Time-Resolved Infrared Emission Studies of CO_2 Formed by Catalytic Oxidation of CO on Pt and Pd Surfaces

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Time-resolved FTIR emission spectroscopy was used to detect vibrationally excited gas phase CO_2 formed by the catalytic oxidation of CO on Pt and Pd surfaces. A continuous molecular beam of O_2 and a pulsed flux of CO (200 μs FWHM) were supplied to the surface at 900 K, and the infrared emission of the CO_2 product was analyzed with 30 μs time resolution to study the dependence of the internal energy on surface oxygen coverage. Analysis of the band width and centroid of the time-resolved infrared spectra (4 cm^{-1} resolution) allows an estimation of the rotational and average vibrational temperatures (T_R and T_V) of the CO_2 molecules. At a low CO nozzle pressure on a Pt surface, the infrared signal intensity almost parallels the time dependent CO flux to the surface with relatively small changes in the infrared spectra. The analysis showed that both T_V and T_R decrease with decreasing surface oxygen coverage and that the change in T_R is more significant than that in T_V. At a high CO nozzle pressure, the reaction can be shut off as the oxygen on the Pt surface is depleted (CO titration behavior). These infrared spectra showed large changes in T_V (from ca. 1700 K to 700 K). In contrast, on a Pd surface no drastic change in T_V was observed even at high CO pressure, but T_V was decreased slightly with decreasing surface oxygen coverage. The T_V values (around 2000 K) on Pd are much higher than on Pt.

The oxidation of CO by O_2 to CO_2 on Pt and Pd surfaces is one of the most-studied surface catalyzed reactions and many aspects of it are well understood.[1] Reaction occurs by a Langmuir–Hinshelwood mechanism between chemisorbed molecular CO and atomic oxygen. However, our interest is not only in the kinetics of this reaction, but also in the structure and dynamics of the activated CO_2 complex.[2] Recently there has emerged some information on the internal energy states of product CO_2 molecules obtained by measurements of their infrared radiation.[3,4] These experiments provide valuable insight into the dynamics of CO oxidation on the metal surface. In our experiments using a steady-state mixed CO–O_2 molecular beam reacting on a Pt foil, we have been able to determine energy distributions in both rotational and vibrational modes by means of Fourier transform infrared emission spectroscopy.[4] We have observed large changes in the vibrational and rotational energy states as a function of surface temperature. At the lower surface temperatures the surface coverage of CO compared to oxygen was relatively high, whereas at the higher surface temperature it was relatively low. Therefore, there is a strong suggestion that the changes in the internal states of CO_2 are due to changes in surface coverages. However, this approach may not allow unequivocal separation of thermal effects on the surface from isothermal coverage effects. On the other hand, it is possible to observe isothermal coverage effects on the dynamics of the activated CO_2 complex by means of time-resolved infrared emission spectroscopy.[5,6] In these experiments a steady flux of O_2 to the suface is maintained while a pulsed nozzle provided a time-dependent flux of CO onto the surface. Such studies are valuable because they permit us to examine the dependence of internal energy on surface oxygen coverage, an important consideration in view of the strong suggestion of the surface coverage effects. In this paper, we report the results of time-resolved infrared emission measurements of CO_2 formed by CO oxidation on Pt and Pd surfaces. Both vibrational and rotational states of the product CO_2 are monitored with time (i.e., with surface oxygen coverage) at different nozzle pressure conditions.

Experimental

The time-resolved infrared emission measurements were performed in the vacuum system described previously.[4] Figure 1 shows the schematic representation of the experimental procedure. A steady-state (continuous) free jet of O_2 was incident on a Pt or Pd foil (Alfa products, 0.025 mm thick) through a stainless steel tube with a small sonic orifice of diameter 150 μm, and a second pulsed beam of CO was simultaneously directed onto the foil. The CO pulses were 200 μs halfwidth at half maximum height with a 2 ms pause between pulses. The 2 ms pause is long enough such that the surface coverage of oxygen could recover to its steady-state value at the given reaction temperature. The number of CO molecules in the pulse could be easily varied by changing the stagnation pressure (P_N(CO)) in the pulsed nozzle source with an orifice of 0.5 mm diameter. At a low pressure the surface coverage of oxygen did not vary much from its steady state value while at a high CO pressure we could effectively perform a titration of the surface oxygen as the CO pulse passed over the surface.[6] Unless otherwise stated, the steady-state nozzle to surface distance (L) was 2.0 cm, and the pulsed-nozzle to surface distance was 2.7 cm. Typically the flux of the steady-state beam of O_2 was about 2×10^{18} molecules/cm^2 s when the

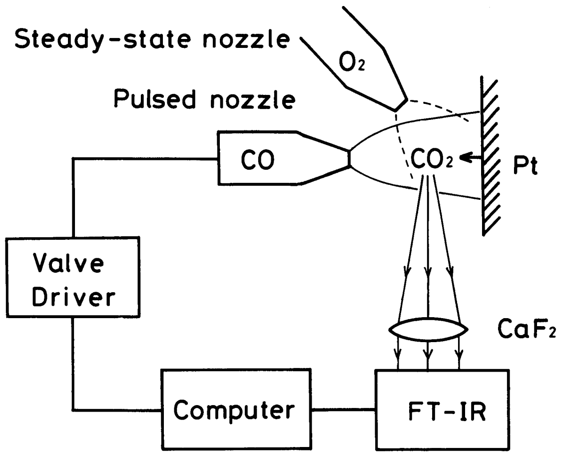

Fig. 1. Schematic view of molecular beam apparatus for the detection of time-resolved infrared emission of the product CO_2 formed by the CO oxidation reaction on metal surface.

stagnation pressure ($P_N(O_2)$) in the O_2 nozzle was 480 Torr, while the CO flux was about 1×10^{19} molecules/cm^2 s at the peak intensity of the pulse when the P_N(CO) was 760 Torr (1 Torr= 133.322 Pa).

The infrared emission from the product CO_2 desorbed from the surface was analyzed with an FTIR spectrometer (Nicolet 7199). The spectrometer was purged by boil-off N_2 and equipped with an InSb detector operated at 77 K. The radiation was collected with a 10 cm focal length CaF_2 lens, as shown in Fig. 1. The time-resolved spectroscopy is accomplished using the FTIR spectrometer and a computer algorithm which allows efficient data collection by varying the time of initiating the beginning of the repetitive event (pulse of CO) and the beginning of the mirror movement in the interferometer.[7] The spectrometer software triggers the nozzle pulse and starts the interferometer scan after a specified time delay which is successively increased. After data points have been collected at all combinations of time intervals into the repetitive event and the mirror position, the data is computer sorted point by point to construct time-resolved interferograms. In our experiments, a total of 65 emission spectra of CO_2 were collected at 30 µs intervals across a CO pulse. The spectral resolution used was 4 cm^{-1}.

In low resolution (4 cm^{-1}) spectra, no individual vibration–rotation lines are resolved. However, from the shape of the envelope of the spectra, it is possible to obtain values that are good approximations for the rotational temperature (T_R) and the average vibrational temperature (T_V).[6,8] From the steady-state results at high resolution (0.06 cm^{-1}), we were able to show that the energy distribution in each internal mode was approximately Boltzmann and could be characterized fairly well by a single temperature for each mode (T_R, T_{SS}, T_B, T_{AS}), where subscripts respectively indicate rotation, symmetric strech, bending, and antisymmetric strech. We were able to compute a spectral envelope that could be compared with low resolution experimental results. Upon analyzing the results we found that the full width at half height of the envelope was a good measure of T_R, whereas the wavenumber location of the centroid was a good measure of T_V.[6,8]

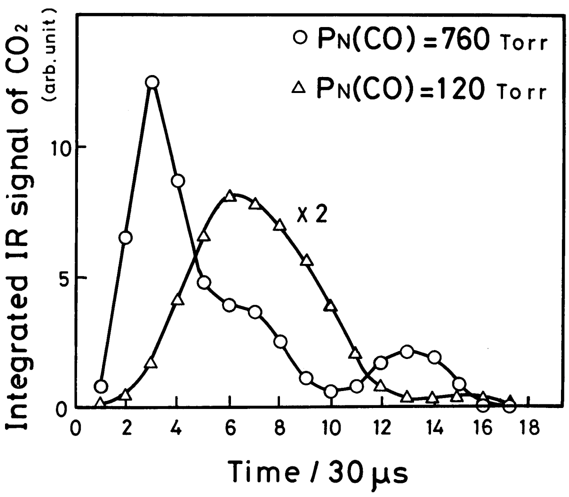

Fig. 2. Integrated infrared emission versus time for CO_2 formed by CO oxidation on Pt at 900 K. The steady-state O_2 flux was kept constant ($P_N(O_2)$= 450 Torr), and the pulsed CO nozzle pressure (P_N(CO)) was varied. L=2.8 cm.

Results

1. CO-Pulsed Experiments on Pt. In Fig. 2, the total infrared signal from CO_2 formed by CO oxidation on Pt at 900 K is plotted as a function of time after the CO pulse begins. At the lower CO pressure behind the pulsed nozzle (P_N(CO)=120 Torr), the reaction rate scales linearly with CO pressure, i.e., we are in the regime of relatively high oxygen coverage where the reaction is first order in CO.[6] Under this condition, the CO_2 emission intensity almost matches the CO flux intensity in the pulse.[5] At the higher CO pressure (P_N(CO)=760 Torr), the integrated emission rises rapidly to a maximum rate (at around 90 µs), then decays as the surface becomes depleted of adsorbed oxygen (the CO titration of the surface oxygen). The emission intensity begins to increase as oxygen adsorption catches up to oxygen consumption by reaction, and finally decays again as the surface becomes depleted in CO at the end of the pulse. Figure 3 shows an example of a sequence of time-resolved spectra obtained on Pt at 900 K with the high CO flux. Because of low resolution spectra, no individual lines are resolved. However, analysis of the band width and centroid allows an estimation of the rotational and average vibrational temperatures (T_R and T_V).[6,8] Figure 4 shows the variation of T_V with time determined from the experiments shown in Fig. 2. At the lower CO pressure (P_N(CO)=120 Torr), T_V stays almost constant but decreases with time very slightly. At the higher CO pressure (P_N(CO)=760 Torr), however, T_V is changed with time dramatically as shown in Fig. 4. During the first 240 µs there is an intermediate dip, and then T_V drops precipitously as the last of the oxygen is consumed (at 330 µs). At this point T_V apparently falls below the surface temperature (T_S=900 K). Then it starts rising as

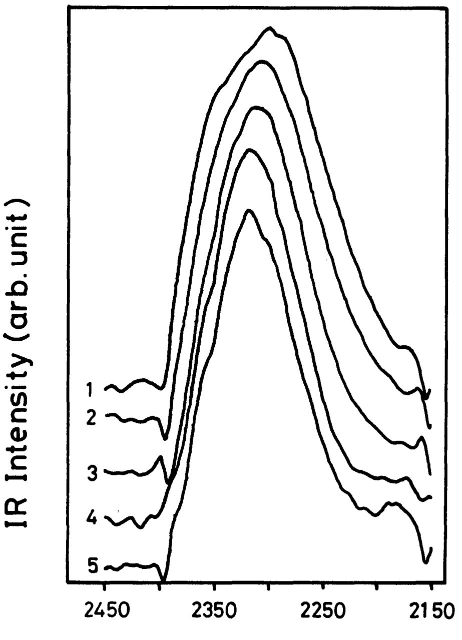

Fig. 3. Time-resolved infrared spectra of CO_2 formed by CO oxidation on Pt at 900 K. The spectra are separated by 30 μs intervals starting with spectrum 1.

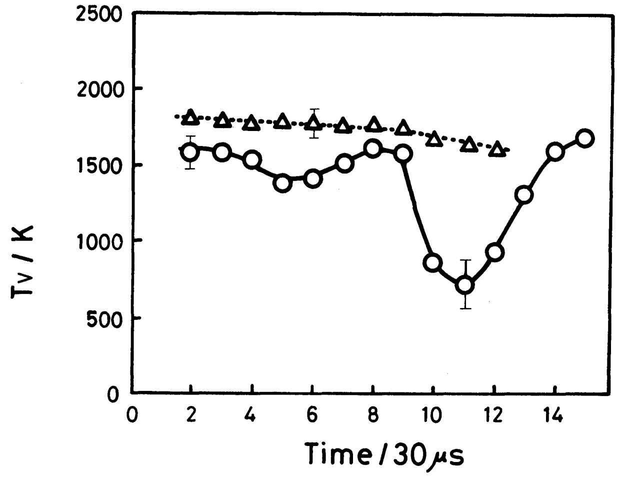

Fig. 4. The variation of the vibrational temperature (T_V) with time. Key as Fig. 2; ○, P_N(CO)=760 Torr; △, P_N(CO)=120 Torr.

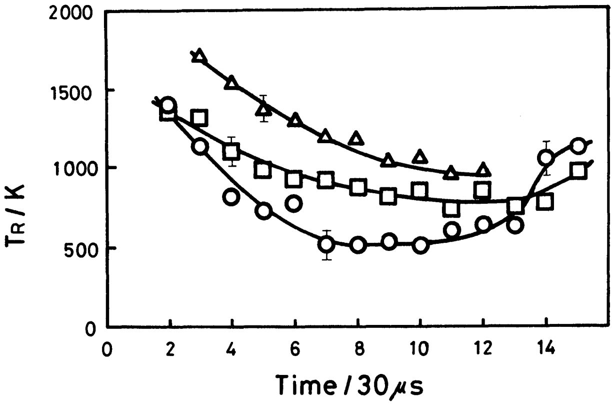

Fig. 5. The variation of the rotational temperature (T_R) with time. Key as Fig. 2; ○, P_N(CO)=760 Torr; △, P_N(CO)=120 Torr. The data for the N_2+CO mixture gas are also plotted: □, P_N(N_2+CO)=760 Torr (the CO partial pressure=120 Torr).

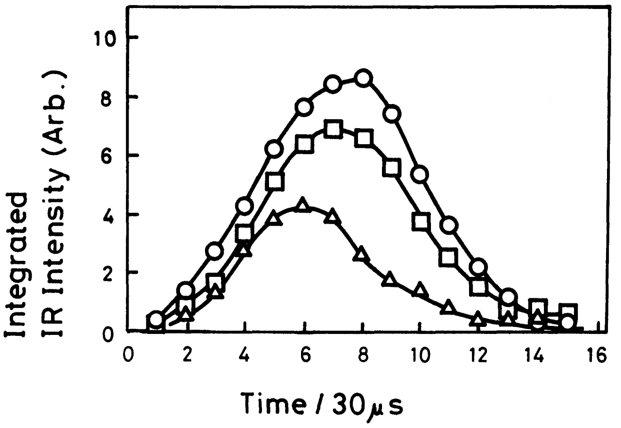

Fig. 6. Integrated infrared emission versus time for CO_2 formed by CO oxidation on Pt at 900 K. The pulsed CO nozzle pressure was kept constant (P_N(CO)=120 Torr), and the steady-state O_2 flux was varied: ○, $P_N(O_2)$=480 Torr; □, $P_N(O_2)$=190 Torr; △, $P_N(O_2)$=50 Torr.

the oxygen is replaced. Figure 5 shows the variation of T_R with time at the different CO pulse conditions. At the lower CO pressure (P_N(CO)=120 Torr), T_R decreases with time monotonously. At the higher CO pressure (P_N(CO)=760 Torr), T_R shows much greater decrease from an initial value of about 1400 K to a minimum of around 500 K when the oxygen is consumed. When the N_2+CO mixture gas (the total pressure of 760 Torr, the CO partial pressure of 120 Torr) was used, T_R became lower than the data at the lower pressure (P_N(CO)=120 Torr). This result suggests that the rotationally "cooling" occurs as the pulsed nozzle pressure is increased to 760 Torr, as will be discussed later.

Figure 6 shows the integrated infrared signals versus time when the amount of steady-state O_2 flux was varied and the pulsed CO nozzle pressure was kept constant at the low pressure (P_N(CO)=120 Torr). The CO_2 emission intesity versus time matches the CO flux intensity in the pulse when the steady-state O_2 pressure is relatively high ($P_N(O_2)$=480 Torr), but it decays earlier, as the O_2 pressure is decreased (i.e., surface oxygen coverage is decreased with time). Figures 7 and 8 show the variation of T_V and T_R, respectively, with time as determined from the experiments in Fig. 6. Both T_V and T_R decrease with time (i.e., with decreasing surface oxygen coverage), but the change in T_R is much more drastic than that in T_V. The effect is more pronounced as the amount of the O_2 flux is decreased.

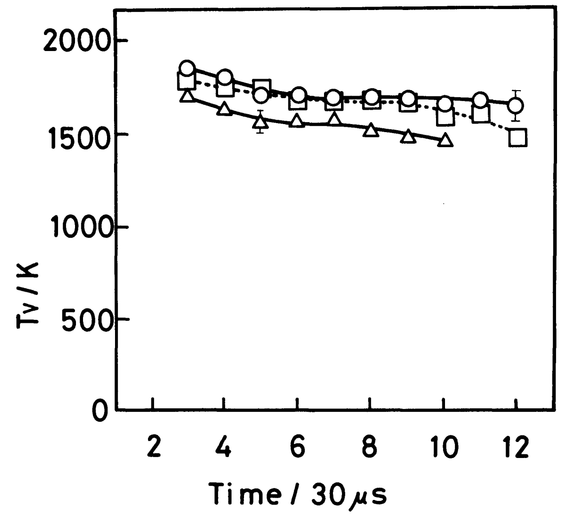

Fig. 7. The variation of the vibrational temperature (T_V) with time: Key as Fig. 6.

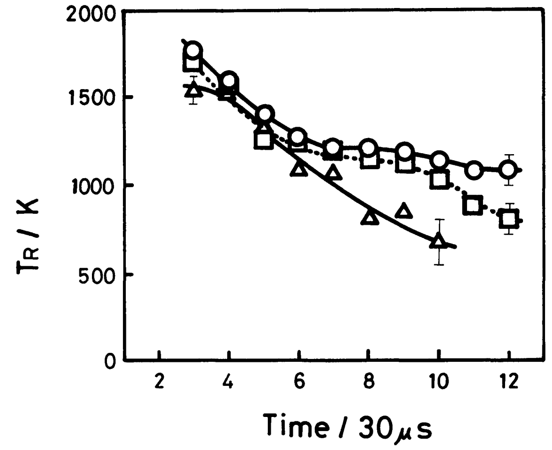

Fig. 8. The variation of the rotational temperature (T_R) with time: Key as Fig. 6.

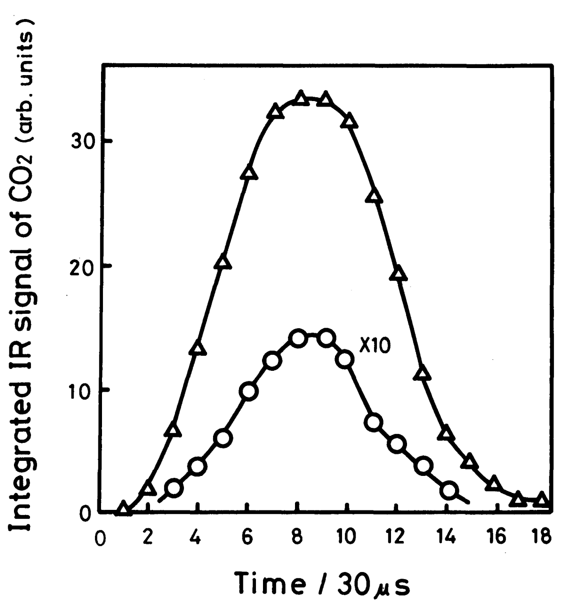

Fig. 9. Integrated infrared emission versus time for CO_2 formed by CO oxidation on Pd at 900 K. The steady-state O_2 flux was kept constant ($P_N(O_2)$= 480 Torr), and the pulsed CO nozzle pressure was varied: △, P_N(CO)=760 Torr; ○, P_N(CO)=120 Torr.

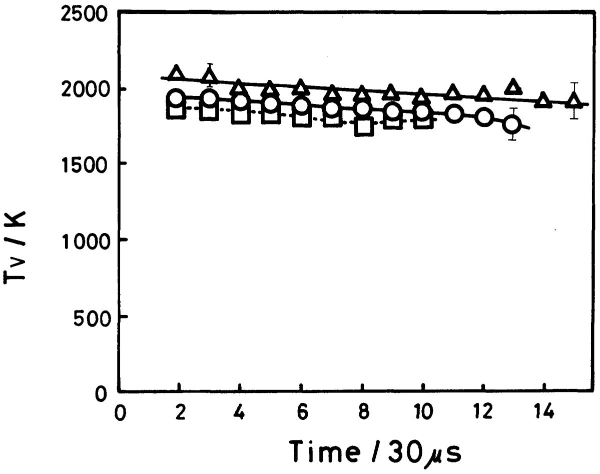

Fig. 10. The variation of the vibrational temperature (T_V) with time for CO_2 formed by CO oxidation on Pd at 900 K. The pulsed CO nozzle pressure was kept constant (P_N(CO)=760 Torr), and the steady-state O_2 flux was varied: △, $P_N(O_2)$=480 Torr; ○, $P_N(O_2)$= 90 Torr; □, $P_N(O_2)$=20 Torr.

2. CO-Pulsed Experiments on Pd. Figure 9 shows the integrated infrared signals versus time for CO_2 formed by CO oxidation on Pd at 900 K. The behavior on Pd is very different from that of Pt (see Fig. 2). Even at the high CO pressure (P_N(CO)=760 Torr), the change in the CO_2 emission intensity appears to match the change in the CO flux intensity with time, and the titration behavior was not observed. At the low CO pressure (P_N(CO)=120 Torr), the infrared intensity is diminished significantly. Figure 10 shows the variation of T_V with time at the high CO pressure condition, where the amount of the steady-state O_2 flux was changed. No big change in T_V is observed on Pd, which is in stark contrast with the case of Pt (see Fig. 4). T_V decreases slightly with time, and the effect is not very pronounced as the amount of the O_2 flux is decreased. On the other hand, T_R showed much greater decrease with time at the high CO pressure conditions. The behavior is, similar to the case of Pt at the high CO pressure condition, due to the rotationally "cooling" to which we will refer later. For the data on Pd at the low CO pressure, no detailed analysis of T_V and T_R was performed because of the low intensity of the infrared signals, but an average T_V value was estimated to be about 2000 K from an analysis of the sums of several consecutive time-resolved spectra.

Discussion

1. Effect of Gas Phase Collisions on T_R. When a high CO flux is used, the rotational relaxation of the CO_2 molecules may take place by gas phase collision between departing (CO_2) and arriving (CO) molecules that occur with increasing frequency as the CO flux is increased.[4] Such collisions are "cooling" in this case because the arriving CO molecules are from a source at only 300 K. This effect was confirmed by the experiment using the N_2+CO mixture gas, as shown in Fig. 5. When the total pressure (N_2+CO) is increased to 760 Torr and the CO partial pressure is kept constant (120 Torr), T_R (indicated by the symbol □) is much lower than the data (the symbol △) at the lower total pressure (P_N(CO)=120 Torr). An experiment using the Ar+CO mixture gas showed similar behavior. When the total flux is constant (760 Torr) but the CO pressure is increased, the decrease in T_R (the symbol ○) became more significant. This result shows that there may also be an effect of the oxygen coverage on T_R: The greater the CO flux, the more significant the change in T_R, although these observations are distorted by the gas phase collisions in the case of the high pressure (P_N(CO)=760 Torr). These experiments may alternatively be the result of more efficient energy exchange of CO–CO_2 collisions relative to N_2–CO_2 collisions. We can decrease the collisional distortion by lowering P_N(CO). In practice, there was no measurable effect on T_R at the low nozzle pressure (120 Torr), as proved by an N_2-pulsed experiment.[4]

There is little effect of the gas phase collisions on T_V in the product CO_2 because the cross section for exchanging vibrational energy is much smaller than that for changing rotational energy.[9] In practice, no effect of collisions on T_V were observable even at the high nozzle pressure (760 Torr).[4]

2. Effect of Surface Oxygen Coverage on T_V and T_R. The effect of surface oxygen coverage on Pt under nearly collision free conditions can be investigated at the low CO pressure conditions (P_N(CO)=120 Torr) in Figs. 6, 7, and 8. At the beginning of the CO pulse, the T_V values in Fig. 7 were in good agreement with the average vibrational temperature of about 1700 K determined for the steady-state reaction on Pt at the same surface temperature (T_S=900 K).[4] T_V decreases slightly with time (i.e., surface oxygen coverage). T_V is lower when the steady-state O_2 pressure is decreased. This trend is in contrast to the results by Brown and Bernasek who reported a decrease in the vibrational temperature as the oxygen pressure is increased.[3] In their experiments using the gas flow technique, the product CO_2 molecules suffer multiple collisions with the surface and other gas phase species prior to detection.[2]

The decrease in T_R is much more drastic than that in T_V, as shown in Fig. 8. At the higher steady-state O_2 pressure condition, T_R went from a maximum value of 1800 K at high oxygen coverage to a minimum value of 1100 K at low oxygen coverage. The coverage effect is more pronounced as the steady-state O_2 pressure is decreased. This is not due to the effect of the gas phase collisions since T_R drops more significantly as the O_2 flux is decreased.

3. Different Behavior of T_V on Pt and Pd. As the CO nozzle pressure is increased (P_N(CO)=760 Torr), the resulting increase in CO arrival rate increases the rate of oxygen consumption so that the depletion of surface oxygen is complete on the Pt surface (the titration behavior). As a result of the large decrease in the surface oxygen coverage, the drastic change of T_V with time was observed in Fig. 4. It should be noted that there is little effect of the gas phase collisions on T_V because the cross section for the vibrational relaxation is much smaller than that for the rotational relaxation, as mentioned before. In practice, the small dip at around 150 μs is not due to the gas phase collisions, because such change in T_V was not observed on the Pd surface at the same high P_N(CO) condition (see Fig. 10). It appears that the vibrational states of the product CO_2 molecules are very sensitive to the reaction sites on the Pt surface when the surface oxygen coverage is relatively low. In other words, the nature of the transition state is reflected much more directly by the energy distribution in the product molecules that are formed at relatively low surface coverage, although at present we don't know the detailed mechanism for the process that results in such drastic change in T_V. With respect to extremely low coverage of surface oxygen, the reaction sites are probably at ledges and kinks where the interactions of the product CO_2 with the surface should be stronger than out on the terrace. It is possible that the abrupt drop in T_V (ca. 700 K) shown in Fig. 4 at 330 μs may be caused by a loss of energy to the surface as a result of such strong interactions. The very low T_V value (below the surface temperature) might imply a simple lowering of the overall vibrational temperatures. However, this cannot be the case because the emission intensity would be too low to detect in our system if the antisymmetric temperature (T_{AS}) were in fact that low. This result suggests that symmetric strech and bending should have cooled to the point where they make very little contribution to the emission. Mantell et al. discussed this effect in terms of a selective population of the antisymmetric (00^01) fundamental[6] or a decrease in the translational kinetic energy of the CO_2.[4]

The behavior on Pd is in stark contrast to those on Pt. First, the reaction rate did not scale linearly with CO pressure: the lowering of the P_N(CO) resulted in a drastic decrease in the signal intensity, as shown in Fig. 9. Secondly, no big change in T_V with time (coverage) was observed on Pd (Fig. 10) even at the high CO nozzle pressure (P_N(CO)=760 Torr). Furthermore, the T_V values are significantly higher than those in the case of the Pt surface. The reactivity of CO appears to be relatively lower on the Pd surface when the CO arrival rate is decreased (P_N(CO)=120 Torr). The activity may be suppressed due to the presence of large surface oxygen concentrations. It is reported that on a Rh surface the near surface regions becomes oxidized (probably to Rh_2O_3) and the catalytic activity is reduced under highly oxidizing conditions.[10] In fact, the surface oxygen coverage may be higher on the Pd surface than on the Pt surface, primarily because of the more oxyphilic nature of Pd. It has been estimated that Pt coverage is of order 0.2 (the O/Pt ratio) and that Pd approaches full coverage (O/Pd=0.5) at 900 K.[11] These estimates are based on known sticking coefficients and heats of adsorption for Pt and Pd (111) and assume equilibrium with the gas phase and a full coverage with O/Pt (or Pd) of 0.5.[11] Although we have no information about the surface characterization, we argue that even at the high P_N(CO) the depletion of surface oxygen on Pd was not complete as on Pt. Therefore, no titration behavior was observed on Pd. During the CO pulse the surface oxygen at ledges and kinks remained unreacted on the Pd surface. Most of the CO_2 molecules with high T_V may be formed on the terrace of the Pd surface.

The higher T_V values on Pd than on Pt are consistent with the results of the steady-state CO oxidation reaction.[12,13] The CO_2 produced by oxidation on Pd is more vibrationally excited than for reaction on Pt, and Coulston and Haller[12] have postulated that the CO_2 activated complex is bent more on Pd than on Pt. A small change in T_V is observed by variation of the flux of O_2. The trend is similar to the case of Pt: T_V decreases slightly with decreasing the surface oxygen coverage. These results are in good agreement with those of the steady-state reaction experiments,[12,13] in which the surface oxygen coverage was varied by changing the CO : O_2 ratio and the surface temperature.

The time-resolved infrared emission experiments here revealed that T_R as well as T_V decreases with decreasing surface oxygen coverage. The change in T_R is more significant than in T_V, if compared at the same experimental condition on Pt (P_N(CO)=120 Torr). The activation energy for the surface reaction step between chemisorbed CO and oxygen is 24 kcal mol^{-1} at low oxygen coverage and decreases to about 12 kcal mol^{-1} when the oxygen coverage is a substantial fraction of a monolayer.[14] It has been proposed that the variation in activation energy with coverage can be understood in terms of chemisorption energies. With increasing coverage, the heats of chemisorption of both reactants (CO, O) should decrease due to repulsive interactions.[1,14] This would decrease the height of the activation barrier, assuming that the energy of the transition state remains almost constant. However, such an interpretation is not adequate to explain the present results. To explain a change in both rotational and vibrational energies of the product CO_2 molecules, one would have to envision a shift in the potential energy of the transition state, which is accompanied with the change in the activation energy.

More detailed studies including surface characterization will be required to elucidate the mechanism of changes in the vibrational and rotational states of the product CO_2. In addition to the information about the internal energies, measurements of the translational energy distribution of the product CO_2 will also be important for the understanding of the dynamics of the formation and desorption of the CO_2 activated complex.[2]

Summary

The time-resolved infrared emission spectra for the product CO_2 formed by CO oxidation on metal (Pt, Pd) surface at 900 K were measured to examine the dependence of the internal energy on the surface oxygen coverage. At the low pressure of the pulsed CO nozzle, the rotational temperature (T_R) as well as the average vibrational temperature (T_V) decreased with decreasing oxygen coverage on Pt surface. At the high CO nozzle pressure, a large decrease in T_V was observed as the oxygen on the Pt surface was almost depleted. The vibrational states of the product CO_2 appeared to be sensitive to the reaction sites on Pt at relatively low surface oxygen coverage. In contrast, no such drastic change in T_V was observed on Pd surface, but T_V was decreased only slightly with decreasing surface oxygen coverage. The higher T_V values on Pd than on Pt are consistent with the results of the steady-state CO oxidation experiments.

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