CO oxidation on Pd(111), Pt(111), and Rh(111) surfaces studied by infrared chemiluminescence spectroscopy

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Abstract

The infrared (IR) chemiluminescence studies of CO_2 formed during steady-state CO oxidation over Pd(111), Pt(111), and Rh(111) surfaces were carried out. Analysis of their emission spectra indicates that the order of the average vibrational temperature (T_V^{AV}) values of CO_2 formed during CO oxidation was as follows: Pd(111) > Pt(111) > Rh(111), and the order is coincident with the potential energy in the transition state expected by the theoretical calculations. Furthermore, it is suggested that the bending vibrational temperature (T_V^B) can also be influenced by the angle of O–C–O ($\angle_{OCO}$) of the activated complex in the transition state, which has also been proposed by the theoretical calculations.

1. Introduction

The catalytic oxidation of carbon monoxide (CO) on platinum group metal surfaces has been one of the most widely studied surface-catalyzed reactions [1-17]. The reaction is of practical importance for the environmental pollution control. On the other hand, the reaction is also of scientific interest because the total reaction can be divided into a few elementary steps and the theoretical approaches can be applied to the reaction to describe the kinetics of the surface-catalyzed reaction. In contrast, in order to elucidate the dynamics of the surface-catalyzed reaction, it is effective to investigate internal (vibrational and rotational) [6-14] and translational [15] energy of product molecules. Measurements of the vibrational and rotational states of the product CO_2 molecules have been performed by infrared chemiluminescence (IR emission) technique [6-14]. Analysis of the vibrational states can give the information on the structure of the activated CO_2 complex (i.e., the dynamics of CO oxidation) from which the gas-phase molecules desorbed.

Coulston and Haller [6] studied the dynamics of CO oxidation on polycrystalline Pd, Pt, and Rh surfaces by measuring high-resolution IR emission spectra and reported that the order of the apparent vibrational temperatures are as follows: Pd > Pt > Rh. Our group has reported IR emission of CO_2 from steady-state CO oxidation on single-crystal Pd and Pt surfaces combined with kinetic results [9-14]. These suggest that the activated complex of CO_2 formation (i.e., the transition state of CO_2 formation from CO(a) + O(a)) had more bent structure on Pd(111) and less bent structure on Pt(111), since the bending mode of CO_2 from Pd(111) was more vibrationally excited than that of CO_2 from Pt(111) [12,13]. Furthermore, we have confirmed that the product CO_2 molecules on Pd(111) and Pd(110) was also rotationally excited [12]. These results indicate that the IR

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chemiluminescence method can provide a direct energetic evidence of the reaction mechanism and the activated complex of CO_2 formation.

In this article, the dynamics of CO_2 formation during the CO oxidation over single-crystal Rh(111) surface is reported, and this corresponds to the first presentation of the IR emission studies on a single-crystal Rh surface. The obtained results were compared with those on Pd(111) and Pt(111), and the tendency was interpreted from the comparison between the experimental results and the reported theoretical studies on the transition state of CO oxidation.

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 just desorbed from metal surfaces during catalytic reactions [10-14]. 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 using mass flow controllers. The CO and O_2 gases (total flux of 8.2×10^{18} cm^{-2} s^{-1}; $CO/O_2 = 1$) were exposed to single-crystal surfaces (Pd(111), Pt(111), and Rh(111)). Steady-state CO oxidation was performed at temperatures of 400–900 K. Another UHV chamber (base pressure $< 2.0 \times 10^{-10}$ Torr) was used to prepare and characterize the clean surfaces. It was equipped with a molecular-beam reaction system, an Ar^+ ion gun, low energy electron diffraction (LEED), and a QMS. Before the molecular-beam

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reaction, the single-crystal surfaces were cleaned using a standard procedure (O_2 treatment, Ar^+ bombardment and annealing) [9-14]. After cleaning, the sharp (1×1) LEED pattern was observed.

The IR emission spectra of the CO_2 molecules desorbed from the surface were measured with 4 cm^{-1} resolution. At that low resolution, no individual vibration-rotation lines were resolved. The IR emission spectra were analyzed based on simulation of model spectra [7,12,13]. The average vibrational Boltzmann temperature (T_V^{AV}: an average temperature of the antisymmetric stretching, symmetric stretching and bending modes), which was calculated from the degree of the red-shift from the fundamental band (2349 cm^{-1}) [7,9-13]. The emission intensity is related to the extent of excitation in the antisymmetric stretching of CO_2 [11-14]. Therefore, the antisymmetric vibrational temperature (T_V^{AS}) can be estimated from the normalized emission intensity [11-14]. Based on T_V^{AV} and T_V^{AS}, 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

$$T_V^{AV} = (T_V^{AS} + T_V^{SS} + 2 T_V^B) / 4, \qquad (1)$$

where $2T_V^B$ corresponds to the degeneration of the bending vibration. 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 [6,8]. 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. It took about 30–90 min for the measurement of the IR emission spectra with 2000–6000 scans. The stable steady-state activity was obtained during the measurement.

3. Results and Discussion

Figure 1(a) shows the rate of CO_2 formation in the steady-state CO oxidation on Pd(111), Pt(111), and Rh(111) as a function of surface temperature (T_S) (CO/O_2 = 1). The CO oxidation proceeded above 500 K on Pd(111) and Rh(111), and 550 K on Pt(111). The surface temperature dependence of the formation rate showed a maximum on all the surfaces. The behavior agrees well with the general Langmuir-Hinshelwood (LH) kinetics of CO oxidation on noble metal (Pd [1,4,6,12], Pt [2,6,13], and Rh [3,5,6]) surfaces. The temperature at which the highest activity was obtained is denoted as T_S^{max}. At temperatures lower than T_S^{max}, the surface coverage of CO is known to be high. 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. This behavior is attributable to the decreased CO coverage. The starting temperatures of reaction and T_S^{max} on Pd(111), Pt(111) and Rh(111), i.e., 650, 775 and 650 K, respectively, are similar to those on polycrystalline surfaces reported by Coulston and Haller [6]. In contrast, the order of production rate of our results (Pd(111) > Rh(111) > Pt(111)) at T_S^{max} is different from results of polycrystalline surfaces (Pd > Pt > Rh [6]). Generally, a polycrystalline surface consists of low-index planes such as (111), (100) and (110) [17]. It has been reported that the maximum production rate was strongly dependent on surface structure. In the case of Pd and Rh, the order is Pd(100) > Pd(110) > Pd(111) [9], and Rh(100) ≈ Rh(111) [3]. Therefore, it is thought that polycrystalline Pd surface can give higher catalytic activity than Pd(111), and polycrystalline Rh surface can be comparable to Rh(111). Unfortunately, there is no report on the comparison in catalytic activity on Pt low-index surfaces, however, the different order between the polycrystalline and single-crystal surfaces presented here suggests Pt(100) > Pt(111) and Pt(110) >

Pt(111). The CO_2 formation rate is plotted as a function of inverse surface temperature in the Arrhenius form as shown Figure 1(b). From the low temperature range T_S = 475–600 K of this plot, the apparent activation energy (E_{app}) of Pd(111) is estimated as 27.8 kcal/mol, from T_S = 550–625 K, that of Pt(111) is estimated as 19.0 kcal/mol, and from T_S = 550–575 K, that of Rh(111) is estimated as 22.2 kcal/mol. These values agree with the value of 28.1 kcal/mol on Pd(111) [4], which was obtained by Goodman et al., that of 24.1 kcal/mol on Pt(111) [2], which was obtained by Ertl et al., and that of 19.9 kcal/mol on Rh(111) [5], which was obtained by Schmidt et al.. It has been reported that the surface is oxidized during the CO oxidation in high reaction pressure (about 10 Torr) or low CO/O_2 ratio conditions (CO/O_2=1/30), especially in the case of Rh surface [3]. However, we think that the surface keeps metallic state, because our reaction pressure ($\sim 10^{-2}$ Torr) is three orders of magnitude lower than their condition, and the pressure ratio is CO/O_2=1/1.

Figure 2 shows IR emission spectra of CO_2 molecules produced by the CO oxidation on Rh(111) surface at various surface temperatures. The CO_2 emission spectra were observed in the region of 2400–2220 cm^{-1}, while the emission spectra centered at 2143 cm^{-1} are due to the IR emission of the non-reacted CO molecules, which are scattered from the surface. The CO_2 emission spectra are considerably red-shifted from 2349 cm^{-1} (the fundamental band of antisymmetric stretch). The degree of the red-shift from the fundamental band, which reflects the average vibrational state of the excited CO_2 molecules, is not strongly influenced by the surface temperatures. The emission intensity is also almost constant under various surface temperatures.

Figure 3 shows the average vibrational temperature (T_V^{AV}) derived from IR emission spectra of CO_2 on Pd(111), Pt(111) and Rh(111) surfaces as a function of surface temperature. The T_V^{AV} values are much greater than T_S, which indicates that the product CO_2 is vibrationally excited. It is shown

that the order of T_V^{AV} is as follows: Pd(111) > Pt(111) > Rh(111). This tendency agrees well with the results of polycrystalline Pd, Pt, and Rh surfaces studied by Coulston and Haller [6]. In addition, the T_V^{AV} values on Pd(111) is much more dependent on the T_S than those on Pt(111) and Rh(111). The reason for different surface temperature dependence on these surfaces is not clear at present.

Eichler [16] has studied CO oxidation on transition metal surfaces using density functional theory (DFT) calculations. He reported that the potential energies of transition state (E_{TS}) and the activation energies (E_a) in CO oxidation on Pd(111), Pt(111) and Rh(111) as listed in Table 1, and the potential energy diagram is illustrated in Figure 4. He exhibited that the E_{TS} values in CO oxidation on Pd(111), Pt(111) and Rh(111) were -0.98, -1.38 and -1.88 eV, respectively [16], that is, the transition state on Pd(111) has the highest potential energy and that on Rh(111) is the lowest one. IR emission measurements are reflected by the excited energy ($E_{excited}$) of the product CO_2, which can be distributed to internal (vibrational and rotational) and translational energies of desorbed CO_2 molecules. Therefore, it is suggested that the excitation level of desorbed CO_2 can be originated from the height of potential energy of the transition state as shown in Figure 4.

Figure 5 shows the bending vibrational temperature (T_V^B) and the antisymmetric vibrational temperature (T_V^{AS}) obtained from the IR emission intensity of CO_2 as a function of surface temperature. The T_V^B values are higher than those of T_V^{AS} on each surface, which means that the bending vibrational mode is more excited than the antisymmetric vibrational mode on each surface. However, the bending vibrational temperature at $T_S = 800$ K is much higher on Pd(111) ($T_V^B = 2200$ K) than on Pt(111) ($T_V^B = 1750$ K) and Rh(111) ($T_V^B = 1400$ K) as shown in Fig. 5(a). The higher vibrational temperatures on Pd(111), compared to Pt(111) or Rh(111), are in good agreement with the polycrystalline results of Coulston and Haller [6]. They argued that the excess bending

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excitation in the case of Pd might be due to the higher density of states at Fermi level compared to Pt or Rh. In fact, the antisymmetric vibrational temperature on Pd(111) was also rather high, and this can be corresponded to higher potential energy of the transition state (Table 1). Regarding Pt(111) and Rh(111), the bending vibrational temperature of Pt(111) was higher than that of Rh(111) and this can be related to the angle of O−C−O ($\angle_{OCO}$) in the transition state. Eichler [16] has also reported that the $\angle_{OCO}$ in the transition states on Pt(111) and Rh(111) were 109° and 112°, respectively, as shown in Table 1. In addition, the smaller the $\angle_{OCO}$ at the transition state, the larger the energy amount in the bending vibrational mode of desorbed CO_2 molecules. This can be explain the difference in the bending vibrational temperature on Pt(111) and Rh(111). On the other hand, in the case of Pd(111), the angle is relatively large like Rh(111). However, the product CO_2 molecules on Pd(111) are much more excited in both bending and antisymmetric vibrations than those on Pt(111) and Rh(111). At present, it is interpreted that the vibrational excited states on Pd(111) can be controlled mainly by the large excited energy ($E_{excited}$) than by the angle of activated complex in the transition state.

4. Conclusions

We measured the steady-state activity of CO oxidation over Pd(111), Pt(111), and Rh(111) surfaces in the temperature range of 400−900 K. Measurements and analyses of IR chemiluminescence of CO_2 formed during the steady-state CO oxidation supplied 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}). The order of the T_V^{AV} values of CO_2

formed during CO oxidation was as follows: Pd(111) > Pt(111) > Rh(111). It is suggested that the order corresponds to the potential energy of the transition state expected from the theoretical studies. The T_V^B values are higher than those of T_V^{AS} on each surface, which means that the bending vibrational mode is more excited than the antisymmetric vibrational mode. The order of the T_V^B was as follows: Pd(111) > Pt(111) > Rh(111), and this can be influenced by both the angle of the activated complex ($\angle_{OCO}$) and $E_{excited}$.

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Figure Captions

Figure 1. (a) The formation rate of CO_2 during CO oxidation on Pd(111), Pt(111), and Rh(111), and (b) the Arrhenius plot obtained from Fig. 1(a). The total flux of reactants of $(CO + O_2)$ was 8.2×10^{18} cm^{-2} s^{-1} at the $CO/O_2 = 1$. The values of Pd(111) and Pt(111) are taken from Ref. [12,13].

Figure 2. IR emission spectra of CO_2 desorbed by CO oxidation on Rh(111). The surface temperature (T_S) was 575–800 K. The flux conditions are as descried in Figure 1. The emission intensity was normalized per unit of CO_2 yield.

Figure 3. Surface temperature dependence of average vibrational temperature (T_V^{AV}) of CO_2 formed in CO oxidation on Pd(111), Pt(111) and Rh(111). The flux conditions are as described in Figure 1. The values of Pd(111) and Pt(111) are taken from Ref. [12,13].

Figure 4. Potential energy diagram for the CO oxidation on noble metal surfaces (Pd, Pt, Rh). The E_{ini} and E_{TS} are the potential energies in the initial and transition states, respectively. The E_a and $E_{excited}$ are the activation energy in CO oxidation and the excited energy of the product CO_2, respectively (see Table 1).

Figure 5. Surface temperature dependence of (a) bending vibrational temperature (T_V^B) and (b) antisymmetric vibrational temperature (T_V^{AS}) of CO_2 formed in CO oxidation on Pd(111) ($\blacksquare$,$\square$), Pt(111) ($\blacktriangle$,$\triangle$) and Rh(111) ($\bullet$,$\bigcirc$). The flux conditions are as described in Figure 1. The values of Pd(111) and Pt(111) are taken from Ref. [12,13].

Table 1 Potential energies in the initial (E_{ini}) and the transition (E_{TS}) states, the activation energies (E_a) and O–C–O angle ($\angle_{OCO}$) at the transition states for the CO oxidation over Pd(111), Pt(111) and Rh(111) surfaces taken from Ref. [16] [a].

	Pd(111)	Pt(111)	Rh(111)
E_{ini} [b] / eV	−2.38	−2.12	−2.91
E_{TS} / eV	−0.98	−1.38	−1.88
E_a [c] / eV	1.40	0.74	1.03
$\angle_{OCO}$	112°	109°	112°

[a] The zero of potential energies based on the free molecules (CO + 1/2O$_2$).

[b] The initial states means the states of CO and O adsorbed on surfaces.

[c] $E_a = E_{TS} - E_{ini}$

Figure 1. (a) The formation rate of CO_2 during CO oxidation on Pd(111), Pt(111), and Rh(111), and (b) the Arrhenius plot obtained from Fig. 1(a). The total flux of reactants of $(CO+O_2)$ was 8.2×10^{18} cm^{-2} s^{-1} at the $CO/O_2 = 1$. The values of Pd(111) and Pt(111) are taken from Ref. [12,13].

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Figure 5. Surface temperature dependence of (a) bending vibrational temperature (T_V^B) and (b) antisymmetric vibrational temperature (T_V^{AS}) of CO_2 formed in CO oxidation on Pd(111) (■,□), Pt(111) (▲,△) and Rh(111) (●,○). The flux conditions are as described in Figure 1. The values of Pd(111) and Pt(111) are taken from Ref. [12,13].