reacted when a Pd/SnO_2(ox) sample was exposed to successive 4.1 μmol CO + O_2 (2 : 1) pulse doses at different temperatures.

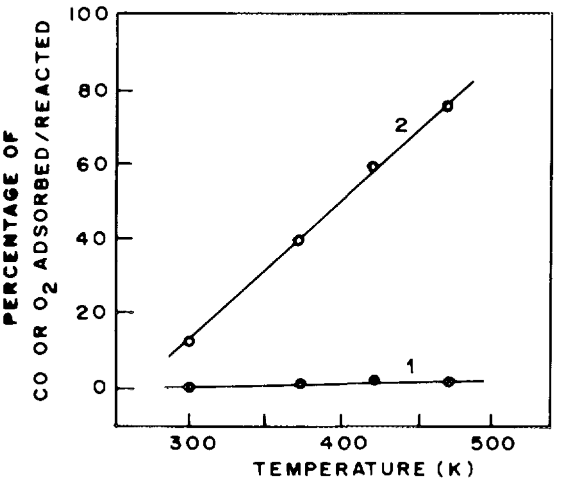

FIG. 7. Average percentage of CO (curve 1) and O_2 (curve 2) adsorbed/reacted when Pd/SnO$_2$(red) was exposed to successive 4.1 μmol CO + O_2 (2 : 1) pulse doses at different temperatures.

from CO + O_2 pulses was adsorbed over the catalyst surface at respective temperatures of 300, 370, 420, and 470 K, as shown in Fig. 7.

Almost similar Q molar values (per mol of CO + O_2 adsorbed/reacted) were observed during successive pulse exposures, though the values were much higher in the case of the Pd/SnO$_2$(red) sample as compared to corresponding oxidized sample at each temperature. Figure 8 presents the average value of heat evolved in these experiments. As compared to Q molar values of 205, 360, 420, and 448 kJ per mol of consumed CO + O_2 over Pd/SnO$_2$(red) at respective temperatures of 300, 370, 420, and 470 K, the corresponding values in the case of Pd/SnO$_2$(ox) were found to be around 75, 125, 150, and 170 kJ mol^{-1}.

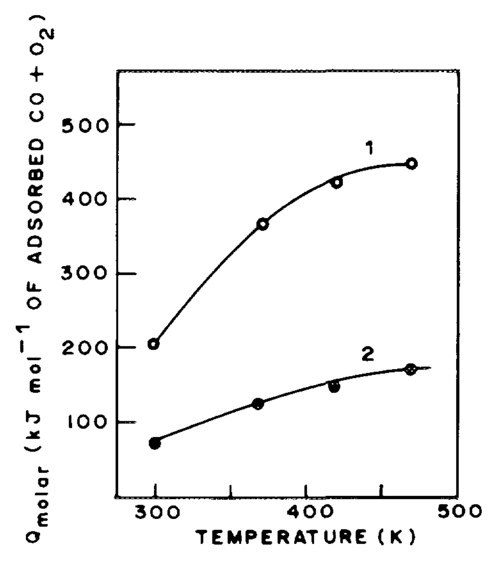

FIG. 8. Average Q molar values observed during exposure of Pd/SnO$_2$(red) (curve 1) and Pd/SnO$_2$(ox) (curve 2) catalysts to 5–6 successive 4.1-μmol CO + O_2 (2 : 1) pulse doses at different temperatures.

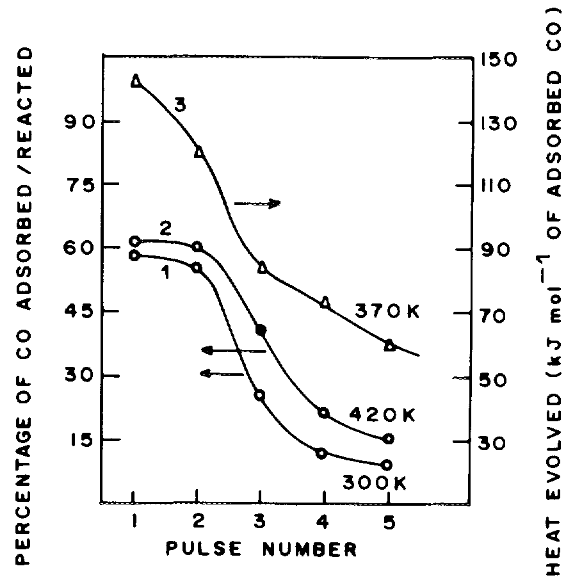

FIG. 9. Percentage of CO adsorbed/reacted (curves 1,2) and the corresponding values of heat evolved when Pd(red) was exposed to successive 4.1-μmol CO pulse doses.

The average value of heat evolved per mol of CO_2 formed during CO + O_2 pulse exposures over Pd/SnO$_2$(ox) was calculated to be around 242 ± 10 kJ mol^{-1}, irrespective of catalyst temperature.

Palladium Metal

CO exposure on Pd metal. The hydrogen-pretreated palladium metal showed different CO chemisorption behaviour than that of a Pd/SnO$_2$(red) sample. A considerable amount of CO was adsorbed at the surface of a Pd(red) sample from the first 2–3 CO pulses, but the adsorption amount reduced drastically during subsequent pulse exposures. A marginal increase in the CO adsorption was observed with a rise in sample temperature as shown by typical data given in curves 1 and 2 of Fig. 9 for two catalyst temperatures. A larger amount of heat was similarly evolved for the initial CO pulse exposures, after which lower Q molar values were recorded during subsequent pulse exposures. Q values varied marginally (±15%) as a function of temperature and the typical data obtained with the catalyst at 370 K are included in curve 3 of Fig. 9.

Subsequent to dosing of 10 CO pulses as mentioned above, when the catalyst was flushed with helium and then exposed to successive O_2 pulses at respective temperatures, a considerable amount of O_2 was adsorbed and about 60–100% of it reacted to form CO_2, depending on

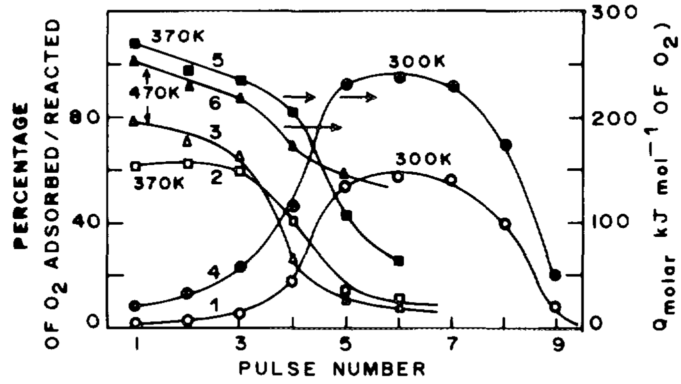

FIG. 10. Percentage of O_2 adsorbed/reacted (curves 1–3) and the corresponding value of heat evolved (curves 4–6) when a Pd(red) sample was exposed to successive 4.1-μmol pulse doses of O_2 following 10 pulse exposures to CO and flushing under helium: Curves 1 and 4, 300 K; curves 2 and 5, 370 K; and curves 3 and 6, 470 K.

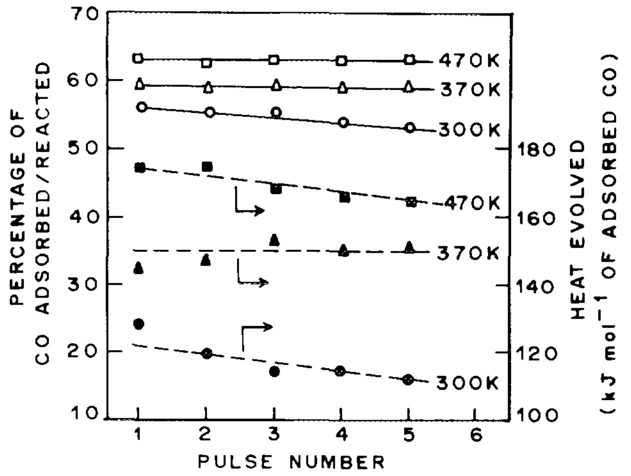

FIG. 11. Percentage of CO adsorbed/reacted and corresponding values of heat evolved when a Pd(ox) sample was dosed with successive 4.1-μmol pulses of CO at different temperatures.

the catalyst temperature and on the pulse number. Thus, at a catalyst temperature of 300 K, no substantial amount of O_2 was consumed during the first 2–3 O_2 pulse exposures and accordingly a negligible amount of CO_2 was observed in the effluent. Further oxygen pulses led to higher amounts of O_2 adsorption, almost all of which reacted to form CO_2. Curve 1 in Fig. 10 shows these data. At higher catalyst temperatures, higher amounts of O_2 were adsorbed/reacted from initial pulses (Fig. 10, curves 2, 3). It was, however, of interest to note that the total amount of reacted oxygen was almost the same at all of the catalyst temperatures under study. The total amount of CO_2 formed, however, declined with the rise in temperature. The amount of heat evolved per mol of adsorbed/reacted O_2 (curve 4) showed a pattern similar to that followed in curve 1 for various pulse exposures at 300 K. Only marginal variation in the *Q* value as a function of temperature was observed, however, although the successive O_2 pulses gave decreasing *Q* molar values as shown in curves 5 and 6 of Fig. 10.

In the case of oxygen-pretreated Pd metal, similar amounts of CO were adsorbed during 6–8 successive CO pulse exposures, and each pulse gave rise to CO_2 formation. The amount of CO consumed varied only marginally with temperature. Thus, on the average, about 55, 59, 61, and 63% of the dosed CO was adsorbed/reacted from each pulse at catalyst temperatures of 300, 370, 420, and 470 K respectively. The CO_2 yield, however, increased considerably with the rise in sample temperature. For example, around 54, 80, 92, and 100% of consumed CO was converted to CO_2 during each successive pulse exposure for catalyst temperatures of 300, 370, 420, and 470 K respectively. The heat evolved per mol of adsorbed/reacted CO also increased with the temperature, the average *Q* molar value being around 118, 159, and 168 kJ mol^{-1} at the sample temperatures of 300, 420, and 470 K respectively. Figure 11 gives typical results of this study for three catalyst temperatures.

CO + O_2 exposure. The fractions of O_2 and CO adsorbed/reacted during interaction of a hydrogen-pretreated palladium metal powder with 4.1 μmol CO + O_2 (2 : 1) pulses depended strongly on catalyst temperature. At 300 K, only a small fraction of oxygen and predominantly carbon monoxide was adsorbed. The amount of

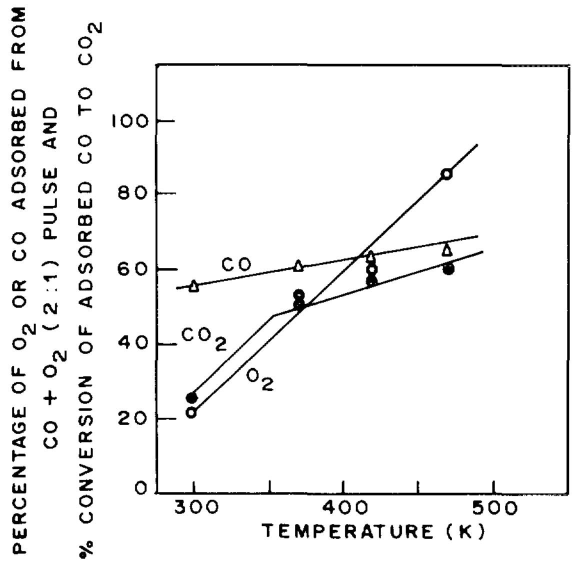

FIG. 12. Average percentage of O_2 or CO adsorbed and the yield of CO_2 from adsorbed CO when a Pd(red) sample was exposed to 5–6 successive 4.1-μmol CO + O_2 (2 : 1) pulse doses at different temperatures.

oxygen adsorbed from each pulse increased progressively with catalyst temperature, whereas the amount of adsorbed CO increased only marginally. The adsorption behaviour during 8–10 successive pulse exposures remained the same at a particular catalyst temperature. Figure 12 shows the temperature effect on the average fraction of O_2 and CO adsorbed from a CO + O_2 pulse. At lower temperatures the CO_2 yield was controlled by the amount of O_2 consumed, whereas at higher temperatures the fraction of adsorbed CO was a determining factor. The amount of heat evolved per mol of reacted CO + O_2 was found to be 170 ± 2 kJ mol^{-1} irrespective of the catalyst temperature.

Almost similar behaviour was observed during interaction of oxygen-pretreated palladium with CO + O_2 pulses, except for the marginally higher CO_2 yields obtained in this case. For example, on the average about 20, 47, 53, and 58% of the oxygen was adsorbed from individual CO + O_2 pulses when exposed over Pd(ox) at 300, 370, 420, and 470 K, the corresponding amounts of adsorbed CO being 54, 59, 63, and 65%. An average Q molar value of 173 ± 3 kJ was observed per mol of CO + O_2 consumed irrespective of the catalyst temperature.

DISCUSSION

Contrary to the results reported by Schreyer and coworkers for a high-activity Pt/SnO_2 catalyst (1), we saw no drastic fall in the CO oxidation activity of Pd/SnO_2 at any reaction temperature under study (Fig. 2) even when the reaction was followed for periods up to 30 h. Also, the catalyst activity in our study was found to deteriorate on hydrogen pretreatment, the effect being more drastic at higher reduction temperatures (Figs. 1b, 1d). Similar behaviour was observed for the catalysts prepared with 1–4 wt.% of Pd. Also, a similar pretreatment effect was observed in our earlier study using Pt/SnO_2 (3). The initial increase in the CO_2 yields as shown in Fig. 2 thus suggests a partial reoxidation of the catalyst surface during exposure to CO + O_2. The effect of pretreatment on catalytic activity (Fig. 1) is commensurate with the results of the microcalorimetry experiment. Thus, whereas a negligible amount of CO was adsorbed over Pd/SnO_2(red), a significant amount of CO was held over Pd/SnO_2(ox) which gave rise to CO_2 formation (Fig. 3). The temperature-dependent CO_2 yields as shown in Fig. 3 reveal that the CO + O_2 reaction and not the CO disproportionation is the source of CO_2 formation. Furthermore, the CO_2 yields observed during successive pulse exposures (Fig. 3) suggest that, in addition to the oxygen adsorbed over Pd, the lattice oxygen contributes significantly to CO_2 formation. This is also reflected in the Q molar values given in Fig. 4. The exothermic heat value for the reaction

$$CO(g) + 1/2\, O_2(ads) \rightarrow CO_2(g) \qquad [i]$$

may be estimated as ca. −143 kJ mol^{-1} (from CO(g) + 1/2 O_2(g) → CO_2(g), $\Delta H = -280$ kJ mol^{-1}, and 2Pd + O_2(g) → 2Pd(O)ad, $\Delta H = -275$ kJ mol^{-1} (17, 18).

Similarly, the enthalpy change occurring during reaction steps

$$CO(ad) + O(ad) \rightarrow CO_2(ad) \rightarrow CO_2(g) \qquad [ii]$$

may also be evaluated to be around −140 kJ mol^{-1}.

The lower Q molar values in the range 60–120 kJ mol^{-1} as shown in Fig. 4 (curves 3–5) thus confirm the significant contribution of the following endothermic step (17).

$$SnO_2 + CO \rightarrow SnO + CO_2 \qquad \Delta H = +11.7 \text{ kJ mol}^{-1} \qquad [iii]$$

The temperature-dependent rise in the Q molar values in Fig. 4 (curves 3–5), however, indicates that step (i) may play an increasing role with a rise in sample temperature. The Q molar values of 15–40 kJ mol^{-1} observed for Pd/SnO_2(red) (Fig. 4, curves 1, 2) indicate weak adsorption of CO in these samples. A comparison between the data given in Table 2 and in Figs. 3, 4, and 9 brings out the following important observations. It is seen that whereas no measurable amount of CO was adsorbed over Pd/SnO_2(red), a substantial amount of CO was adsorbed over Pd(red) under identical conditions without giving rise to any CO_2 formation. The progressive decrease in the CO adsorption from successive pulse doses as shown in Fig. 9 indicates a multilayer CO adsorption which is also reflected in the observed enthalpy values. The Q molar value of ~145 kJ mol^{-1} observed for the first CO injection (Fig. 9, curve 3) is in agreement with the reported value of heat of CO adsorption over polycrystalline palladium (18). The progressive fall in the enthalpy values as seen in Fig. 9 (curve 3) matches the decreasing amount of adsorbed CO from each pulse dose (Fig. 9, curves 1, 2). As a larger amount of CO was adsorbed over Pd(ox) (Fig. 11) and about 54–100% of this CO was reacted to produce CO_2 depending on catalyst temperature, it can be concluded that the oxygen adsorbed over palladium is very reactive to gaseous CO. This view is supported by the observed Q molar values of ~115–170 kJ mol^{-1} which correspond to the heat of reaction [i]. The marginally lower Q values at a lower reaction temperature may be attributed to the heat required for the release of some $(CO_2)_{ad}$ molecules formed during the reaction.

Interesting results are presented in Fig. 10 which show that smaller amounts of oxygen were adsorbed during exposure of Pd(red) to the first few O_2 pulses following the introduction of 10 successive CO pulse doses at 300 K. A correspondingly smaller amount of heat was evolved. The larger amounts of O_{ad} and the Q molar values observed during subsequent O_2 pulses match the results obtained at higher temperatures (Fig. 10, curves 2, 3). When the Q molar values of 240–250 kJ mol^{-1} as reported in Fig. 10 are compared with the enthalpy values of 115–170 kJ mol^{-1} observed during CO exposure over Pd(ox), it becomes clear that the oxygen adsorption over Pd ($\Delta H \approx -280$ kJ mol^{-1} (17)) plays an important role in this case. It may therefore be concluded that unlike the reaction of CO molecules with O_{ad}, the oxygen reaction with $(CO)_{ad}$ involves the L–H mechanism. The data obtained at 300 K (Fig. 10) thus suggest that the initial O_2 pulse doses displace some adsorbed CO molecules, making Pd sites available for the interaction with the next oxygen doses. The enthalpy data shown in curve 4 of Fig. 10 tend to support this view.

In the case of a Pd/SnO_2 sample, the O_2 pulse dosing following exposure to CO (Fig. 5) gave rise to higher enthalpy changes in the case of a reduced sample. The Q molar values in the range 380–480 kJ mol^{-1} as shown by curves 1–3 in Fig. 5 indicate the important role of the highly exothermic reaction between SnO and O_2; e.g.,

$$SnO + 1/2O_2 \rightarrow SnO_2, \qquad \Delta H = -295 \text{ kJ mol}^{-1}.$$

Data in Fig. 6 show that a higher fraction of dosed CO was adsorbed/reacted than that of O_2 when a Pd/SnO_2(ox) sample was exposed to CO + O_2 (2 : 1) pulses. A similar trend was observed at elevated sample temperatures when higher amounts of CO or O were adsorbed. On the other hand, only O_2 and no CO was adsorbed/reacted during the exposure of Pd/SnO_2(red) to CO + O_2 pulse doses. The Q molar values observed during interaction of CO + O_2 (Fig. 8, curve 1) are similar to those observed for the exposure of Pd/SnO_2(red) to O_2 alone (Fig. 5, curves 1–3). On the other hand, the lower Q molar values as shown by curve 2 of Fig. 8 obtained for a Pd/SnO_2(ox) sample correspond with the data in curves 4–6 of Fig. 5. It may therefore be concluded that out of the various reactions, such as CO(g) + O(ad) → CO_2(g), CO(ad) + O(ad) → CO_2(g), CO(g) + O(lattice) → CO_2, and $SnO + 1/2O_2 \rightarrow SnO_2$, the dominance of one over the other will depend on the chemical nature of the catalyst surface at the time of interaction. Thus, on an oxygen-rich surface the interaction of CO with adsorbed oxygen or with lattice oxygen plays a dominant role depending on the catalyst temperature; the reduced surface on the other hand tends to get oxidized first. These views are in agreement with our earlier reported study on the zeolite-supported platinum catalysts (19).

The results of similar experiments carried out with the Pd metal show that the CO is adsorbed preferentially on Pd(red) at lower temperatures and the fraction of adsorbed O_2 increased with the rise in temperature. The CO_2 yields shown in Fig. 11 suggest that at lower temperatures the reaction is controlled by the fraction of O_2 held on catalyst surface, whereas at the temperatures above 450 K the amount of adsorbed CO is the controlling factor. These results help us to conclude that both the CO and O_2 compete for metal sites and the simultaneous chemisorption of CO and O_2 at metal sites governs the overall reaction. At the lower sample temperatures the CO is held more strongly, inhibiting O_2 adsorption, but the removal of CO at higher temperatures resulted in a greater consumption of O_2.

The following conclusions may thus be drawn from the results discussed above.

(1) Whereas simultaneous adsorption of CO and O_2 governs the CO oxidation over Pd metal, the lattice oxygen abstraction plays an important role in the case of a Pd/SnO_2 catalyst, particularly at the lower catalyst temperatures. The presence of Pd facilitated this process, as is discussed in Ref. 3 in detail.

(2) The behaviour of a Pd/SnO_2 catalyst towards adsorption of CO or O_2 and for the CO oxidation reaction depends on the chemical nature of the surface at the time of interaction. The CO may react from both the gaseous and the adsorbed states but the oxygen takes part only in the adsorbed form. The reactions $CO_g + O_{ad} \rightarrow CO_2g$, $CO_g + SnO_2 \rightarrow CO_2 + SnO$, $CO_{ad} + O_{ad} \rightarrow CO_2(g)$, and $2SnO + O_2 \rightarrow 2SnO_2$ are equally probable and the preponderance of one over the other is decided by the oxidation states of Pd and Sn at the time of the reaction.

(3) In contrast to the behaviour shown by reduced Pd metal, the hydrogen-reduced Pd/SnO_2 exhibited very poor activity for the adsorption and the oxidation of CO. The x-ray photoelectron spectroscopy results (20) showed that the binding energy of $Pd_{3d5/2}$ and $Sn_{3d5/2}$ peaks shifted to a lower value by 1.4 and 1.1 ev, respectively, when a Pd/SnO_2 sample was subjected to a reducing pretreatment at 470 K. These results are in agreement with the detailed investigations of Gardner *et al.* (21, 22) showing that the reduction of Pt/SnO_2 led to the removal of lattice oxygen and the formation of Pt–O–Sn or Pt/Sn alloy moieties at the catalyst surface. The decrease in the metal surface area of Pd/SnO_2 on hydrogen pretreatment (Table 1) further supports this contention. The alloy species reoxidise to some extent to form Pd/SnO_2 or $Pd–O/SnO_2$ upon oxygen exposure, as is evident from the large amount of heat evolved in this process (Fig. 5, curves 1–3; Fig. 8, curve 1) and from the initial increase in the catalytic activity as shown in Fig. 2. Furthermore, these species show lack of Pd metal character for CO adsorption (Fig. 7) and are therefore responsible for the poor catalytic activity of the Pd/SnO_2(red) sample (Fig. 1).

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