JOURNAL OF CATALYSIS **140**, 443–452 (1993)

Microcalorimetric Study of the Adsorption and Reaction of CO, O_2, CO + O_2, and CO_2 on NaX Zeolite, Pt/NaX, and Platinum Metal: Effect of Oxidizing and Reducing Pretreatment

N. D. GANGAL, N. M. GUPTA, AND R. M. IYER

Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India

Received March 25, 1991; revised October 22, 1992

Pt/NaX and Pt powder showed very similar behaviour in both chemisorption and heat release (Q) when CO, O_2, CO + O_2, or CO_2 were dosed in the temperature range 300–500 K. However, an oxidizing or a reducing treatment given to a sample had a different effect on the Q values. Thus, CO adsorption on H_2-pretreated Pt/NaX and Pt powder gave constant Q values of about 130 and 140 kJ mol^{-1}, respectively, at all the temperatures studied. In the case of an oxygen pretreatment, the Q values were about 167 kJ mol^{-1} for both samples, with the exception of CO dosed to Pt/NaX at 305 K when a lower Q value of 83 kJ mol^{-1} was observed. The heat evolved when CO + O_2 were dosed was higher by about 40–60 kJ mol^{-1} compared with that observed when CO was dosed under identical conditions. The metal-free zeolite showed negligible adsorption and heat release during exposure to both CO and CO + O_2 at 300–500 K. The results provide evidence for exclusive participation of metal sites in the CO oxidation over Pt/NaX catalyst, the diffusion of reactants or products through zeolite pores playing an insignificant role. The chemisorption properties of the metal were nevertheless modified by the support. Both reactant species (CO and oxygen) are chemisorbed simultaneously and compete for metal sites. The results suggest that the three reactions, namely, $2CO(ad) \rightarrow C + CO_2(g)$, $CO(g) + O(ad) \rightarrow CO_2(g)$, and $CO(ad) + O(ad) \rightarrow CO_2(g)$ are equally probable over the platinum surface, and the preponderance of one of them may be decided by the chemical nature of the surface at the time of reaction. The study supports the view that the CO and O interact at a Pt site in a cyclic order, and the sequence in which these species are chemisorbed may have a significant effect on the catalytic activity.

INTRODUCTION

In a calorimetric study of the interaction of CO, O_2, and CO + O_2 with SnO_2 and Pt/SnO_2 catalysts (*1*), we showed that the amount of evolved heat depended significantly on the chemical nature of adsorbent surface. The thermochemical data supported the view that lattice oxygen abstraction from SnO_2 plays an important role in the CO oxidation reaction at 300–475 K. Furthermore, the presence of platinum was found to augment $Sn^{4+} \rightarrow Sn^{2+}$ conversion during interaction with CO. These data led us to propose a reaction scheme in which the heat evolved in the interaction of CO with metal sites promotes lattice oxygen abstraction at the metal/support interface and thus accelerates the rate of CO oxidation.

On the other hand, much work on metals supported on nonreducing oxides has shown that CO oxidation over these catalysts proceeds at metal sites (for reviews, see Refs. (*2*, *3*)). A few studies also suggest the involvement of support hydroxyl groups in the process (*4*). Different views have been expressed on the mechanistic routes followed in CO oxidation over transition metals (*2*, *3*). As is brought out in our previous work (*1*), microcalorimetry is sensitive to each step in a catalytic process, and the heat evolved in the interaction/reaction of an adsorbate represents the overall effect of the processes occurring on the catalyst surface. This technique is therefore well suited for elucidation of intermediate steps involved in a catalysed process. Although some thermochemical data are now available for che-

0021-9517/93 $5.00

misorption on polycrystalline and single-crystal transition metal surfaces (*5, 6*), there are very few studies on supported metal catalysts, particularly with zeolites as supports, where adsorption and diffusion in structural cavities may play an important role (*7–11*).

The present study was therefore undertaken to evaluate the adsorption and the heat evolved in the interaction of CO,O_2, CO + O_2, and CO_2 with NaX zeolite and Pt/NaX catalyst. Similar data were also obtained for polycrystalline platinum powder for a comparative evaluation. The effect of pretreatment given under oxygen or hydrogen flow to a catalyst was evaluated to understand the role and the activity of preadsorbed surface species. Reaction routes involved in the CO oxidation reaction over zeolite-based catalysts are discussed in the light of these thermochemical data.

EXPERIMENTAL

Calorimetry. A heat flow microcalorimeter equipped with stainless steel gas circulation cells (Setaram, France, model C80) was employed for the heat measurements. One end of the calorimeter vessel was connected to a vacuum system and a gas manifold so as to have provision for evacuation or alternatively to maintain a sample under helium, oxygen or hydrogen flow. The other end was connected to a gas chromatograph equipped with a thermal conductivity detector for on-line analysis of effluents. An injection port was provided at the entry point of the calorimeter vessel to introduce 100-μl (~4.9-μmol) pulses of a required adsorbate, such as CO or CO + O_2 mixture, using a gas-tight hypodermic syringe. An identical but empty calorimeter vessel connected similarly to the vacuum line or gas flow system was used as a reference cell.

One hundred mg of a Pt (1%)/NaX or NaX sample (~250 μm particle size) or alternately 100 mg of platinum powder (50 μm particle size) was used for each experiment. Catalysts of larger particle size, rather than samples containing fine binder-free zeolites, were preferred in this study, as the latter tended to agglomerate in the calorimeter vessel leading to uneven distribution and hence to non-reproducible results. Prior to calorimetric measurements, a sample was treated in situ in flowing hydrogen or oxygen (20 ml min^{-1}) at 475 K for 1 h, followed by evacuation (475 K, 30 min) and heating the sample for 1 h under helium flow at 475 K. The samples pretreated in oxygen or hydrogen are represented by using (ox) or (red) as a suffix, e.g., Pt/NaX(red) stands for a zeolite-supported platinum pretreated under hydrogen. While maintaining a sample under helium flow (~10 ml min^{-1}) several 100-μl (~4.9-μmol) pulses of an adsorbate were successively introduced to a sample with an interval of about 10 min. The heat evolved and the effluents released were measured simultaneously. The symbol Q indicates the heat liberated in the process.

As the sample amount used in each experiment was very small as compared to the mass of calorimeter vessel, the dissymmetry produced by using the sample only in one of the cells was negligible. Also, no significant heat change was observed when an adsorbate pulse was introduced into the empty calorimeter vessel at different temperatures.

The amount of adsorbed or reacted adsorbate was evaluated from the difference between the amounts of the injected and the eluted gas or gas mixture.

Each set of experiments was repeated atleast two or three times and the data reported here indicate the average values. The accuracy of heat values was constrained by the accuracy of the gas chromatographic analysis as discussed previously (*1*) and the Q values reported in this study may be considered to be accurate within 5–10%, depending on catalyst temperature.

Catalysts. A 60–80 mesh fraction of sodium X zeolite (Union Carbide, Si/Al ratio = 1.2) was washed repeatedly to remove binder material as far as possible and was then dried in vacuum at 425 K for several hours. The characteristics of the zeolite used are given in detail elsewhere (*12, 13*). Samples with the particle size used in this study showed an N_2 BET surface area of about 350 m^2 g^{-1} and had a pore size in the range of 0.02–0.8 μm. The X-ray diffraction pattern corresponded to the reported data for a crystalline NaX zeolite (*13, 14*).

A catalyst sample containing 1 wt% Pt was prepared by incipient impregnation using the required amount of aqueous chloroplatinic acid solution. The pH of the slurry was maintained at about 5. After drying in air at 365 K, the catalyst was finally reduced under hydrogen flow at 575 K. The reduced sample showed an X-ray diffraction pattern almost similar to that of NaX zeolite, confirming its crystalline nature. The Pt/NaX sample had a N_2 BET surface area of about 330 m^2 g^{-1}.

A fine powder of platinum metal used for parallel thermochemical measurements was prepared by complete reduction of chloroplatinic acid in flowing hydrogen at 575 K, and this sample showed a N_2 BET surface area of less than 1 m^2 g^{-1}.

Gases. He(99.9%) carrier gas (from Airco, USA) was used after passing through a bed of a deoxo catalyst and then through a molecular sieve trap to remove away any moisture. Traces of carbonyl impurities were removed from carbon monoxide (from Airco) by passing through a solidified carbon dioxide (195 K) trap. Carbon dioxide (99.5% purity) was used without further purification.

RESULTS

Pt/NaX Catalyst

Interaction of CO. Figure 1 shows the fraction of CO adsorbed/reacted and the yield of CO_2 formed at 300–500 K when a 100-μl (4.9-μmol) pulse was introduced to Pt/NaX catalyst after an oxygen or a hydrogen pretreatment as mentioned above. These data show that except at the catalyst temperature of 375 K when the amount of CO adsorbed/reacted over Pt/NaX(ox) was much less than in the case of Pt/NaX(red), almost similar amounts of CO were adsorbed/reacted over these two samples.

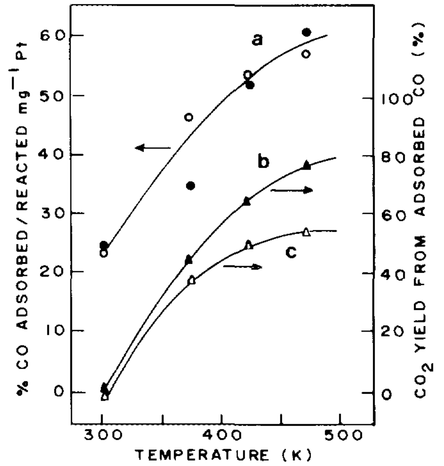

FIG. 1. Amount of CO adsorbed/reacted and the CO_2 yield from 4.9-μmol CO pulse injection over Pt/NaX(red) and Pt/NaX(ox) samples at different temperatures:

—●—, —▲— } Pt/NaX(ox), —○—, —△— } Pt/NaX(red).

The conversion of adsorbed CO to CO_2 was, however, always higher in the case of the Pt/NaX(ox) sample (Fig. 1b) as compared to the yield obtained with the Pt/NaX(red) sample (Fig. 1c). It is also of interest to observe that the CO_2 yields were normally less than 50% for the Pt/NaX(red) sample (Fig. 1c), whereas the conversion reached a value of 80% for the Pt/NaX(ox) sample (Fig. 1b).

Curves a and b of Fig. 2 give the heat evolution results corresponding to a 4.9-μmol CO pulse admitted to Pt/NaX(ox) and Pt/NaX(red) samples, respectively. Whereas a constant Q value of ~130 kJ mol^{-1} was obtained during interaction of CO over Pt/NaX(red) sample at different temperatures, in the case of Pt/NaX(ox) the amount of evolved heat varied with sample temperature (Fig. 2a), the value being low at 300 K.

Successive pulse injections gave rise to decreasing amounts of CO adsorption and also that of Q values for both the Pt/NaX(red) and Pt/NaX(ox) samples. Typical data obtained for heat evolution from a

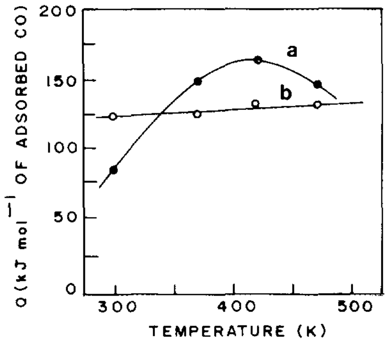

FIG. 2. Heat evolved following admission of a 4.9-μmol CO pulse to (a) Pt/NaX(ox) and (b) Pt/NaX(red) catalysts at different temperatures.

Pt/NaX(red) sample as a function of CO adsorbed during successive pulse exposures at different temperatures are given in Fig. 3.

Interaction of oxygen following CO. Subsequent to 8 to 10 pulse injections of carbon monoxide as mentioned above at different sample temperatures, the sample was flushed with helium for about an hour and was exposed to a pulse of 100 μl (4.9 μmol) oxygen. A small fraction of the gas was adsorbed but no CO_2 was found to be formed for both the Pt/NaX(ox) and Pt/NaX(red) samples. Correspondingly, a small amount of heat was evolved as shown in the typical data in Table 1 for Pt/NaX(red) sample.

Interaction of CO + O_2. Figures 4 and 5 show the heat evolved as a function of gas mixture adsorbed during successive 4.9-μmol pulse exposures at different temperatures using Pt/NaX(red) and Pt/NaX(ox) samples. For the experiment with Pt/NaX(red) at 305 K (Fig. 4a), the amount of gas adsorbed was very small and therefore the heat values in this case are expressed per gram of Pt metal rather than per mol of adsorbate. The data in Figs. 4 and 5 show that the amount of gas mixture adsorbed is very similar for both the Pt/NaX(ox) and Pt/NaX(red) samples at all the temperatures investigated. Also, the successive CO + O_2 pulse injections gave rise to almost the same adsorption and heat evolution, in contrast to the data in Fig. 3. Furthermore, an almost constant Q value of about 170 kJ mol^{-1} was observed for experiment with Pt/NaX(red) at different temperatures (Fig. 4), whereas in the case of Pt/NaX(ox) the heat evolved depended somewhat on catalyst temperature (Fig. 5), a behaviour similar to that observed in CO exposure over Pt/NaX(ox) (Fig. 2a).

Figure 6 shows the carbon dioxide yield obtained in the interaction of the first 4.9-μmol CO + O_2 pulse injection over the two respective catalyst samples. Notwithstanding the slightly different Q_{molar} values (Figs. 4, 5), the yield of CO_2 was similar from the two catalyst samples at all the temperatures studied.

Heat of CO_2 evolution. The Q values involved in the evolution of a mole of CO_2 in the interaction of CO and CO + O_2 on Pt/NaX are given in Table 2. As is seen in these data, the Q values for a particular adsorbate are almost independent of the pretreatment given to a sample, though the heat of CO_2 evolution was marginally higher in CO + O_2 interaction as compared to that observed for CO exposures.

Adsorption of CO_2. An appreciable amount of CO_2 was adsorbed on Pt/NaX

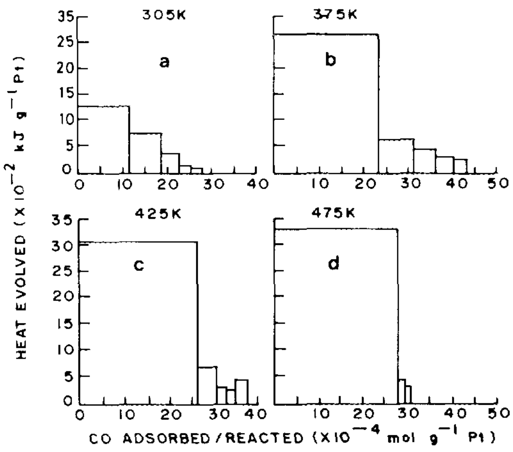

FIG. 3. Heat evolved as a function of adsorbed gas during successive CO pulse (4.9 μmol each) injections to Pt/NaX(red) catalyst at different temperatures.

TABLE I

The Yield of CO_2 and the Heat Evolved on Injection of a 100-μl (4.9-μmol) Oxygen Pulse after 1 h of 8–10 Successive CO Pulse Injections over 100 mg of Pt(1%)/NaX or Pt Powder Samples at Different Temperatures

Catalyst temperature (K)	Pt/NaX(red)			Pt(red)		
	Oxygen adsorbed μl mg^{-1} of Pt	CO_2 yield (%)	Q (kJ g^{-1} platinum $\times 10^{-3}$)	Oxygen adsorbed (μl mg^{-1} of Pt)	CO_2 yield (%)	Q (kJ g^{-1} platinum $\times 10^{-3}$)
305	4.3	Not measurable	67	0.25	88	276
375	4.4	Not measurable	90	0.29	78	289
425	3.5	Not measurable	102	0.29	62	312
475	8.6	Not measurable	207	0.28	43	277

only at a temperature of 305 K. The heat evolved in CO_2 adsorption was found to vary in the range of 40 to 50 kJ mol^{-1}, depending on the sample pretreatment conditions, the values being higher in the case of Pt/NaX(red) samples. Successive CO_2 pulse exposures gave rise to slightly reduced heat values which became constant after a second or third pulse exposure. At sample temperatures above 375 K, the amount of CO_2 adsorbed and that of the heat evolved were negligibly small under present experimental conditions. Table 3 gives typical data obtained at various sample temperatures.

NaX Zeolite

No significant adsorption or formation of CO_2 was observed when CO or CO + O_2 pulses were introduced to a metal-free NaX zeolite sample at different temperatures. The amount of heat evolved in these interac-

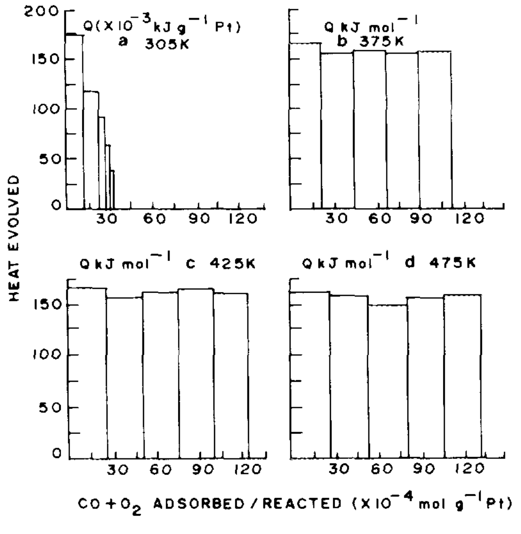

FIG. 4. Heat evolved as a function of adsorbed gases during successive 4.9-μmol CO + O_2 (1 : 1) pulse injections to Pt/NaX(red) catalyst at different temperatures.

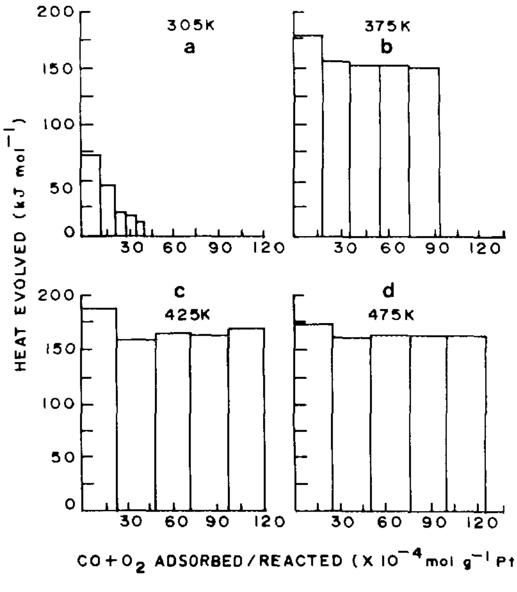

FIG. 5. Heat evolved as a function of adsorbed gases during successive 4.9-μmol CO + O_2 (1 : 1) pulse injections to Pt/NaX(ox) catalyst at different temperatures.

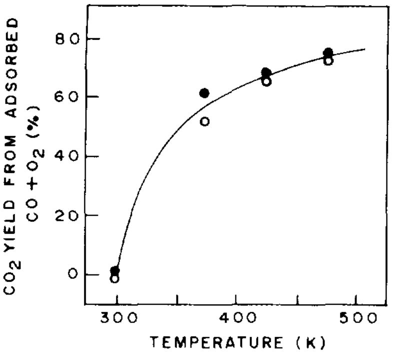

FIG. 6. Yield of CO$_2$ from adsorbed/reacted CO + O$_2$ when a 4.9-μmol gas mixture (1 : 1) pulse was admitted to Pt/NaX(ox) (—●—) and Pt/NaX(red) (—○—) samples at different temperatures.

tions was also very low (in the range of about 0.02 to 0.2 J g^{-1} of catalyst sample). The pretreatment given to a sample under hydrogen or oxygen flow had only a marginal effect on the *Q* values. Exposure of NaX to CO$_2$ gave a thermochemical result similar to that shown in Table 3 and an average value of about 40 kJ mol^{-1} was obtained which is commensurate with the value reported in the literature (*15*).

Platinum Metal

CO interaction. An almost similar amount of carbon monoxide was adsorbed/reacted on platinum metal powder when 4.9-μmol gas pulses were introduced over hydrogen- or oxygen-pretreated samples. The amount of carbon dioxide formed in the process, however, was higher in the case of the Pt(ox) sample (Fig. 7). The variation in temperature had a less pronounced effect on CO adsorption on platinum metal as compared to the case of Pt/NaX in Fig. 1.

Almost constant *Q* values of about 165 kJ mol^{-1} from Pt(ox) and about 140 kJ mol^{-1} from Pt(red) were obtained at all temperatures in the range 300–500K in the exposure of platinum powder to CO pulses (Fig. 8).

O$_2$ interaction. Following CO exposure, when a platinum sample was maintained under helium flow for 1 h at adsorption temperature and was then exposed to an oxygen pulse, a considerable fraction was adsorbed and converted to carbon dioxide. The extent of oxygen adsorption and the yield of CO$_2$ formed were higher in the case of Pt(ox) as compared to Pt(red). Further oxygen pulses, however, resulted in negligible adsorption.

A similar heat was evolved for oxygen pulses with both the Pt(red) and Pt(ox) samples, irrespective of temperature. Results with the Pt(red) sample are included in Table 1.

CO + O$_2$ interaction. As in the case of CO adsorption (Fig. 8), exposure of platinum powder to CO + O$_2$ gave rise to similar *Q* values at all temperatures. The *Q* values, however, were marginally higher with CO + O$_2$ as compared with CO. Thus, the average *Q* value for CO + O$_2$ interaction with Pt(ox) was about 190 kJ mol^{-1}, the corresponding value for Pt(red) being 170 kJ.

As was observed with CO + O$_2$ on Pt/NaX (Fig. 6), the amount of CO$_2$ formed from adsorbed/reacted CO + O$_2$ over platinum at different temperatures was independent of the pretreatment given to a sample. Figure 9 presents these data.

CO$_2$ interaction. No measurable amount of CO$_2$ was adsorbed on Pt(ox) or Pt(red) samples when pulses were admitted at the temperatures under study, and correspondingly a negligible amount of heat was evolved in the process.

TABLE 2

Enthalpy Change per mol of CO$_2$ Evolved in the Interaction of CO or CO + O$_2$ Pulse Injections over Pt/NaX(ox) and Pt/NaX(red) Samples at Different Temperatures

Temperature (K)	Pt/NaX(red) (kJ mol^{-1})		Pt/NaX(ox) (kJ mol^{-1})	
	CO	CO + O$_2$	CO	CO + O$_2$
375	290	305	274	277
425	246	272	252	284
475	200	224	218	236

TABLE 3

Amount of CO_2 Adsorbed and That of the Heat Evolved when a 100-μl (4.9-μmol) CO_2 Pulse Was Admitted to 100 mg of Pt/NaX(red) and Pt/NaX(ox) Samples at Various Temperatures

Temperature (K)	Pt/NaX(red)		Pt/NaX(ox)	
	CO_2 adsorbed (μl)	Q (kJ mol^{-1})	CO_2 adsorbed (μl)	Q (kJ mol^{-1})
305	52.8	48	56.0	37
375	10.1	54	Unmeasurable	39[a]
425	Unmeasurable	37[a]	Unmeasurable	29[a]
475	Unmeasurable	15[a]	Unmeasurable	8[a]

[a] Values refer to total heat evolved in mJ in the exposure to 100 μl of CO_2, expressed per g of the catalyst.

DISCUSSION

The following points may be highlighted on the basis of the results obtained in this study.

1. Since only a limited quantity of CO was adsorbed/reacted on NaX zeolite under the present experimental conditions, the data in Figs. 1 and 2 may be considered to arise exclusively from chemisorption of CO on platinum sites.

2. A comparison of the data in Figs. 1 and 7 reveals a parallelism in CO chemisorption over Pt/NaX and over polycrystalline platinum powder. It is seen that the extent of CO chemisorption/reaction is similar after both the reducing and oxidizing pretreatments. On the other hand, the CO_2 yields were always larger for Pt/NaX(ox) and Pt(ox) samples.

Higher CO_2 yields from oxygen-pretreated samples suggest that the CO chemisorption on platinum and its reaction with adsorbed oxygen are two competitive processes occurring with similar probability. About 50% conversion of consumed CO to CO_2 in the case of CO exposure to Pt/NaX(red) (Fig. 1c) and to Pt(red) (Fig. 7c) may indicate the occurrence of a CO dispro-

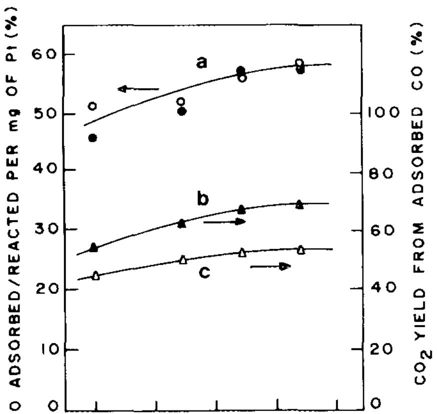

FIG. 7. Amount of CO adsorbed/reacted and the CO_2 yield from 4.9 μmol CO pulse injection to polycrystalline Pt(red) and Pt(ox) samples:

—●—, —▲— } Pt(ox), —○—, —△— } Pt(red).

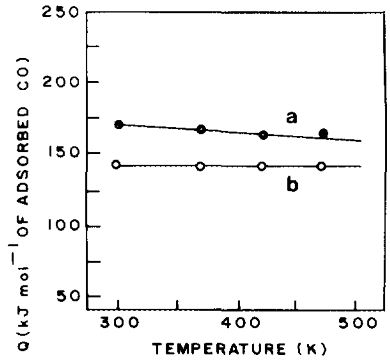

FIG. 8. Heat evolved following admission of a 4.9 μmol CO pulse to (a) Pt(ox) and (b) Pt(red) samples at different temperatures

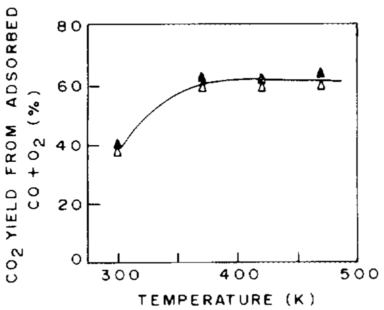

FIG. 9. Yield of CO_2 from adsorbed/reacted Co + O_2 when a 4.9-μmol gas mixture (1 : 1) pulse was admitted to Pt(ox) (—●—) and Pt(red) (—○—) samples at different temperatures.

portionation reaction, whereas in the case of Pt/NaX(ox) and Pt(ox) samples, the reaction of CO with O_{ad} may play an important role. High reactivity of chemisorbed oxygen with CO is a well documented phenomenon (*3*, *16*).

3. A negligible amount of CO_2 was formed in the interaction of CO or CO + O_2 with Pt/NaX at 305 K (Figs. 1, 6) whereas almost similar CO_2 yields were observed in the interaction of these adsorbates with platinum powder at all the temperatures in the range 300–500 K (Figs. 7, 9).

The low activity of Pt/NaX at 305 K may arise either due to CO_2 remaining adsorbed in the zeolite, if formed, or due to strongly chemisorbed oxygen at this temperature which may not be reactive to CO. It has indeed been shown that the chemisorption properties of a metal are dependent on its dispersion. For example, the oxygen chemisorbed over highly dispersed platinum in Pt/SiO_2 had poor activity for reaction with CO at low temperatures (*17*, *18*).

4. Data in Table 3 show that about 40 kJ mol^{-1} of heat is evolved in the adsorption of CO_2 on Pt/NaX or NaX at 305 K, whereas at higher temperatures the CO_2 adsorption and heat release was negligible for both the oxidized and reduced samples. The CO_2 formed in the interaction of CO or CO + O_2 which may remain adsorbed on the zeolite may thus influence *Q* values in Figs. 2–5 for experiments performed at 305 K only. However, in that case, higher *Q* values would be expected using Pt/NaX(ox) than with Pt/NaX(red) as the former showed higher CO oxidation activity (Figs. 1, 6). On the contrary, a smaller *Q* value (80 kJ mol^{-1}) was observed in the interaction of CO and CO + O_2 with Pt/NaX(ox) at 305 K (Fig. 2) as compared to the values of about 130–160 kJ mol^{-1} obtained with Pt/NaX(red) under identical conditions.

These data thus confirm that the CO_2 adsorption in zeolites or its desorption played no significant role in the heat values obtained in this study.

5. The almost constant *Q* value of about 130 kJ mol^{-1} observed when CO was introduced to Pt/NaX(red) and Pt(red) is of the order of heat values reported in the literature (130–180 kJ mol^{-1}) for CO chemisorption on polycrystalline and single crystal platinum (*5*, *6*). The rather lower value of this *Q* in our study may be attributed to the contribution of an endothermic process associated with the desorption of produced CO_2 though the net contribution of this step cannot be assessed at this stage. The data in Figs. 2, 8 thus again confirm that the CO adsorption on Pt/NaX involves mainly metal sites and that the entrapment and diffusion through zeolite channels play an insignificant role.

The higher *Q* values observed for CO on Pt/NaX(ox) and Pt(ox) samples as compared to the values obtained for the respective reduced samples (Figs. 2, 8) may be attributed to the occurrence of the CO(g) + O(ad) → CO_2(g) reaction (from CO(g) + O_2(g) → CO_2(g); $\Delta H = -280$ kJ mol^{-1} and O_2(g) + Pt → Pt(O)(ad); $\Delta H = -120$ kJ mol^{-1}, enthalpy change for CO(g) + O(ad) → CO_2(g) may be calculated as ~ −160 kJ mol^{-1}).

An anomalous lower *Q* value of 85 kJ mol^{-1} in the interaction of CO over Pt/NaX(ox) at 305 K (Fig. 2a) may be explained by poor catalyst activity for the CO oxidation reaction at this temperature as has been discussed above. A poor reactivity of chemisorbed oxygen at low temperatures has been demonstrated by Sárkány *et al.* using well dispersed metal catalyst (*18*).

6. The *Q* values observed with CO + O_2 pulses were higher than those obatined with CO pulses under identical conditions. Thus, whereas the value of *Q* was about 130 kJ mol^{-1} for CO on Pt/NaX(red) (Fig. 2), the average value observed for CO + O_2 was about 170 kJ mol^{-1} (Figs. 4, 5). Higher *Q* values with CO + O_2 pulses were similarly observed in experiments using platinum powder. Thermochemical data given in Refs. (*6, 7*) show that the heat evolved in the chemisorption of oxygen on polycrystalline platinum is of the order of 210–270 kJ mol^{-1}, whereas the *Q* in CO chemisorption is found to be in the range 125–165 kJ mol^{-1}. The values observed with CO + O_2 pulses in our experiments may thus be considered to be intermediate values obtained in simultaneous CO and O_2 chemisorption on metal sites. Our data may thus be taken as evidence for simultaneous and competitive chemisorption of both the reactants over platinum sites. This contention is supported by the fact that, for both the supported and the metallic platinum samples, a similar fraction of adsorbed CO + O_2 gas mixture was converted to CO_2 irrespective of a H_2 or a O_2 pretreatment given to a sample (Figs. 6, 9).

7. A comparison of the data in Figs. 3–5 shows that successive CO pulses introduced to Pt/NaX(red) give rise to decreasing CO adsorption and to correspondingly lower *Q* values at all temperatures. On the other hand, successive CO + O_2 pulses gave rise to almost constant values of *Q* and CO_{ad}, particularly at temperatures above 300 K (Figs. 4, 5).

These results again suggest that the two reactions, namely $2CO_{ad} \rightarrow C + CO_2$ and $CO_{ad} + O_{ad} \rightarrow CO_2$ are equally probable over the platinum surface. In the case of the latter reaction, the surface is simultaneously regenerated (Fig. 4) whereas the carbon deposition in the disproportionation reaction would lead to progressive catalyst poisoning (Fig. 3).

8. The data in Table 1 suggest that although the zeolites do not actively participate in the chemisorption process, they do modify the characteristics of the supported metal. Thus, in the case of platinum metal, the surface species formed in CO chemisorption were reactive to oxygen even after a lapse of 1 h the species formed on Pt/NaX under identical conditions being completely inactive. The nature and the reactivity of the species formed in CO chemisorption in the two cases are now under investigation.

In conclusion, the present data provide evidence that the CO oxidation process over platinum catalyst using a nonreducible support is mainly governed by the simultaneous chemisorption of CO and O at metal sites, though the support may considerably modify the adsorption characteristics of a metal, as discussed by various authors (*19*). The pretreatment effect on the chemisorption properties and on the *Q* values are in agreement with our views (*1*) that the initial chemical nature of a catalyst surface governs the sequence of subsequent reaction steps. It may be suggested that the CO and O are chemisorbed at a metal site in a cyclic order, and the sequence in which these species are chemisorbed and reacted may play an important role in deciding the overall reactivity of a catalyst (*1, 20*). This is supported by our finding that a hydrogen pretreatment leads to a much higher CO oxidation activity of a Pt/NaX catalyst as compared to that of a sample pretreated in oxygen under identical conditions (*21*). For example, in the reaction of CO + O_2 + He (2 : 1 : 17) gas mixture using a flow-through catalytic reactor, a conversion of 100% was observed at all temperatures in the range 325–500 K for Pt/NaX(red) catalyst, whereas the conversion was around 25 and 50% when Pt/NaX(ox) catalyst was used at temperatures of 375 and 425 K, respectively.

REFERENCES

1. Gangal, N. D., Gupta, N. M., and Iyer, R.M., *J. Catal.* **126,** 13 (1990).

2. Golodets, G. I., *in* "Heterogeneous Catalytic Reactions Involving Molecular Oxygen," Studies in Surface Science and Catalysis, Vol. 15, p. 280. Elsevier, Amsterdam, 1983.

3. Boreskov, G. K., *in* "Catalysis: Science and Technology" (J. R. Anderson and M. Boudart, Eds.), Vol. 3, p. 92. Springer-Verlag, Berlin/New York, 1982.
4. Gel'bshtein, A. I., Mischchenko, yu. A., Dulin, D. A., Kolotyrkin, I. Ya, and Kakhniashvili, G. N., *Dokl. Adkad. Nauk SSSR* **284,** 900 (1985).
5. Toyoshima, I., and Somorjai, G. A., *Catal. Rev–Sci. Eng.* **19,** 105 (1979).
6. Engel, T., and Ertl, G., *Adv. Catal.* **28,** 1 (1979).
7. Chou, P., and Vannice, M. A., *J. Catal.* **104,** 1 (1987).
8. Chou, P., and Vannice, M. A., *J. Catal.* **104,** 17 (1987).
9. Herrmann, J. M., Gravelle-Rumeau-Maillot, M., and Gravelle, P. C., *J. Catal.* **104,** 136 (1987).
10. Gatte, R. R., and Phillips, J., *J. Catal.* **116,** 49 (1989).
11. Gelin, P. Auroux, A., Ben Taarit, Y. and Gravelle, P. C., *Appl. Catal.* **46,** 227 (1989).
12. Kamble, V. S., Gupta, N. M., and Iyer, R. M., *J. Catal.* **113,** 398 (1988).
13. Gupta, N. M., Kamble, V. S., Annaji Rao, K., and Iyer, R.M., *J. Catal.* **120,** 432 (1989).
14. Barrer, R. M., Baynham, J. W., Bultitude, F. W., and Meier, W. M., *J. Chem. Soc. (London)*, 195 (1959).
15. Meier, W. M., and Uytterhoeven, J. B., "Advances in Chemistry Series," Vol. 121, p. 376. Amer. Chem. Soc., Washington, DC, 1973.
16. Behm, R. J., Thiel, P. A., Norton, P. R., and Bindner, P. E., *Surf. Sci.* **147,** 143 (1984).
17. Bennett, C. O., Laporta, L. M., Cutlip, M. B., *Stud. Surf. Sci. Catal.* **30,** 143 (1987).
18. Sárkány, J., and Gonzalez, R. D., *Appl. Catal.* **5,** 85, (1983); Barshad, Y., Zhou, X., and Gulari, E., *J. Catal.* **94,** 128 (1985); Dijkgraaf, P. J. M., Duisters, H. A. M., Kuster, B. F. M., and van der Wiele, K., *J. Catal.* **112,** 337 (1988).
19. Imelik, B., Naccache, C., Coudurier, G., Praliaud, H. Mériaudeau, P., Gallezot, P., Martin, G. A., and Védrine, J. C. (Eds.), "Metal–Support and Metal–Additive Effects in Catalysis." Elsevier, Amsterdam, 1982.
20. Slin'ko, M. M., Jaeger, N. I., and Svensson, P., *J. Catal.* **118,** 349 (1989).
21. Gangal, N. D., Gupta, N. M., and Iyer, R. M., unpublished work.