Evidence for a Carbonate Species During CO Oxidation on Deactivated Rh(111)[1]

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In earlier work from this laboratory on the oxidation of CO over a single-crystal Rh(111) model catalyst, it was found that the kinetics of the reaction change dramatically when the reaction conditions were varied from reducing to oxidizing. These earlier studies suggested the possibility that the observed changes in reaction kinetics arose from the formation of a surface carbonate species, i.e., Rh–O–(CO_2), on oxidized Rh which alters the kinetics and decreases the reaction rate because of the tenacious bonding of this complex. In order to further investigate this suggestion, we have recently performed a high-resolution electron energy loss, HREELS (surface vibrational spectroscopy), study of the intermediate species present on the Rh surface under various reaction conditions in conjunction with temperature-programmed desorption (TPD) measurements. The results provide further evidence that such a carbonate complex is present on the surface after reaction under oxidizing conditions. However, we also observed that under these conditions the surface is hydroxylated, probably arising from the presence of impurity H_2O or H_2 in the reactor. TPD results confirm the importance of these –OH groups in stabilizing the carbonate complex. For example, CO_2 adsorbed on a "clean" oxide (prepared by high temperature oxygen exposures in ultrahigh vacuum) was found to desorb at temperatures more than 100°C lower than CO_2 desorption from a hydroxylated Rh-oxide surface. In the latter case, CO_2 desorption likely arises from the reaction-limited decomposition of the carbonate species. In fact, the earlier kinetic studies are most consistent with an overall reaction mechanism for CO oxidation under oxidizing conditions involving the rate-limited decomposition of such a surface-bound carbonate species.   © 1991 Academic Press, Inc.

INTRODUCTION

The catalytic oxidation of CO by O_2 over group VIII metals is important for the control of automotive exhaust emissions (*1–3*). As such, considerable attention has been focused on the kinetics and mechanisms of this reaction (*4*). Furthermore, the relative simplicity of the reaction on a metal surface makes it an ideal model system of a heterogeneous catalytic process—a process involving molecular and dissociative (atomic) adsorption, surface reaction, and desorption of products. This additional motivation has led to numerous fundamental studies of the various elementary steps of the reaction;

for example, the adsorption and desorption of CO and O_2, and the surface reaction between chemisorbed CO molecules and O atoms ($\equiv$ CO(ad) and O(ad), respectively) (*5*).

The present study is part of a continuing effort in this laboratory (*6–9*) to understand the mechanism(s) of the CO oxidation reaction over, and the deactivation of, a number of transition metal catalysts. In particular, we focus here on a kinetic regime observed at low CO/O_2 ratios (highly oxidizing conditions) on Rh, Pd, and Ir in which the catalytic activity decreases dramatically due to an oxidation of the near-surface region of the metal (*7–10*). On Rh this regime is characterized by a zero-order pressure dependence for either of the reactants (CO or O_2). Such behavior is in stark contrast to reaction at higher CO/O_2 ratios (reducing condi-

tions), where the dependence is first-order in O_2 and negative first-order in CO. The kinetics displayed under these reducing conditions are consistent with a mechanism involving a reaction on the metal surface between CO(ad) and O(ad), rate-limited by the dissociative chemisorption of O_2. At steady state, the latter process is poisoned by high coverages of chemisorbed CO which must desorb to open sites for O_2 adsorption. Previously (8), we have suggested that the zero-order pressure dependence observed under highly oxidizing conditions may result from a mechanism involving the rate-limited decomposition of a carbonate-like species which forms as an intermediate on oxidized Rh. Besides being consistent with the observed kinetics, such a mechanism was also suggested by an observation of an unusually high CO_2 desorption temperature in TPD measurements made subsequent to reaction on Rh (and Pd and Ir) (8, 9).

In this paper, we describe high-resolution electron energy loss (HREELS) vibrational spectroscopic measurements of a Rh surface subsequent to high-pressure (<1 Torr) reaction for a variety of CO/O_2 partial pressures in order to verify the presence of a carbonate species for such reaction conditions. In addition to the HREELS measurements, we again use TPD of CO_2 in order to make a connection with our previous studies (8). Besides the additional evidence for the presence of carbonate intermediates, new information is obtained concerning a possible role for hydroxyl species on the oxidized Rh surface in the mechanism of CO oxidation on such a surface.

EXPERIMENTAL

The experiments reported here involved the use of a small high-pressure (≤1 atm) reactor directly coupled to an ultrahigh vacuum (UHV) surface-science apparatus. The Rh(111) single crystal, mounted on the sealed end of a reentrant tube connected to a retractable bellows, could be transferred in vacuum from the reactor to the UHV analysis chamber. The sample was heated

resistively by passing current through two 0.020-in. high-purity tungsten leads spot welded to the back of the crystal. Cooling was accomplished by partially filling the reentrant tube with liquid nitrogen.

The surface analysis apparatus consisted of a Vacuum Generators ADES 400 system with capabilities including a single-pass CMA for Auger electron spectroscopy (AES), a quadrupole mass spectrometer for temperature-programmed desorption (TPD), a low-energy electron monochromator and an angle-resolved energy analyzer for high-resolution electron energy loss spectroscopy. The HREELS measurements were taken with an incident beam energy of 2.14 eV and the spectrometer resolution, as measured by the energy width of the elastic peak (full width, half maximum, FWHM), was typically <130 cm^{-1}. Loss energies were measured relative to the peak energy corresponding to the elastically scattered electrons.

Rh single crystals commonly show significant levels of surface segregated C and B impurities as the principal problems to achieving clean surfaces (11). Carbon was removed by repeatedly dosing the sample surface (through a microchannel-plate doser) to 100 Langmuir (L) of O_2 (1 L = 10^{-6} Torr-sec) at a temperature of 1000 K followed by a vacuum anneal at 1100 K. The B impurity, which was detected in HREELS as a loss feature at 1405 cm^{-1} (assigned to the symmetric O–B stretch for surface BO_2 on Rh (11)) was removed by a 24-hr bake in 1-atm H_2 at 1200 K prior to mounting of the crystal on the UHV manipulator.

High-pressure (<1 Torr) reactions were performed by heating the Rh crystal for several minutes after charging the reactor with the premixed gases (CO and O_2). CO and O_2 were both ultrahigh purity grades and the CO was further purified prior to mixing by passing it through a liquid-nitrogen-cooled trap to prevent the introduction of volatile metal carbonyls into the reactor. It should be noted here that a direct comparison between the reaction conditions used in this
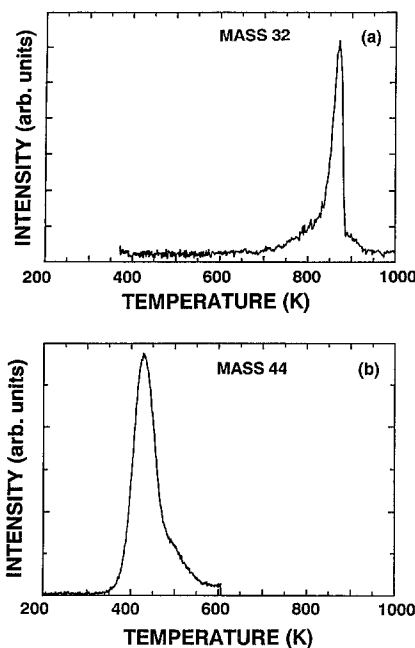
FIG. 1. TPD spectra obtained after adsorption of CO_2 onto a Rh(111) surface at 100 K preoxidized in 5 × 10^{-8} Torr of O_2 at 550 K for several minutes: (a) Mass 32; (b) mass 44.

observation (8) that the CO_2 TPD spectra were diagnostic of the various kinetic regimes.

RESULTS

CO_2 Adsorption on UHV-Oxidized Rh

As background experiments, CO_2 was adsorbed on clean and oxygen-covered Rh(111) prior to HREELS and TPD measurements. On clean Rh at 100 K, no evidence for CO_2 chemisorption or dissociative adsorption [$CO_2(g) \rightarrow CO(ad) + O(ad)$] was observed in either the vibrational or TPD spectra. However, when the Rh crystal was oxidized in the UHV chamber prior to CO_2 adsorption, a significant CO_2 desorption peak was observed in TPD (Fig. 1b) with a peak maximum near 430 K. (The oxidation was performed at 500–600 K in ≈ 5 × 10^{-8} Torr O_2 for several minutes, and a typical O_2 TPD from this surface is shown in Fig. 1a (13).) The HREELS spectrum for CO_2 adsorbed on the UHV oxidized surface is shown in Fig. 2b. For comparison, the HREELS spectrum obtained before CO_2 ad-

study and results described previously (8) was not possible due to the limitations of the present reactor design. For example, Fig. 3b was obtained after reaction at 500 K in 0.5 Torr of reactant gas pressure (CO/O_2 = 1), while similar CO_2 TPD spectra in Ref. (8) were found after reaction at 475 K in 508 Torr (CO/O_2 = 0.016). This apparent discrepancy can be explained by noting that the precise CO/O_2 partial pressure ratio at which the reaction mechanism appears to change, i.e., when the kinetics change from being first-order in oxygen pressure to negative-order (8), is very sensitive to temperature and total pressure (12). Because the present apparatus did not allow for the measurement of reaction rates, the CO_2 TPD spectra were used to indirectly indicate that the chosen reaction conditions (temperature and partial and total pressures) yielded the various regimes of reactivity described in Ref. (8). This assumption is based on the
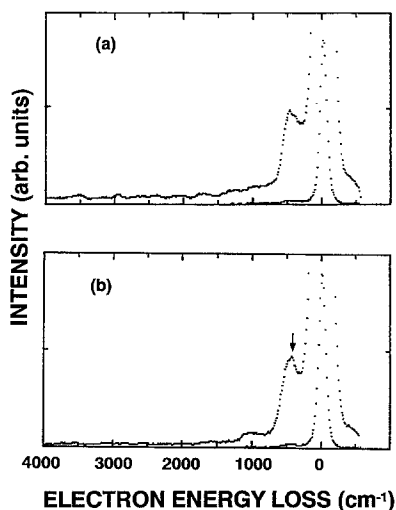

FIG. 2. HREEL spectra obtained at 100 K before (a) and after (b) CO_2 adsorption on a Rh(111) surface preoxidized in UHV, conditions given in Fig. 1 caption. (Figure 1b was obtained subsequent to the data in (b). Upon desorption of CO_2 (i.e., after the TPD experiment giving Fig. 1b), an HREEL spectrum identical to (a) was obtained.)

sorption is included in Fig. 2a. Clearly evident in Fig. 2b is the appearance of a broad feature (likely two or more unresolved peaks) near 1000 cm^{-1} which is *not* present in Fig. 2a. A closer comparison of the two spectra in Fig. 2 also reveals the development of a feature (at ≈ 400 cm^{-1}, see arrow in Fig. 2b) on the low-energy side of the metal–oxygen stretch (at ≈ 480 cm^{-1} (*13*)), *following* CO_2 adsorption.

Both spectral techniques demonstrate a significant increase in CO_2 bonding to the Rh surface upon oxidation. However, the CO_2 TPD peak temperature observed here (430 K) is approximately 100°C lower than that observed previously in TPD spectra obtained after high-pressure reaction (*8*) (see also Fig. 3 below). This, and differences in the HREEL spectra shown in Figs. 2b and 4c, suggest that *the species responsible for CO_2 desorption on UHV oxidized surfaces and those present following high-pressure reaction are distinctly different.* That is, the species giving rise to CO_2 desorption from UHV-oxidized surfaces may not be important to the understanding of the high-pressure kinetics since it is *not* observed after reactions under oxidizing conditions as we show below.

TPD and HREEL Spectra After High-Pressure Reaction

In order to make a connection with the previous kinetics study [8], CO_2 TPD and HREEL spectra were obtained after high-pressure reaction in CO and O_2 for various partial pressures of the reactants. Figures 3 and 4 show the results of these measurements. Under reducing conditions (CO/O_2 = 11/1), the nature of the surface subsequent to reaction is characterized by the spectra shown in Figs. 3a and 4a. Virtually no CO_2 is observed to desorb from the surface (3a), and the peaks in the vibrational spectrum (at ≈ 2000 and 430 cm^{-1}, Fig. 4a) can be readily assigned to adsorbed CO. In fact, the broad feature at 2000 cm^{-1} consists of two peaks (which were not resolved by our spectrometer) due to linear and bridged
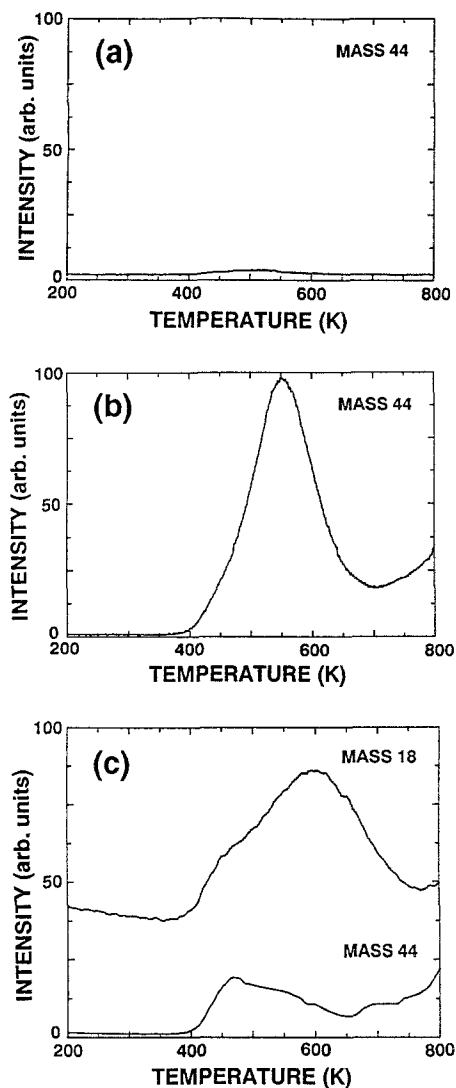

FIG. 3. CO_2 TPD spectra obtained subsequent to "high-pressure" reaction for 2 min in 0.5 Torr of a gas mixture of CO and O_2 at: (a) $T = 500$ K, P(CO)/P(O_2) = 11/1 (reducing conditions); (b) $T = 500$ K, P(CO)/P(O_2) = 1/1 (intermediate conditions); and (c) $T = 600$ K, P(CO)/P(O_2) = 1/32 (oxidizing conditions). Also shown is the H_2O (mass 18) desorption spectrum from this surface.

CO species present at saturation CO coverages on this Rh surface (*14*). Small quantities of chemisorbed oxygen could be missed in the HREEL spectra due to the similarity of the metal–oxygen and metal–carbon stretching frequencies (*11a*). However, the
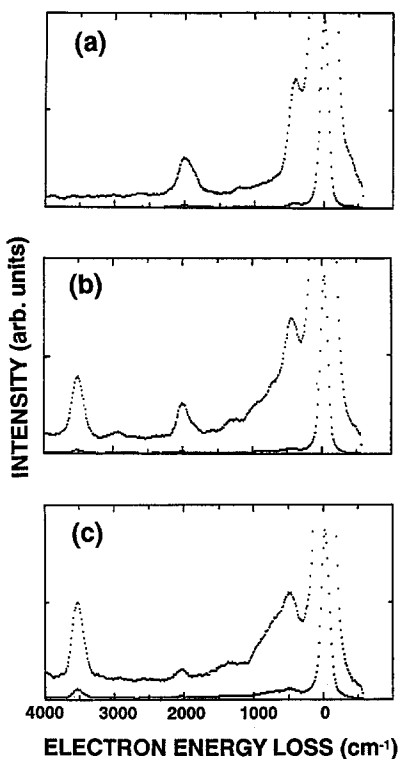
FIG. 4. HREEL spectra for high-pressure reaction under (a) reducing, (b) intermediate, and (c) oxidizing conditions. These spectra were obtained at 100 K prior to the corresponding TPD spectra shown in Fig. 3.

tures are apparent at $\approx$ 1400, 900, and 750 cm^{-1}. In addition, a small CO peak at 2000 cm^{-1}, the metal–oxygen (and metal–carbon?) band at $\approx$480 cm^{-1}, and a sharp feature at $\approx$3530 cm^{-1} are evident in the spectrum. We assign the 3530 cm^{-1} peak to the O–H stretch of a hydroxyl species on the oxidized Rh surface (15, 16). The δ(OH) mode for adsorbed hydroxyl is expected to be near 750 cm^{-1} and, thus, should be at least partially responsible for the HREELS scattering intensity observed in this spectral region. While this latter feature is usually the larger of the two for adsorbed hydroxyls on metal and semiconductor (Si) surfaces (15, 17), the reverse may be true on oxide surfaces (15). In addition, hydroxyls on metal surfaces are not stable much above room temperature in contrast to the temperatures of 450 K or more required to dehydroxylate oxide surfaces (16). As discussed below, the hydroxyl bands observed here are not removed until $\approx$600 K. Apparently, these –OH species recombine on the surface to produce water. This is evidenced by the fact that while no mass 2 (H_2) desorption was observed in TPD spectra from this surface, Fig. 3c demonstrates that a large H_2O (mass 18) desorption signal is obtained. Note that H_2O desorption occurs at a somewhat higher temperature than does CO_2.

Similar vibrational spectra are observed under intermediate conditions. Figure 4b was obtained subsequent to reaction at CO/ O_2 partial pressures of 1/1. The notable differences between the spectra shown in Figs. 4b and 4c are the larger contribution from adsorbed CO (at 2000 cm^{-1}) and smaller hydroxyl band (at 3530 cm^{-1}) in the spectrum 4b. Both indicate that the extent of oxidation of the surface is smaller under intermediate conditions as expected (8). The CO_2 TPD spectrum obtained subsequent to reaction at intermediate conditions, shown in Figure 3b, is identical to that observed previously (8). In both studies, a large, sharp CO_2 desorption feature, with a peak maximum of $\approx$560 K is observed.

To aid in the identification of the various

spectrum in Fig. 4a indicates that the surface is predominantly covered with adsorbed CO under these reaction conditions; a result in excellent agreement with previous studies (7, 8) (see discussion below).

At higher relative oxygen pressures, the post-reaction HREEL and TPD spectra are significantly different. After reaction under very oxidizing conditions (CO/O_2 = 1/32), the CO_2 TPD and HREEL spectra shown in Figs. 3c and 4c were obtained. A broad CO_2 TPD peak is observed with a desorption peak temperature considerably higher than that shown in Fig. 1a for CO_2 adsorbed on UHV oxidized Rh. However, the TPD profile in Fig. 3c is virtually identical to that obtained previously in a study of the reaction kinetics over deactivated Rh (8). In the vibrational spectrum (Fig. 4c), broad fea-
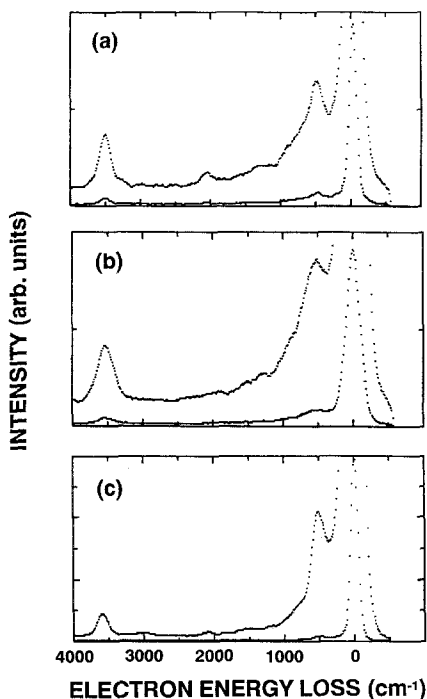
FIG. 5. HREEL spectra showing the effect of annealing after high-pressure reaction under oxidizing conditions. (a) Before annealing (see Fig. 3c caption for surface preparation conditions. (b) After flashing the sample to 450 K and recooling to ≈100 K. (c) After annealing a separately prepared sample (see text) to 525 K for 30 sec.

HREELS features, Fig. 5 shows the effect on the vibrational spectra of annealing surfaces obtained after reaction under oxidizing conditions. The annealing temperatures (450 and 525 K) were chosen to be just below and in the middle of the CO_2 desorption profile shown in Fig. 3c. In addition, H_2O desorption from the recombination of the surface hydroxyl groups was found to occur at somewhat higher temperatures (peak maximum ≈600 K, Fig. 3c). After a flash anneal to 450 K, the HREEL spectrum shown in Fig. 5b was obtained. The removal of the small amount of adsorbed CO was evidenced by the absence of the ≈2000-cm^{-1} peak in this spectrum. The intensity of the remaining features was not altered significantly. However, all bands (including the elastic peak, which now shows a FWHM of

≈220 cm^{-1}) were broadened significantly, presumably due to a disordering of the oxide surface. Unfortunately, further heating of this sample continued to degrade the spectral resolution making it difficult to identify the loss of features on the trailing edge (500 ≤ ν ≤ 1500 cm^{-1}) of the Rh–O stretching mode of the oxide at ≈500 cm^{-1}. However, in a separate experiment starting with a surface which gave a spectrum very similar to that shown in Fig. 5a, annealing to 525 K for 30 sec gave rise to the spectrum shown in Fig. 5c. (In this case, the spectral resolution of ≈130 cm^{-1} was maintained for reasons we do not understand at the present time (18).) A comparison between Figs. 5a and 5c reveals that there is no loss intensity above 1000 cm^{-1} in Fig. 5c, and that the broad, structured feature between 500 and 1000 cm^{-1} in Fig. 5a appears to be a single and significantly less intense band after annealing (Fig. 5c). Now, the only identifiable spectral features are those from adsorbed hydroxyl on the oxide surface at 3530 and ≈750 cm^{-1}, and the Rh–O stretching peak of the oxide at 480 cm^{-1}.

DISCUSSION

In previous publications, reactivity of a Rh single crystal for CO oxidation under two extreme sets of conditions was described (7, 8). These can be usefully defined as reducing, where the CO/O_2 partial pressure ratio is greater than 1, and highly oxidizing with CO/O_2 ratios much less than 1. In the first case (≡case 3 reaction in Ref. (8)), the formation of CO_2 was shown to proceed by reaction on the Rh surface between chemisorbed CO molecules and O atoms. Since the surface under these conditions is predominantly covered by CO (Fig. 6a), desorption of CO is required to vacate the sites needed for the rate-limiting dissociative adsorption of O_2. This regime of reactivity is characterized by kinetics that are first-order in O_2 pressure, negative first-order in CO, and which yield an apparent activation energy (≈25 kcal/mol) very nearly equal to
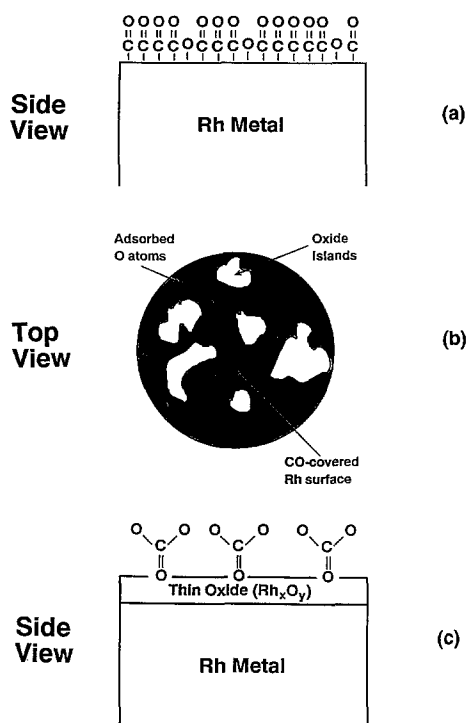
FIG. 6. Models of the surface of Rh under (a) reducing, (b) intermediate, and (c) oxidizing reaction conditions corresponding to the conditions used to obtain the TPD and HREEL spectra in Figs. 3 and 4, respectively. The structure of a carbonate species schematically drawn in (c) is one of many possible coordination geometries for such a species.

the desorption energy of CO from Rh at saturation coverages (7).

In contrast to the above behavior, reaction under highly oxidizing conditions, which proceeds at much slower rates ($\equiv$case 1 reaction (8)), occurs with no dependence (zero-order) on the partial pressure of either reactant and with a significantly higher activation energy (29 kcal/mol) (8). A mechanism consistent with these results, involving the rate-limited decomposition of a carbonate-species on oxidized Rh (Fig. 6c), has been proposed (8). CO and CO_2 TPD measurements obtained after reaction under the above two reaction conditions provide additional support for the two proposed mechanisms. For example, post-reaction TPD following high-pressure reaction under

reducing conditions consisted of large quantities of CO (8) and virtually no CO_2 (Fig. 3a). However, Fig. 3c shows significant CO_2 desorption at unexpectedly high temperatures (>500 K) following highly oxidizing reaction. No CO was found to desorb from this latter surface (8).

Interestingly, reaction kinetics in intermediate regimes (mildly oxidizing, $\equiv$case 2 reaction (8)) appeared to be a superposition of the two extremes (8). It has been suggested (8) that oxide on the Rh surface nucleated in islands as the oxygen pressure was increased which allowed for the operation of both CO_2 production mechanisms simultaneously. Figure 6b schematically illustrates this situation. Reference (8) proposes that the surface reaction between chemisorbed CO and atomically adsorbed O takes place on the unoxidized regions of the surface. Likewise, carbonate-decomposition-limited reaction occurs on the islands of Rh-oxide. Of course, the oxide islands will eventually coalesce across the entire surface as the oxygen partial pressure is further increased, yielding the activity associated with highly oxidizing conditions (Fig. 6c).

The present vibrational spectroscopic (HREELS) measurements provide additional support for the proposed mechanisms described above. Specifically, vibrational bands in the spectra can be assigned to a carbonate-like species on the surface on the basis of previous assignments for such a species (19, 20). TPD has been used to provide a connection with the previous kinetics study since the CO_2 TPD spectra are diagnostic of the various reaction regimes (8). Unexpectedly, the current HREELS and TPD data suggest an important role for hydroxyl species, present on oxidized Rh during high-pressure reaction, in the stabilization of the carbonate species. These results have important implications for the catalytic oxidation of CO under oxidizing conditions since the CO_2 formation rate is apparently rate-limited by the decomposition of such a species (8). Before discussing the results ob-

tained after high-pressure reaction, we first identify the nature of CO_2 adsorption on a Rh surface oxidized in UHV.

The HREEL spectrum from a UHV-oxidized Rh surface is shown in Fig. 2a. It consists of a single vibrational band at ≈480 cm^{-1} which can be readily assigned to the metal–oxygen stretching motion (13). This spectrum is considerably simpler than that obtained by Dubois (11a) by heating Rh(100) to 1200 K in 5×10^{-7} Torr of O_2. In fact, we obtain a spectrum (Fig. 2b) virtually identical to that reported by Dubois (Fig. 3 in Ref. (11a)) by adsorbing CO_2 onto the oxidized Rh surface at 100 K. This implies that CO_2 (or CO) may have been a contaminant in the O_2 gas used to oxidize Rh in the previous study (11a). The HREEL spectrum in Fig. 2b consists of three features; two poorly resolved peaks at ≈480 and 400 cm^{-1}, and a broad peak at ≈1000 cm^{-1}. A significant quantity of CO_2 was observed to desorb from this surface as shown in the TPD spectrum obtained subsequent to the HREELS data (Fig. 1b). A recent study of CO_2 adsorption on Ni(110) (20) made assignments of HREELS features at 390, 730, and 1110 cm^{-1} to the molecule–substrate vibration, and the bending and stretching mode of a bent CO_2-anion, respectively. The bonding geometry for the species was uncertain with either a bidentate structure (metal coordination to both oxygen atoms) or bonding through the carbon atom to the metal proposed (20), both structures having C_{2v} symmetry. On this basis, we tentatively assign the losses at 1000 cm^{-1} (broad and possibly including a band at lower frequency) and 400 cm^{-1} to a CO_2^- ion adsorbed on an oxidized Rh site, possibly Rh^+. Despite the tentative nature of this assignment, the main point here concerns the very different spectra obtained subsequent to high-pressure reaction (Figs. 3 and 4) which we discuss next.

The lack of CO_2 desorption in TPD (Fig. 3a), and the large CO features in the HREEL spectra (at ≈450 cm^{-1}, M–C stretch, and 2000 cm^{-1}, C–O stretch, Fig. 4a) are consis-

tent with the previously proposed mechanism for reaction under reducing conditions as described above. Again in this case, CO_2 is formed by the reaction between chemisorbed CO molecules and O atoms, both bound to the Rh metal surface.

For reaction under highly oxidizing conditions, the CO_2 TPD and HREEL spectra obtained subsequent to reaction are shown in Figs. 3c and 4c, respectively. In this case, significant CO_2 desorption is observed, and broad vibrational features at ≈3530, 1400, 900, 750, and 500 cm^{-1} are present in the HREEL spectrum. As discussed above, the 3530 and (at least a portion of) the 750 cm^{-1} peaks can be assigned to hydroxyl species on the oxidized surface, and the 500 cm^{-1} band is due to the Rh–O stretching motion of the oxide. Previously, Stuve et al. have attributed peaks at 1360, 1050, and 830 cm^{-1} to a carbonate species (CO_3) on Ag(110) (19). Similar features at 1565, 1310, 1013, and 828 cm^{-1} are analogously assigned to CO_3 on Ni(110) (20). On this basis, we conclude that the broad features near 1400, 900, and 750 cm^{-1} arise from a CO_3 species on the hydroxylated oxide surface present after reaction under oxidizing conditions (21). Such an assignment is supported by the results shown in Fig. 5 which demonstrate that these features (except perhaps the 750 cm^{-1} band) are absent from the spectrum (5c) obtained after an anneal in which most if not all of the CO_2 would have been removed. This spectral evidence for adsorbed CO_3 lends strong support to the previously proposed mechanism for CO_2 formation on Rh under highly oxidizing conditions.

The CO_3 species is remarkably stable on the surface as evidenced by the CO_2 TPD spectrum in Fig. 3c. By comparison of the CO_2 TPD spectra shown in Figs. 1b and 3b–3c, it is clear that the CO_2 desorption temperature is significantly higher on the surface oxidized at high pressures. That is, the decomposition of the carbonate species takes place at higher temperatures than that for the desorption of the species obtained after CO_2 adsorption on UHV-oxidized Rh

(tentatively assigned above as a bent-CO_2^- anion). Analysis of the carbonate CO_2 TPD spectra (Fig. 3b) using a simple Redhead procedure (22) yields a CO_2 desorption activation energy of about 31 kcal/mol. It is tempting to favorably compare this number to that obtained for steady-state CO_2 formation under oxidizing conditions (29 kcal/mol (8)) as further evidence for our proposed reaction mechanism. This is so because the energetics of the rate-limiting step should dominate the overall reaction kinetics. In the proposed mechanism, CO_3 decomposition limits the reaction rate under oxidizing conditions, which is consistent with the activation energy for CO_2 desorption (presumably limited by CO_3 decomposition) being very similar to the measured steady-state activation energy. However, such a simple analysis of TPD spectra can often yield erroneous desorption activation energies (22). (Unfortunately, our data is not suitable for a more complicated and precise analysis.)

A possible explanation of the difference in the nature of CO_2 adsorption on the UHV and high-pressure oxidized surfaces is the marked difference in the state of the surface oxide formed in the two experiments. Importantly, the Rh surface exposed to high-pressure reaction under oxidizing conditions leads not only to oxidation of the surface but to hydroxylation of the surface oxide as well. This is clearly evident by the strong band in Figs. 4b and 4c at ≈ 3530 cm^{-1}. This surface species is likely formed by impurity H_2 and/or H_2O which are both very difficult to remove from the high-pressure reactor. (Hydrocarbon impurities were also evident in the spectra obtained after reaction during the early stages of this work, although they were successfully suppressed by baking the reactor for several days.) On the basis of this data, it is not possible to define precisely the role of the hydroxyl species in the reaction mechanism. However, since we only observed carbonate species on oxidized surfaces which are hydroxylated, it may well be that hydroxyls directly contribute to the stabilization of carbonate.

For example, nearby hydrogen atoms in the hydroxyl species could hydrogen bond to the carbonate oxygen atoms. Conversely, hydroxylation may generate sites for carbonate formation on the oxidized Rh surface. In any case, the present results support the mechanistic arguments concerning the importance of a carbonate intermediate for CO oxidation under oxidizing conditions on Rh made previously (8) on the basis of kinetic studies. Such a mechanism may well be operative in a working automotive exhaust catalyst since conditions cycle between oxidizing and reducing. Further, such catalysts operate at much higher temperatures (900 K or more) than those used here (≤ 600 K). Thus, real catalysts may well be more likely to oxidize, even at higher CO/O_2 ratios (12) than needed in the present study to generate reactivity associated with oxidized Rh surfaces.

SUMMARY AND CONCLUSIONS

Vibrational spectroscopic and TPD data have been used to provide further evidence for the existence of a stable carbonate species on oxidized Rh surfaces. Such a species had previously been implicated (8) as an important intermediate in the oxidation of CO over Rh under highly oxidizing conditions. In fact, the mechanism of reaction under such conditions appears to involve the rate-limited decomposition of carbonate. However, new information obtained in the present study suggests that surface hydroxyl species on oxidized Rh may play an important role in the formation and/or stabilization of the carbonate species. In particular, carbonate was not observed on oxide surfaces where surface hydroxyls were absent. On such surfaces, an adsorbed CO_2 species (tentatively assigned to a bent-CO_2^- anion) is formed by adsorption of CO_2, probably on Rh$^+$ sites. In this regard, it is interesting to note that recent molecular orbital calculations for CO_2 adsorption on ZnO (23) conclude that bent CO_2^- binds to Zn$^+$ sites, while a carbonate species is formed on anionic surface oxygen sites. As a caveat, it

should be noted that the presence or absence of hydroxyls may not be the only difference between oxide surfaces formed in UHV or at high pressures. Thus, it is possible that an oxide surface structure unique to high-pressure oxidation leads to the formation of sites for carbonate formation. This point is underscored by the fact that oxide structures thermally grown on Rh(111) are very sensitive to oxygen pressure and surface temperature (24). Finally as with any kinetics study, while consistent, the results reported here and elsewhere (8) cannot unambiguously confirm the proposed mechanism.

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tably higher temperatures), this effect may have important practical implications. There is another possible explanation for the different CO/O_2 ratios needed to give "intermediate reaction conditions" in this and the previous study (8). This concerns the possible role of impurity H_2O in changing the gas mixture to be more oxidizing. However, on the basis of the similarity of the CO_2 TPD data in this and the previous study (8), it seems likely that impurity H_2O plays a role in both sets of experiments. Thus, we prefer the explanation given in the experimental section and elaborated on above.

13. A direct comparison between the present HREEL and O_2 TPD spectra for UHV-oxidized Rh with published results for chemisorbed oxygen on Rh(111) (Ref (11b) and Root, T. W., Schmidt, L. D., and Fisher, G. B., Surf. Sci. 134, 30 (1983), respectively) shows interesting differences. This is noted to possibly explain differing chemical properties of UHV-oxidized Rh surfaces and Rh(111) covered with chemisorbed oxygen. However, a detailed comparison is beyond the scope of this paper.
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18. In fact, other attempts were made to reproduce this experiment. In all cases except for the sample shown in Fig. 5c, the resolution was significantly degraded upon annealing. However, there is very qualitative agreement between these experiments and Fig. 5c.
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