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Catalysis Today 111 (2006) 316–321

www.elsevier.com/locate/cattod

Reaction mechanism and structure of activated complex of CO_2 formation in CO oxidation on Pd(1 1 0) and Pd(1 1 1) surfaces

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Received 10 May 2005; accepted 13 October 2005
Available online 19 December 2005

Abstract

The infrared (IR) chemiluminescence spectra of CO_2 were measured during steady-state CO oxidation over Pd(1 1 0) and Pd(1 1 1). CO_2 formation rate always gave a maximum in the surface temperature dependence, and the maximum temperature was denoted as T_S^{max}. Analyses of IR emission spectra at surface temperatures higher than T_S^{max} showed that the bending vibrational temperature (T_V^B) was higher for Pd(1 1 1) than for Pd(1 1 0). These results suggest that the activated CO_2 complex of CO_2 formation is more bent on Pd(1 1 1), and straighter on Pd(1 1 0). On the other hand, at surface temperatures lower than T_S^{max}, antisymmetric vibrational temperature (T_V^{AS}) was much higher than T_V^B on both Pd surfaces, suggesting that the activated complex is much straighter at the lower surface temperatures. Considering adsorption sites and their energy levels, the model of the activated complex of CO_2 formation at the transition state is discussed and proposed.

Keywords: CO oxidation; Pd; Infrared chemiluminescence; Activated complex; Transition state

1. Introduction

The infrared chemiluminescence (IR emission) technique has been applied to measure the vibrational states of product molecules desorbed during catalytic reaction [1–4]. This method can contribute to obtain information on the structure of the activated complex just before the desorption (i.e., the dynamics of CO oxidation) [1–7]. CO oxidation on Pt and Pd surfaces is one of the prototype reactions for the studies of the dynamics, and measurements of internal energy states of the produced CO_2 molecules have been performed by the IR chemiluminescence method [5–7]. Furthermore, the vibrational energy state of product CO_2 depends on its surface structure [1–4]. Consequently, information about the active sites is obtainable in situ from the IR emission spectra of CO_2 under a steady-state catalytic reaction.

Our group has reported the IR chemiluminescence of CO_2 from steady-state $CO + O_2$ reaction on single crystal Pd surfaces combined with kinetic results [1–3]. The activated complex of CO_2 formation (the transition state of CO_2 formation from CO(a) + O(a)) has more bent structure on Pd(1 1 1) and a straighter structure on Pd(1 1 0) at higher surface temperatures ($T_S > 650$ K) because CO_2 from Pd(1 1 1) is more excited vibrationally than CO_2 from Pd(1 1 0) [1–3]. Results of kinetic investigations show that the CO_2 formation rate in $CO + O_2$ reaction increases with increasing surface temperature in the low-temperature range. On the other hand, it decreases with increasing surface temperature. The temperature at which the catalytic activity of CO_2 formation is maximal is denoted herein and in previous studies by our group as T_S^{max} [1–3]. We have specifically examined higher temperature conditions than T_S^{max}. In the higher temperature region, the catalytic activity of $CO + O_2$ reaction is greatly dependent on the CO coverage. It decreases with increasing surface temperature. 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

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doi:10.1016/j.cattod.2005.10.043

greater practical value. This article is focusing on such reaction conditions.

2. Experimental

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 CO_2 molecules that desorbed on metal surfaces during catalytic reaction [1–4]. A UHV chamber (base pressure $<1.0 \times 10^{-9}$ Torr) was equipped with: a CaF_2 lens, which collected IR emission, an Ar^+ ion gun for sample cleaning, and a quadrupole mass spectrometer (QMS, QME200; 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 by mass flow controllers. The CO and O_2 gases (total flux of $8.2 \times 10^{18}\ \mathrm{cm^{-2}\ s^{-1}}$; $CO/O_2 = 1$) were exposed to single-crystal Pd surfaces (Pd(1 1 0) and Pd(1 1 1)). Steady-state $CO + O_2$ reaction 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(1 1 0) and Pd(1 1 1) surfaces. It was equipped with an identical molecular-beam reaction system, an Ar^+ ion gun, low energy electron diffraction (LEED), and a QMS. Before the molecular-beam reaction, the Pd(1 1 0) and Pd(1 1 1) were cleaned using a standard procedure (O_2 treatment, Ar^+ bombardment and annealing) [1–4].

The IR emission spectra of the CO_2 molecules desorbed from the surface were measured with 4 $\mathrm{cm^{-1}}$ resolution. At the low resolution, no individual vibration–rotation lines were resolved. The IR emission spectra 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), which could be calculated from the degree of red-shift from the fundamental band (2349 $\mathrm{cm^{-1}}$) [5,7]. Although the IR emission observed here is in the antisymmetric stretch vibrational region $[(n_{SS}, n_B^l, n_{AS}) \rightarrow (n_{SS}, n_B^l, n_{AS}-1)]$, the vibrational excitation levels of symmetric stretch (n_{SS}) and bending (n_B) also affect this region [3,5]. 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 CO_2 production. Consequently, the emission intensity is related to the extent of excitation in the antisymmetric stretch of CO_2, which is given by following equation [3,5]:

$$f \propto \exp\left(\frac{-\Delta E_V}{k_B T_V^{AS}}\right), \tag{1}$$

where f is the emission intensity normalized per unit of CO_2 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 $\mathrm{cm^{-1}}$) [5] show the energy distribution in respective vibrational modes, T_V^{SS}, T_V^B, T_V^{AS}, where the superscripts, respectively, indicate symmetric stretch, bending and antisymmetric stretch. Here, the steady-state $CO + O_2$ reaction on polycrystalline Pt foil was performed with the previous conditions [5] ($CO = O_2 = 4.1 \times 10^{18}\ \mathrm{cm^{-2}\ s^{-1}}$). The IR emission spectra of CO_2 molecules were measured with 4 $\mathrm{cm^{-1}}$ resolution at the surface temperature (T_S) of 900 K. The obtained spectrum was compared with previous results ($T_V^{AS} = 1600$ K) [5]. We estimated the emission intensity at $T_V^{AS} = 1600$ K. This emission intensity and T_V^{AS} on polycrystalline Pt surface were used as standards for various conditions on Pd surfaces. Based on 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 respective vibrational temperature is represented as

$$T_V^{AV} = \frac{T_V^{AS} + T_V^{SS} + 2T_V^B}{4}, \tag{2}$$

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 [6,8], T_V^B is expected to be $(4T_V^{AV} - T_V^{AS})/3$. This assumption is plausible on the basis of previous reports [5,8]. It should be added that T_V^{AV}, T_V^{AS} and T_V^B were used here as parameters to characterize the extent of the vibrational excitation of the product CO_2. 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 CO_2 states under steady-state conditions.

3. Results and discussion

Fig. 1 shows the rate of CO_2 formation in the steady-state $CO + O_2$ reaction on Pd(1 1 0) and Pd(1 1 1) as a function of surface temperature (T_S). At temperatures greater than 500 K, the CO oxidation proceeds and the temperature dependence of the formation rate is maximal on both surfaces. The temperature at which the highest activity was obtained is denoted as T_S^{max}. These behaviors agree well with the general

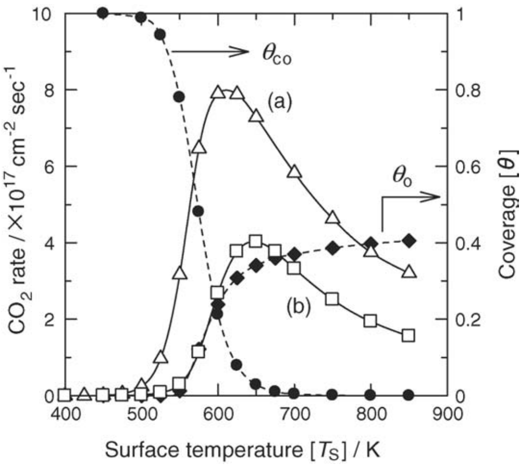

Fig. 1. The formation rate of CO_2 during the $CO + O_2$ reaction (a) on Pd(1 1 0), (b) on Pd(1 1 1), and the coverage of CO and oxygen on Pd(1 1 0) as a function of surface temperature (T_S).

Langmuir–Hinshelwood (LH) kinetics of CO oxidation on Pd surfaces [3,9,10].

As is known well, the mechanism of the CO + O_2 reaction on Pd surface is as follows [9,10]:

$$\mathrm{CO(g)} + \mathrm{V} \leftrightarrow \mathrm{CO(a)}, \tag{3}$$

$$\mathrm{O_2(g)} + 2\mathrm{V} \rightarrow 2\mathrm{O(a)}, \tag{4}$$

$$\mathrm{CO(a)} + \mathrm{O(a)} \rightarrow \mathrm{CO_2(g)} + 2\mathrm{V}, \tag{5}$$

where V represents a vacant site. It is possible to make the equations regarding the coverage of each intermediate as shown below [11,12]

$$\frac{d\theta_{CO}}{dt} = f_{CO}s_{CO}(1-\theta_{CO}-\theta_{O}) - k_{CO}^{des}\theta_{CO} - r_{CO_2}, \tag{6}$$

$$\frac{d\theta_{O}}{dt} = 2f_{O_2}s_{O_2}(1-\theta_{CO}-\theta_{O})^2 - r_{CO_2}. \tag{7}$$

Here, the rate of O_2 desorption is small enough to be neglected [9,11,12]. The CO_2 formation rate, $r\mathrm{CO}_2$, was obtained from the experimental results shown in Fig. 1. The initial sticking coefficients of CO and O_2 and the kinetic parameters used are listed in Table 1. The results of the coverage calculation in CO + O_2 reaction on Pd(1 1 0) are also shown in Fig. 1. It is known that at temperatures lower than T_S^{max}, the surface coverage of CO (θ_{CO}) is high, and the rate-determining step is O_2 adsorption on the vacant site, which is formed by the desorption of CO(a). At temperatures higher than T_S^{max}, the formation rate of CO_2 decreased gradually with increasing surface temperature, and this behavior is due to the drastic decrease of θ_{CO}. Generally, in CO + O_2 reaction on Pd surface at lower surface temperatures, reaction order of CO is negative-first-order, and that of O_2 is positive-first-order [9]. On the other hand, at higher temperatures, θ_{CO} can be very small (θ_{CO} « 0.01) and oxygen coverage (θ_O) approaches almost saturation level ($\theta_O \sim 0.5$) [16]. Therefore, the reaction orders of CO and O_2 are, respectively, inferred to be positive-first-order and zero-order. The formation rate of CO_2 can be plotted as a function of inverse surface temperature in Arrhenius form, as in Fig. 1. From the temperature range T_S = 475–600 K of this plot, the apparent activation energies of Pd(1 1 1) and Pd(1 1 0) are estimated to be 27.8 kcal/mol and 34.3 kcal/mol, respectively. It is known that the apparent activation energy is roughly equal to the desorption energy of CO at lower temperatures or at higher CO coverage conditions because the rate-determining step is CO desorption [9]. According to present and previous results [9,10,17], the apparent activation energies were approximately consistent with the desorption energy of CO. Our present values agree with the value of 28.1 kcal/mol on Pd(1 1 1) [17] and that of 33.1 kcal/mol on Pd(1 1 0) [10] reported by Goodman et al. under high pressure conditions or that of 25 kcal/mol on Pd(1 1 1) obtained by Engel and Ertl [9] in UHV studies. The agreement of activation energy of CO oxidation over Pd surfaces suggests that the surface structure is maintained during catalytic and steady-state reactions. Generally speaking, the planer surface prepared by treatments such as annealing can be changed to a rough surface during reactions. However, Pd(1 1 0) and Pd(1 1 1) have considerably stable surface structure even under reaction conditions. Based on this inference, we can estimate the TOF of CO_2 formation over

Table 1
Kinetic parameters for the CO + O_2 reaction on Pd(1 1 0)

Reaction equation	Rate constant (s^{-1})	ν (s^{-1})	E_a (kcal mol^{-1})	Ref.
(3)	k_{CO}^{des}	1×10^{17}	35.5	[13,14]
		Initial sticking coefficient		
(3)		$s_{CO} = 0.93$		[15]
(4)		$s_{O_2} = 0.86$		[16]

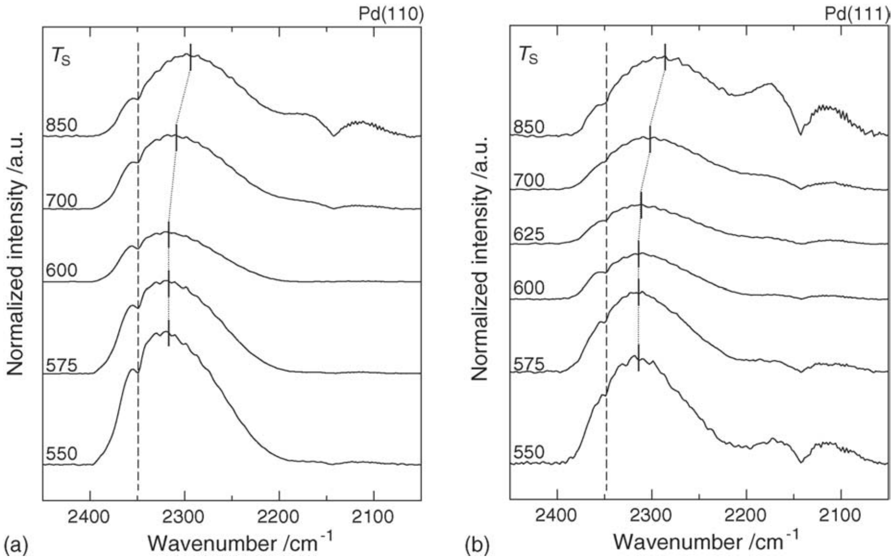

Fig. 2. IR emission spectra of CO_2 desorbed by the CO + O_2 reaction (a) on Pd(1 1 0) and (b) on Pd(1 1 1). The surface temperature (T_S) was 550–850 K. The emission intensity was normalized per unit of CO_2 yield.

Pd(1 1 0) and Pd(1 1 1). At $T_S = 575$ K, TOFs over Pd(1 1 0) and Pd(1 1 1) are calculated, respectively, as 440 and 74 s^{-1}.

Fig. 2 (a and b) shows IR emission spectra of CO_2 molecules produced by $CO + O_2$ reaction on Pd(1 1 0) and Pd(1 1 1) surfaces for various surface temperatures. The peaks centered at 2143 cm^{-1} are IR emission from the non-reacted CO molecules, which are fully accommodated to the surface. The higher the surface temperature, the greater the red-shift from the antisymmetric stretch fundamental (2349 cm^{-1}) was observed in the CO_2 emission spectra. In contrast, at low surface temperatures ($T_S = 550$–600 K), the degree of red-shift from 2349 cm^{-1} was almost constant, even though the emission intensity is extremely large in this temperature range. Fig. 3(a) shows the average vibrational temperature (T_V^{AV}) on Pd(1 1 0) and Pd(1 1 1) surfaces derived from IR emission spectra of CO_2 as a function of T_S. The T_V^{AV} values are much greater than that of T_S, which indicates that the product CO_2 is excited vibrationally. This is related to the exothermic reaction heat, which can be distributed to translational and internal (vibrational and rotational) energies of desorbed molecules, and it can also be distributed to the surface [18]. The T_V^{AV} value increases with increasing T_S at temperatures greater than 600 K. It is thought that the energy distribution to the surface can become lower at the higher surface temperatures. In all the temperature range, the T_V^{AV} values on Pd(1 1 1) are higher than those on Pd(1 1 0), and the difference was more significant in higher T_S range. The difference can be due to the surface structure, therefore the discussion on basis of the adsorption site and adsorption energy will be given later.

Fig. 3(b and c) shows antisymmetric vibrational temperature (T_V^{AS}) and bending vibrational temperature (T_V^{B}) derived from IR emission intensity of CO_2 as a function of T_S. For surface temperatures above 600 K, the T_V^{AS} and T_V^{B} values increase gradually with increasing T_S. In this temperature range, T_V^{AS} was higher than T_V^{B} on Pd(1 1 0), and in contrast, T_V^{B} was higher than T_V^{AS} on Pd(1 1 1). This behavior indicates that more energy is distributed to antisymmetric vibrational mode on Pd(1 1 0) and to bending vibrational mode on Pd(1 1 1). This fact is reflected in the structure of the activated complex of CO_2 formation [3,4]. Particularly in the bending vibrational mode, CO_2 on Pd(1 1 1) is excited. For that reason, the structure of the activated complex is more bent. In contrast, CO_2 on Pd(1 1 0) is slightly more excited in the antisymmetric stretching vibration than in the bending one. Therefore, the activated complex has a straighter form. The different behavior was observed on both surfaces at the lower surface temperatures (e.g., 550 K). Under these conditions, it is characteristic that T_V^{AS} was much higher than T_V^{B}. This result indicates that the desorbed CO_2 is much more highly excited in antisymmetric vibrational mode than bending vibrational mode. This suggests that structure of the activated complex is rather linear.

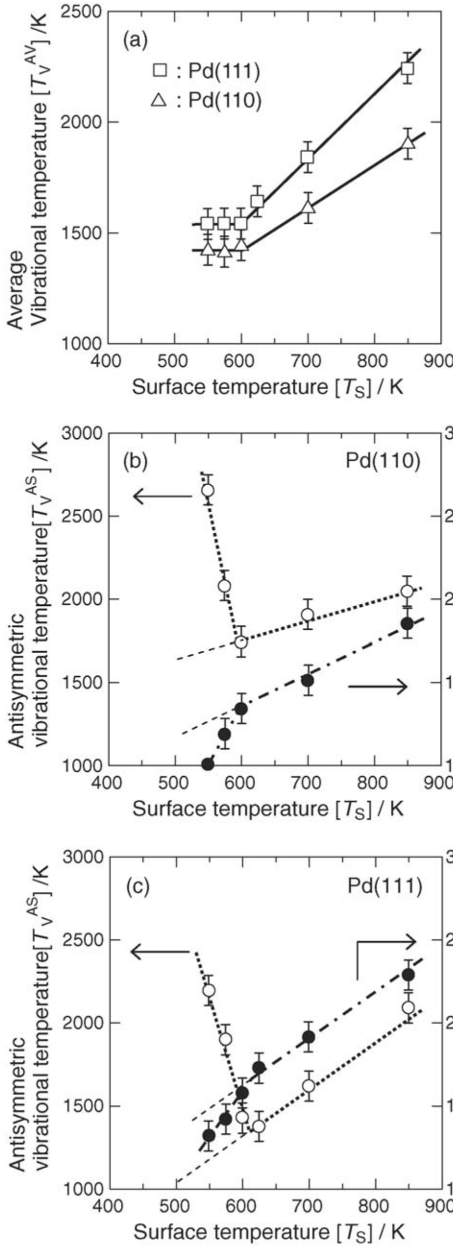

Fig. 3. (a) Surface temperature dependence of average vibrational temperature (T_V^{AV}) of CO_2 formed in $CO + O_2$ reaction on Pd(1 1 0) and on Pd(1 1 1). (b) and (c) Surface temperature dependence of antisymmetric vibrational temperature (T_V^{AS}) and bending vibrational temperature (T_V^{B}) (b) on Pd(1 1 0) and (c) on Pd(1 1 1).

From these results and analysis, it is suggested that the structure of the activated complex is much dependent on surface structure and reaction conditions, and the structure can be influenced by adsorption site and adsorption energy. Therefore, we discuss the transition state and the structure of the activated complex of CO_2 formation. For reaction temperatures above 600 K, it is thought that the coverage of CO is so small, and that of oxygen almost reaches the saturation level. Under these conditions, oxygen atoms are located at a three-fold hollow site on Pd(1 1 1) [19–21], and they are also located at a three-fold hollow site between the first layer and the second one on Pd(1 1 0) [22,23]. The adsorption sites of oxygen are similar in both cases, and this suggests that the adsorption energy is also similar. In contrast, the adsorption site of CO can be different. In higher reaction temperature range, the coverage of CO is very small judging from the results of our coverage estimations (Fig. 1). This suggests that CO can be adsorbed on the most stable site. It has been reported that the site is a three-fold hollow site on

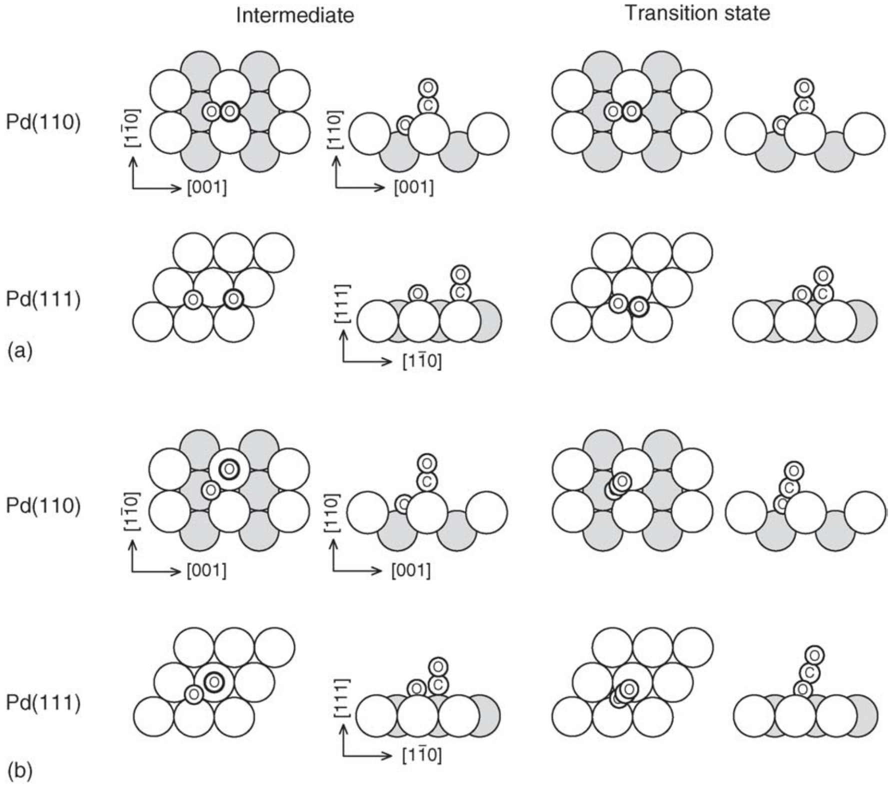

Fig. 4. Model structures of adsorption and activated complex in $CO + O_2$ reaction (a) at T_S above T_S^{max} and (b) at T_S below T_S^{max}.

Pd(1 1 1) [20,21,24], and a bridge site in the first layer on Pd(1 1 0) [23,25]. Considering the local relation between CO and oxygen, it is expected that the activated complex of CO_2 formation on flat Pd(1 1 1) has more bent structure than that on rough Pd(1 1 0). This can explain that bending vibrational mode was more excited than antisymmetric one in CO_2 formed on Pd(1 1 1), and antisymmetric one was more excited than bending one on Pd(1 1 0) at high T_S. On the other hand, the T_V^{AV} on Pd(1 1 1) was higher than that on Pd(1 1 0). Here, we try to explain this tendency on the basis of the adsorption energy and the energy of the transition state. It is expected that higher T_V^{AV} of desorbed CO_2 can be related to high energy level of adsorption and transition states. The adsorption energy level of CO on Pd(1 1 1) is lower than that on Pd(1 1 0) because of the difference in adsorption sites [20,21,23–25]. This does not agree with the behavior of T_V^{AV}. Therefore, we discuss the transition state on the basis of previous reports.

According to the report by Hu et al. [20] on coadsorption system of CO and oxygen on Pd(1 1 1) by means of the density functional theory (DFT) calculations, the most stable adsorption states of adsorbed CO and oxygen are a three-fold hollow site, and CO oxidation process can be divided into three distinguished periods. First, CO(a) moves freely from its initial position (three-fold hollow site), while O(a) vibrates around the three-fold hollow position. The energy change in this period is very small. Second, O(a) becomes activated and moves toward a bridge site. If CO(a) moves toward O(a) in the correct direction, then transition state can be achieved. In this period, the energy increases dramatically. Third, O(a) and CO(a) move toward each other, to form CO_2. In addition, Salo et al. [21] have also reported that the most stable sites of CO and oxygen are a three-fold hollow site, however, they have proposed that at the transition state both CO and oxygen are located near the bridge sites next to each other. Anyway, the transition state is much more unstable than stable adsorption site. This can be related to CO_2 desorption with high vibrational excitation. On the other hand, only a few groups have studied the coadsorption of CO and oxygen system on Pd(1 1 0) surface [23]. It has been reported that a three-fold hollow site between the first and second layer is more stable as the adsorption site of oxygen, and that of CO is a bridge site in the first layer on Pd(1 1 0) [23]. We illustrate the model structures of $CO + O_2$ reaction in T_S range above T_S^{max} in Fig. 4(a).

In the lower surface temperature range, the coverage of CO is much higher and that of oxygen is much lower compared to high surface temperature conditions. Under high CO coverage condition, bridge or on-top sites can appear on Pd(1 1 1) [24] and on-top sites can appear on Pd(1 1 0) [20]. In addition, Salo et al. have shown that the reaction barrier of CO adsorbed on-top and oxygen on three-fold hollow site is lower than that of CO adsorbed on a three-fold hollow site and oxygen on a hollow site. Iwasawa et al. [23] have investigated adsorption and oxidation of CO on Pd(1 1 0)-C(2 × 4)-O, and they have considered that at high CO coverage CO is linearly bound to the first layer Pd, which is directly coordinated by oxygen atoms, and that the linear CO mainly reacts to form CO_2 with oxygen below 250 K. Therefore in our case, considering the CO pressure in the gas phase is much higher than UHV conditions, CO can be adsorbed on more unstable site, e.g., on-top site rather than three-fold hollow and bridge sites on both surfaces in high CO coverage range. In addition, at the lower T_S, the antisymmetric vibrational mode was much more excited than bending vibrational mode. Especially, T_V^{AS} on Pd(1 1 0) at the low T_S (e.g., 550 K) was higher than T_V^{AS} on Pd(1 1 0) at the high T_S (e.g., 850 K). This result suggests that the activated complex of CO_2 formation in this low temperature range has more linear structure than that on Pd(1 1 0) in high temperature range. Therefore, it is thought that the linear activated complex can be formed by CO mounting on adsorbed oxygen (Fig. 4(b)). Considering that the coverage of adsorbed CO is rather high at the temperatures lower than T_S^{max}, the structure of the activated complex can be influenced by the CO coverage. Since the activated complex can be bound with the surface through one oxygen atom, its structure is not so influenced by the surface structure.

Regarding angular and velocity distribution measurements for CO_2 molecules produced in CO oxidation on Pd(1 1 0), Matsushima et al. [26] showed that the translational energy of CO_2 increases with increasing CO pressure, and increases with decreasing surface temperature ($T_S < 500$ K). They concluded 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 this behavior agrees with the report on the translational energy [26].

4. Conclusions

(1) We measured the steady-state activity of CO oxidation over Pd(1 1 0) and Pd(1 1 1) surfaces in the temperature range 400–900 K. The CO_2 formation rate profile with regard to surface temperature was maximal. This surface temperature was denoted as T_S^{max}.

(2) Measurements and analyses of IR chemiluminescence of CO_2 formed during the steady-state CO oxidation obtained the vibrational energy states of CO_2, as the average vibrational temperature (T_V^{AV}), antisymmetric vibrational temperature (T_V^{AS}) and bending vibrational temperature (T_V^{B}). Results showed that T_V^{AV}, T_V^{AS} and T_V^{B} values were much higher than surface temperature (T_S), indicating that the product CO_2 was excited vibrationally.

(3) At surface temperatures higher than T_S^{max}, T_V^{B} was higher than T_V^{AS} on Pd(1 1 1) and T_V^{AS} was higher than T_V^{B} on Pd(1 1 0). This fact suggests that the activated CO_2 complex is more bent on Pd(1 1 1), and relatively linear on Pd(1 1 0) at the higher surface temperatures, where the CO coverage is rather low.

(4) The T_V^{AV} values of CO_2 formed in CO oxidation were similar on Pd(1 1 0) and Pd(1 1 1) surfaces when the surface temperature was lower than T_S^{max}. Furthermore, the T_V^{AS} value of CO_2 increased drastically with decreasing T_S ($< T_S^{max}$), thereby indicating that antisymmetric vibration is much more highly excited than other vibrational modes. The high excitation suggests that the structure of the activated complex of CO_2 formation is in more linear form at the lower surface temperatures.

(5) From the comparison of T_V^{AS} and T_V^{B}, the model of the activated complex of CO_2 formation in $CO + O_2$ reaction over Pd(1 1 1) and Pd(1 1 0) is proposed, and the transition state of reaction is discussed.

Acknowledgment

This work was supported by the 21st Century Center of Excellence (COE) Program under the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

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