Structure of Activated Complex of CO_2 Formation in a $CO + O_2$ Reaction on Pd(110) and Pd(111)

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Examinations of CO₂ formed during steady-state CO oxidation reactions were performed using infrared (IR) chemiluminescence. The CO₂ was formed using a molecular-beam method over Pd(110) and Pd(111). The CO₂ formation rate is temperature dependent under various partial pressure conditions. The temperature of the maximum formation rate is denoted as T_S^{max} . Analyses of IR emission spectra at surface temperatures higher than T_S^{max} showed that the average vibrational temperature (T_V^{AV}) is higher for Pd(111) than for Pd-(110). The antisymmetric vibrational temperature (T_V^{AS}) is almost equal on both surfaces. These results suggest that the activated CO₂ complex is more bent on Pd(111) and straighter on Pd(110). Furthermore, the difference in the T_V^{AV} value was small for surface temperatures less than T_S^{max} . The T_V^{AS} value was much higher than T_S^{max} : they became more pronounced at lower temperatures, suggesting that the activated complex of CO₂ formation is much straighter on both Pd surfaces than that observed at higher surface temperatures. Combined with kinetic results, the higher CO coverage at the lower surface temperatures is inferred to be related to the linear activated complex of CO₂ formation.

Introduction

Elucidation of reaction mechanisms is important for catalyst design and control of reaction routes. Single-crystal surfaces can be used to elucidate reaction mechanisms over heterogeneous catalysts.^{1,2} An effective method is spectroscopic observation of reaction intermediates, which are surface species in a metastable state, to obtain information about reaction mechanisms. Another method is the investigation of internal (vibrational and rotational) energy and translational energy of desorbed molecules, which are the products of catalytic reactions, from the catalyst surface.^{3–19} The energy states of desorbed molecules can reflect the catalytic reaction dynamics, which can correspond to a transition state.³⁻¹⁹ Numerous investigations of CO oxidation on Pt and Pd surfaces have revealed the elemental steps of surface catalyzed reactions.¹⁻²⁴ Furthermore, CO oxidation is a prototype reaction for the study of dynamics; measurements of internal energy states of the produced CO₂ molecules have been performed using the infrared chemiluminescence (IR emission) method under steady-state catalytic reactions using molecular-beam techniques.³⁻¹⁵ Analyses of vibrational and rotational states can yield information about the structure of the activated CO₂ complex (i.e., the dynamics of CO oxidation) from which the gas-phase molecules desorbed. Furthermore, the vibrational energy state of product CO₂ depends on its surface structure.8-16 Consequently, information about the active sites is obtainable from the IR emission spectra of CO2 under a steady-state catalytic reaction.

Our group has reported IR chemiluminescence of CO₂ from the steady-state CO + O₂ reaction on single-crystal Pd surfaces combined with kinetic results.^{11–15} The activated complex of CO₂ formation (the transition state of CO₂ formation from CO-(a) + O(a)) has a more bent structure on Pd(111) and a straighter

structure on Pd(110) at higher surface temperatures ($T_{\rm S} > 650$ K) because CO_2 from Pd(111) is more excited vibrationally than CO₂ from Pd(110).^{14,15} Results of kinetic investigations show that the CO_2 formation rate in the $CO + O_2$ reaction increases with increasing surface temperature in the low-temperature range. The temperature at which the catalytic activity of CO₂ formation is maximal is denoted herein and in previous studies by our group as $T_{\rm S}^{\rm max}$.^{14,15} We have specifically examined higher temperature conditions than $T_{\rm S}^{\rm max}$ and find that as the catalytic activity in the $CO + O_2$ reaction is greatly dependent on the CO coverage in this range, it decreases with increasing surface temperatures. However, catalytic reactions using real and practical catalysts are usually carried out at lower reaction temperatures. For that reason, chemiluminescence investigation at a lower temperature range is of greater practical value. This study specifically examines such reaction conditions.

Experimental Procedures

A molecular-beam reaction system, in combination with a FT-IR spectrometer (InSb detector Nexus670; Thermo Electron Corp.), was used to measure IR emissions of product CO₂ molecules that desorbed on metal surfaces during catalytic reactions.^{14–16} A UHV chamber (base pressure $<1.0 \times 10^{-9}$ Torr) was equipped with a CaF₂ lens, which collected IR emission; an Ar⁺ ion gun for sample cleaning; and a quadrupole mass spectrometer (OMS, OME200; Pfeiffer Vacuum Technology AG) with a differential pumping system. Two free-jet molecular-beam nozzles (0.1 mm diameter orifice) supplied the reactant gases. The reactant fluxes were controlled using mass flow controllers. The CO and O₂ gases (total flux of $2.1-20 \times$ $10^{18} \text{ cm}^{-2} \text{ s}^{-1}$; CO/O₂ = 0.3-7) were exposed to single-crystal Pd surfaces (Pd(110) and Pd(111)). Steady-state CO + O_2 reactions were performed at temperatures of 400-900 K. Another UHV chamber (base pressure $< 2.0 \times 10^{-10}$ Torr) was used to prepare the samples and to characterize Pd(110) and

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Figure 1. IR emission spectra of CO₂ desorbed by the CO + O₂ reaction on Pd(111). The surface temperature (T_S) was 850 K. The total flux of reactant CO and O₂ was 8.2 × 10¹⁸ molecules cm⁻² s⁻¹ at CO/O₂ = 1. The spectral resolution was 1 cm⁻¹.

Pd(111) surfaces. It was equipped with an identical molecularbeam reaction system, an Ar^+ ion gun, low energy electron diffraction (LEED), and a QMS. Before the molecular-beam reaction, Pd(110) and Pd(111) were cleaned using a standard procedure (O₂ treatment, Ar⁺ bombardment, and annealing).^{14–16}

The IR emission spectra of the CO₂ molecules desorbed from the surface were measured with 4 cm⁻¹ resolution unless stated otherwise. At that low resolution, no individual vibration– rotation lines were resolved. Figure 1 shows an IR emission spectrum of CO₂ produced by the CO + O₂ reaction on Pd-(111) at surface temperature (T_S) = 850 K. It was taken with 1 cm⁻¹ resolution. The CO₂ emission spectrum was observed in the region of 2400–2200 cm⁻¹, whereas the emission spectrum of the nonreacted CO, which was scattered from the surface, was centered at 2143 cm⁻¹. In the spectrum with a 1 cm⁻¹ resolution, the rotational lines (P and R branches) of CO molecules are clearly visible; notwithstanding, those of the CO₂ molecules were not resolved.

The IR emission spectra of product CO₂ were analyzed based on simulations of model spectra. They yielded an average vibrational Boltzmann temperature (T_V^{AV} : an average temperature of antisymmetric stretch, symmetric stretch, and bending modes) and a rotational Boltzmann temperature $(T_R)^{4,6} T_V^{AV}$ was calculated from the degree of red-shift from the fundamental band (2349 cm⁻¹), and then T_R was derived from the emission bandwidth (Figure 2a,b). Although the IR emission observed here is in the antisymmetric stretch vibrational region— (n_{SS}, n_B^l) , $(n_{\rm AS}) \rightarrow (n_{\rm SS}, n_{\rm B}^l, n_{\rm AS} - 1)$ —the vibrational excitation levels of symmetric stretch (n_{SS}) and bending (n_B) also affect this region.^{4,15} Here, n_{SS} , n_B , and n_{AS} are the vibrational quantum numbers of respective modes. The quantum number of vibrational angular momentum in linear molecules is denoted by *l*. Note that the emission intensity is normalized using the rate of CO₂ production. Consequently, the emission intensity is related to the extent of excitation in the antisymmetric stretch of CO_2 , which is given by the following equation:

$$f \propto \exp(-\Delta E_{\rm V}/k_{\rm B}T_{\rm V}^{\rm AS}) \tag{1}$$

where *f* is the emission intensity normalized per unit of CO₂ yield, ΔE_V is the energy spacing, k_B is the Boltzmann constant, and T_V^{AS} is the antisymmetric temperature. High-resolution steady-state results (0.06 cm⁻¹)⁴ show the energy distribution in respective vibrational modes, T_V^{SS} , T_V^B , and T_V^{AS} , where the superscripts, respectively, indicate symmetric stretch, bending, and antisymmetric stretch. Here, the steady-state CO + O₂ reaction on polycrystalline Pt foil was performed with the previous conditions as (CO = O₂ = 4.1×10^{18} cm⁻² s⁻¹;⁴ Figure 3). The IR emission spectra of CO₂ molecules were measured with 4 cm⁻¹ resolution at the surface temperature (T_S) of 900 K (Figure 4). The obtained spectrum was compared with

previous results ($T_V^{AS} = 1600$ K).⁴ We estimated the emission intensity at $T_V^{AS} = 1600$ K. This emission intensity and T_V^{AS} on the polycrystalline Pt surface were used as standards for various conditions on Pd surfaces (Figure 2c). On the basis of T_V^{AS} and T_V^{AV} , it is possible to deduce the bending vibrational temperature (T_V^B). The relation between T_V^{AV} and the respective vibrational temperatures is represented as

$$T_{\rm V}^{\rm AV} = (T_{\rm V}^{\rm AS} + T_{\rm V}^{\rm SS} + 2 T_{\rm V}^{\rm B})/4$$
 (2)

where $2T_V{}^B$ corresponds to the degeneration of two bending vibrational modes. Assuming that $T_V{}^B$ is equal to $T_V{}^{SS}$ because of the Fermi resonance,^{5,23} $T_V{}^B$ is expected to be $(4T_V{}^{AV} - T_V{}^{AS})/3$. This assumption is plausible on the basis of previous reports.^{4,23} It should be added that $T_V{}^{AV}$, $T_V{}^{AS}$, $T_V{}^B$, and T_R were used here as parameters to characterize the extent of the vibrational and rotational excitation of the product CO₂. About 900–1800 s were required to measure the IR spectra with 1000–2000 scans. The activity was stable during measurement. Therefore, we infer that the results reflected the CO₂ states under steady-state conditions.

Results and Discussion

Figure 5 shows the rate of CO₂ formation in the steady-state $CO + O_2$ reaction on Pd(110) as a function of surface temperature ($T_{\rm S}$) for various total fluxes of reactants (CO/O₂ = 1). The CO oxidation proceeded at temperatures greater than 500 K. The formation rate profiles showed maxima on the Pd-(110) surface. The temperature at which the highest activity was obtained is denoted as $T_{\rm S}^{\rm max}$. It is shifted to a higher temperature, and the formation rate of CO2 increases with the increasing total flux of reactants. These behaviors agree well with the general Langmuir-Hinshelwood (LH) kinetics of CO oxidation on Pd surfaces.^{1,2} At temperatures lower than $T_{\rm S}^{\rm max}$, the surface coverage of CO is known to be high. The rate-determining step is O₂ adsorption on the vacant site, which is formed by the desorption of CO(a). At temperatures greater than $T_{\rm S}^{\rm max}$, the formation rate of CO₂ decreases gradually with increasing surface temperature. This behavior is attributable to the decreased CO coverage. Generally, in the $CO + O_2$ reaction on Pd surfaces at lower surface temperatures, the reaction order of CO is negative first-order and that of O_2 is positive first-order. Consequently, the formation rate of CO₂ is zero-order with respect to total pressure. Goodman et al. reported that the reaction rate of CO oxidation on Pd(110) at temperatures $T_{\rm S} =$ 450-600 and at a total pressure of 16 Torr is zero-order with respect to total pressure.²² On the other hand, at higher surface temperatures, the CO coverage ($\theta_{\rm CO}$) can be minute ($\theta_{\rm CO} \ll$ 0.01), and oxygen coverage (θ_0) approaches the saturation level $(\theta_{\rm O} \approx 0.5)$ ²⁵ Therefore, the reaction orders of CO and O₂ are, respectively, inferred to be positive first-order and zero-order. The total formation rate of CO₂ included the reaction order of total pressure as positive first-order with a constant CO/O2 ratio. These explanations are true for our cases, in which the gas pressure range is lower than those reported previously.²²

Figure 6 shows IR emission spectra of CO₂ molecules produced by CO + O₂ reactions on Pd(110) at $T_S = 650$ K for the various total fluxes (CO/O₂ = 1). The CO₂ emission spectra observed in the region of 2400–2200 cm⁻¹ are considerably red-shifted from 2349 cm⁻¹ (fundamental band of antisymmetric stretch). The degree of red-shift from the fundamental band, which reflects the vibrational state of excited molecules, is nearly equal for all total flux conditions. On the other hand, the emission intensity increases with increasing total flux, indicating



Figure 2. Analyses of average vibrational temperature (T_V^{AV}) , rotational temperature (T_R) , and antisymmetric vibrational temperature (T_V^{AS}) : (a) T_V^{AV} as a function of degree of red-shift from fundamental bands; (b) T_R as a function of full-width half-maximum $(T_V^{AV} = 1500, 1700, \text{ and } 2100 \text{ K})$; and (c) T_V^{AS} as a function of relative emission intensity normalized per unit of CO₂ yield.



Figure 3. Formation rate of CO₂ during the CO + O₂ reaction (CO/ O₂ = 1) on polycrystalline Pt foil as a function of surface temperature. The total flux of reactant CO and O₂ was 8.2×10^{18} molecules cm⁻² s⁻¹ at CO/O₂ = 1.



Figure 4. IR emission spectra of CO₂ desorbed by the CO + O₂ reaction on polycrystalline Pt foil. The surface temperature (T_S) was 900 K. The total flux of reactant CO and O₂ was 8.2 × 10¹⁸ molecules cm⁻² s⁻¹ at CO/O₂ = 1.

changes in the antisymmetric vibrational excited state (T_V^{AS}) , as explained later.

Figure 7a shows the vibrational temperature (T_V^{AV}) and rotational temperature (T_R) derived from IR emission spectra of CO₂ at $T_S = 650$ K as a function of the total flux. Each



Figure 5. Formation rate of CO₂ during the CO + O₂ reaction (CO/ O₂ = 1) on Pd(110). The total flux of reactants (CO + O₂) was $2.1-20 \times 10^{18}$ molecules cm⁻² s⁻¹.

 $T_{\rm V}^{\rm AV}$ value is shown as much higher than $T_{\rm S}$, indicating that the product CO₂ is vibrationally excited. However, it is almost constant under all flux conditions. The $T_{\rm R}$ value is also shown as higher than $T_{\rm S}$, indicating that the product CO₂ is rotationally excited. The $T_{\rm R}$ value is shown as nearly constant between 2.1 and 8.2 \times 10¹⁸ cm⁻² s⁻¹. However, the value decreases gradually beyond the total flux = 1.0×10^{19} cm⁻² s⁻¹. The decrease of the $T_{\rm R}$ value is attributable to rotational relaxation by the gas-phase collision between departing (CO₂) and arriving $(CO + O_2)$ molecules.⁷ Therefore, we measured the IR emission spectra of CO₂ molecules with no rotational relaxation conditions where the total flux of reactants is 8.2×10^{18} cm⁻² s⁻¹. Figure 7b shows the antisymmetric vibrational temperature (T_V^{AS}) and the bending vibrational temperature (T_V^B) derived from IR emission intensity of CO2 as a function of the total flux. The T_V^{AS} value increases gradually with increasing total flux

Figure 8 shows the CO_2 formation rate in the steady-state $CO + O_2$ reaction on Pd(110) as a function of surface



Figure 6. IR emission spectra of CO₂ desorbed by the CO + O₂ reaction on Pd(110). The surface temperature (T_S) was 650 K. The total flux of reactants was $2.1-20 \times 10^{18}$ molecules cm⁻² s⁻¹ at CO/O₂ = 1. The emission intensity was normalized per unit of CO₂ yield.



Figure 7. (a) Total flux dependence of vibrational temperature (T_V^{AV}) and rotational temperature (T_R) of CO₂ formed in CO + O₂ reaction on Pd(110). (b) Total flux dependence of antisymmetric vibrational temperature (T_V^{AS}) and bending vibrational temperature (T_V^B) . The surface temperature (T_S) was 650 K. The total flux of reactants was $2.1-20 \times 10^{18}$ molecules cm⁻² s⁻¹ at CO/O₂ = 1.

temperature ($T_{\rm S}$) for various CO/O₂ ratios. The total flux of reactants is shown as constant at 8.2 × 10¹⁸ cm⁻² s⁻¹. The temperature dependence of the curves shows the maximum value: the observed behavior resembles that shown in Figure 5. In Figure 8, $T_{\rm S}^{\rm max}$ is shown to increase considerably with the increasing CO/O₂ ratio. At surface temperatures lower than $T_{\rm S}^{\rm max}$ (e.g., 525 K) under all pressure conditions, the CO₂ formation rate decreases sharply with the increasing CO/O₂ ratio, which is explainable by the reaction orders with respect to CO and O₂, as depicted in Figure 5. In stark contrast, at surface temperatures higher than $T_{\rm S}^{\rm max}$ (e.g., 700 K) for CO/O₂ ratios



Figure 8. Formation rate of CO₂ during the CO + O₂ reaction (CO/ O₂ = 0.3-7.0) on Pd(110). The total flux of reactants (CO + O₂) was 8.2×10^{18} molecules cm⁻² s⁻¹.



Figure 9. IR emission spectra of CO₂ desorbed by the CO + O₂ reaction on Pd(110). The surface temperature (T_S) was 600 K. The total flux of reactants was 8.2×10^{18} molecules cm⁻² s⁻¹ at CO/O₂ = 0.3–7.0. The emission intensity was normalized per unit of CO₂ yield.

of 0.3-2.1, the CO₂ formation rate increases with increasing CO/O₂ ratio. This behavior is implied by the reaction orders. Furthermore, the CO₂ formation rate at $T_{\rm S}^{\rm max}$ under each CO/O₂ ratio increases concomitant with the increasing CO/O₂ ratio of 0.3-2.1 but decreases for ratios of 3.0-7.0. Especially at very high CO/O₂ ratios, the oxygen coverage decreases, thereby lowering the CO₂ formation rate. This study measured the IR emission spectra at $T_{\rm S} = 600$ K because this temperature is lower than $T_{\rm S}^{\rm max}$ under CO/O₂ = 1.4-7.0. It is higher than $T_{\rm S}^{\rm max}$ under CO/O₂ = 0.3-1.0. Observations at this temperature reveal the relation between the vibrational state of CO₂ and $T_{\rm S}^{\rm max}$.

Figure 9 depicts the IR emission spectra of CO₂ molecules produced by the CO + O₂ reaction on Pd(110) at $T_{\rm S} = 600$ K for various CO/O₂ ratios. The red-shift from the fundamental band is shown to be almost equal for various CO/O₂ ratios. However, the emission intensity increases concomitant with the increasing CO/O₂ ratio. Figure 10a shows T_V^{AV} and T_R , obtained from IR emission spectra of CO₂, as a function of the CO/O₂ ratio. The $T_{\rm R}$ value is almost identical (1000 K), indicating that the rotationally excited state is independent of the CO/O₂ ratio. The T_V^{AV} value increases slightly with the increasing CO/O₂ ratio, whereas the value remains nearly unchanged at a low value of CO/O₂ (CO/O₂ < 0.6). Figure 10b shows T_V^{AS} and T_V^B obtained from IR emission intensity of CO2 as a function of CO/O₂. In the low CO/O₂ region, the T_V^{AS} value is nearly constant, but the T_V^{AS} increases sharply in the higher CO/O₂ region. This result indicates that the antisymmetric vibrational mode of product CO₂ is much more excited with higher CO/



Figure 10. (a) CO/O₂ ratio dependence of vibrational temperature (T_V^{AV}) and rotational temperature (T_R) of CO₂ formed in CO + O₂ reaction on Pd(110). (b) CO/O₂ ratio dependence of antisymmetric vibrational temperature (T_V^{AS}) and bending vibrational temperature (T_V^{B}) . The total flux of reactants was 8.2 × 10¹⁸ molecules cm⁻² s⁻¹ at CO/O₂ = 0.3-7.0.



Figure 11. CO₂ formation rate during the CO + O₂ reaction (CO/O₂ = 1) on (a) Pd(110) and (b) Pd(111). The total flux of reactants (CO + O₂) was 8.2×10^{18} molecules cm⁻² s⁻¹.

O₂. Particularly, much higher T_V^{AS} is apparent at CO/O₂ = 7.0, where $T_S < T_S^{max}$. These results suggest that the vibrational state of CO₂ at T_S lower than T_S^{max} differs from that at T_S higher than T_S^{max} .

Figure 11 shows the rate of CO₂ formation in the steadystate CO + O₂ reaction on Pd(110) and Pd(111) as a function of surface temperature. At temperatures greater than 500 K, the CO oxidation proceeds, and the temperature dependence of the formation rate is maximal on both Pd surfaces. Descriptions similar to those of Figures 5 and 8 are applicable to these behaviors. The $T_{\rm S}^{\rm max}$ and the formation rate of CO₂ also differed for each surface. Comparison of the two surfaces revealed that the CO oxidation on Pd surfaces is structure-sensitive under the steady-state reaction condition with the total pressure of ca. 10^{-3} to 10^{-2} Torr. The CO₂ formation rate can be plotted as a function of inverse surface temperature in the Arrhenius form,

as in Figure 11. From the temperature range $T_{\rm S} = 475-600$ K of this plot, the apparent activation energies of Pd(111) and Pd(110) are estimated, respectively, as 27.8 and 34.3 kcal/mol. These values agree with the value of 28.1 kcal/mol on $Pd(111)^{21}$ and that of 33.1 kcal/mol on Pd(110),²⁰ which were obtained by Goodman et al. in high-pressure conditions, or that of 25 kcal/mol on Pd(111), which was obtained by Engel and $Ertl^1$ in UHV studies. The agreement of activation energies of CO oxidation over Pd surfaces suggests that the surface structure was maintained during catalytic and steady-state reactions. Generally speaking, the planar surface prepared by treatments such as annealing can be changed to a rough surface during reactions. However, Pd(110) and Pd(111) have considerably stable surface structures even under reaction conditions. On the basis of this inference, we can estimate the TOF of CO₂ formation over Pd(110) and Pd(111). At $T_{\rm S} = 575$ K, TOFs over Pd(110) and Pd(111) are calculated, respectively, as 440 and 74 s^{-1} .

Figure 12a,b shows IR emission spectra of CO₂ molecules produced by the CO + O₂ reaction on Pd(110) and Pd(111) surfaces (CO/O₂ = 1) for various surface temperatures. The peaks centered at 2143 cm⁻¹ are IR emissions from the nonreacted CO molecules, which are fully accommodated to the surface. The higher the surface temperature, the greater was the red-shift from the antisymmetric stretch fundamental (2349 cm⁻¹) observed in the CO₂ emission spectra. In contrast, at low surface temperatures ($T_{\rm S} = 550-600$ K), the degree of redshift from 2349 cm⁻¹ is almost constant, even though the emission intensity is extremely high in this temperature range.

Figure 13a,c shows the average vibrational temperature (T_V^{AV}) and the rotational temperature (T_R) on Pd(110) and Pd(111) surfaces derived from IR emission spectra of CO2 as a function of $T_{\rm S}$. The $T_{\rm V}^{\rm AV}$ and $T_{\rm R}$ values are much greater than that of $T_{\rm S}$, which also indicates that the product CO₂ is excited both vibrationally and rotationally. The $T_{\rm R}$ value is almost constant, thereby indicating that the rotationally excited state is independent of the surface temperature. The T_V^{AV} value increases with increasing $T_{\rm S}$ at temperatures greater than 600 K. In particular, the T_V^{AV} values on Pd(111) are much higher than those of Pd-(110), whereas it was almost constant at low surface temperatures ($T_{\rm S}$ < 600 K) on both surfaces. Figure 13b,d shows $T_{\rm V}^{\rm AS}$ and $T_{\rm V}{}^{\rm B}$ derived from IR emission intensities of CO₂ as a function of $T_{\rm S}$. For surface temperatures above 600 K, the $T_{\rm V}^{\rm AS}$ value increases gradually with increasing $T_{\rm S}$. In contrast, the $T_{\rm V}^{\rm AS}$ value increases drastically with decreasing $T_{\rm S}$ at low temperatures of 550-600 K, indicating that the vibrational states of desorbed CO₂ change at about 600 K on both surfaces. The T_V^{AS} values of Pd(111) are similar to those of Pd(110) in Figure 13b,d at the higher surface temperatures. However, the T_V^B values of Pd(111) are much higher than those of Pd(110), meaning that the bending vibrational mode is more highly excited than the antisymmetric vibrational mode on Pd(111) at the higher $T_{\rm S}$. This fact is reflected in the structure of the activated complex of CO₂ formation. Particularly, in the bending vibrational mode, CO_2 on Pd(111) is excited. For that reason, the structure of the activated complex is more bent. In contrast, CO₂ on Pd(110) is slightly more excited in the antisymmetric stretching vibration than in the bending one. Therefore, the activated complex has a straighter form.

On the basis of those behaviors, Figure 14a,b presents the structure of the activated complex at 800 K, higher than $T_{\rm S}^{\rm max}$. Along with them, an appropriate model is presented and described. At higher temperatures, adsorbed oxygen and CO are diffused on the surface. However, it is known that a 3-fold



Figure 12. IR emission spectra of CO₂ desorbed by the CO + O₂ reaction on (a) Pd(110) and (b) Pd(111). The surface temperature (T_S) was 550–850 K. The total flux of reactants was 8.2 × 10¹⁸ molecules cm⁻² s⁻¹ at CO/O₂ = 1. The emission intensity was normalized per unit of CO₂ vield.



Figure 13. (a and c) Surface temperature dependence of vibrational temperature (T_V^{AV}) and rotational temperature (T_R) of CO₂ formed in CO + O₂ reaction on (a) Pd(110) and (c) Pd(111). (b and d) Surface temperature dependence of antisymmetric vibrational temperature (T_V^{AS}) and bending vibrational temperature (T_V^{B}) on (b) Pd(110) and (d) Pd(111). The total flux of reactants was 8.2×10^{18} molecules cm⁻² s⁻¹ at CO/O₂ = 1.

hollow site is more stable as an adsorption site of oxygen.^{26,27} A stable adsorption site of CO is a 3-fold hollow site on Pd- $(111)^{2,28}$ and a bridge site on Pd(110).^{2,29} Therefore, the model describes that CO₂ is formed by the reaction between two adsorbed species at each stable site. For Pd(111), adsorbed oxygen and carbon atoms in CO are located at a similar distance from the surface. The activated complex of CO₂ formation can be bent. On the other hand, in the case of Pd(110) because the adsorbed oxygen is located at the lower level, it is expected that the activated complex has a straighter structure than that on Pd(111). In contrast to the profile at higher temperatures, a different tendency is apparent on both surfaces at lower temperatures (e.g., 550 K; Figure 14c,d). Under such conditions, it is characteristic that T_V^{AS} is much higher than T_V^B . This result indicates that desorbed CO₂ is highly excited in the antisym-

metric vibrational mode and that the excitation level of the bending vibrational mode is low, which is explainable by the linear structure of the activated complex. At low temperatures such as 550 K, adsorbed CO has some mobility, but the adsorbed oxygen's mobility is much lower because its adsorption energy is much higher than that of CO₂. Therefore, we infer that CO, mounted on adsorbed oxygen, can form a linear activated complex. The coverage of adsorbed CO is high at lower surface temperatures. Therefore, the structure of the activated complex can be influenced by the CO coverage.

Regarding angular and velocity distribution measurements for CO₂ molecules produced in CO oxidation on Pd(110), Matsushima et al.¹⁸ showed that the translational energy of CO₂ increases with increasing CO pressure and increases with decreasing surface temperature ($T_{\rm S} < 500$ K). They concluded



Figure 14. Structure of the activated complex of CO₂ formation and vibrationally excited state of desorbed CO₂ molecules: (a) Pd(111) at the higher temperature region; (b) Pd(110) at the higher temperature region; (c) Pd(111) at the lower temperature region; and (d) Pd(110) at the lower temperature region. The temperatures described in each model are based on the reaction under the total flux of reactants, which was 8.2×10^{18} molecules cm⁻² s⁻¹ at CO/O₂ = 1.

that these phenomena are closely related to CO coverage because the amount of CO(a) increases at low surface temperature and at high CO pressure. Our study showed that the T_V^{AS} value increases at the low surface temperature and at the high CO/O₂ flux ratio in a high CO coverage region. High CO coverage can render the activated complex of CO₂ formation as linear.

Conclusions

(1) We measured the steady-state activity of CO oxidation over Pd(110) and Pd(111) surfaces in the temperature range of 400–900 K under various reactant pressure conditions. The CO₂ formation rate profile with regard to the surface temperature was maximal. This surface temperature was denoted as $T_{\rm S}^{\rm max}$.

(2) Measurements and analyses of IR chemiluminescence of CO₂ formed during the steady-state CO oxidation obtained vibrational and rotational energy states of CO₂ as the average vibrational temperature (T_V^{AV}), antisymmetric vibrational temperature (T_V^{AS}), and rotational temperature (T_R). Results showed that T_V^{AV} , T_V^{AS} , and T_R values were much higher than surface temperature (T_S) under all conditions, indicating that the product CO₂ was excited both vibrationally and rotationally.

(3) The average vibrational temperature (T_V^{AV}) of CO₂ formed CO oxidation on Pd(111) was much higher than those of CO₂ on Pd(110) at surface temperatures higher than T_S^{max} . This fact suggests that the activated CO₂ complex is more bent on Pd-(111) and straighter on Pd(110) at the higher surface temperature, where the CO coverage was rather low.

(4) The T_V^{AV} values of CO₂ formed in CO oxidation were similar on Pd(110) and Pd(111) surfaces when the surface

temperature was less than $T_{\rm S}^{\rm max}$. Furthermore, the $T_{\rm V}^{\rm AS}$ value of CO₂ increased drastically with decreasing $T_{\rm S}$ ($< T_{\rm S}^{\rm max}$), thereby indicating that antisymmetric vibration is much more highly excited than other vibrational modes. In turn, that high excitation suggests that the structure of the activated complex of CO₂ formation is straighter.

(5) The high T_V^{AS} value was always observed at T_S lower than T_S^{max} , a fact that can be related to high CO coverage. The structure of an activated complex of CO₂ formation with the interaction of the surrounding CO(a) molecules is in a more linear form.

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