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# Vibrationally excited $CO_2$ formed in CO + NO reaction on Pd(110) surface in high surface temperature range

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The infrared chemiluminescence spectra of $CO_2$ formed during steady-state CO + NO reaction over Pd(110) indicated that the temperature of the bending vibrational mode was much higher than that of the antisymmetric one at higher surface temperatures such as 800–850 K. Especially, in the high temperature range, more vibrationally excited $CO_2$ was formed from CO + NO reaction than $CO + O_2$ reaction. On the basis of the result, we propose the model structure of reaction intermediates for $CO_2$ formation in CO + NO reaction, which is different from that in $CO + O_2$ reaction.

**KEY WORDS:** dynamics; carbon dioxide; carbon monoxide; nitric oxide; infrared chemiluminescence; palladium.

## 1. Introduction

The reaction of CO and NO to form $CO_2$ and $N_2$ is one of the most important automobile exhaust control reactions catalyzed by noble metals such as Pd, Rh and Pt. Recently, there has been considerable interest in using Pd-only catalysts for three-way exhaust gas conversion [1]. Hence, a fundamental understanding of the reaction mechanism of the CO + NO reaction on Pd surfaces is of vital importance. Many ultra high vacuum (UHV) studies have focused on the nature of CO and NO chemisorption on single-crystal Pd surfaces [2–5], however, only a few groups have studied the steady-state CO + NO reaction over well-defined surfaces [6–10]. The utilization of single crystal surfaces can be useful for the elucidation of the reaction mechanism over heterogeneous catalysts. An effective method is an investigation of internal (vibrational and rotational) energy and translational energy of product molecules desorbed from the catalyst surface [8–15]. This is because the energy states of desorbed molecules can reflect the dynamics of catalytic reaction, which correspond to a transition state (i.e., structure of activated complex). The infrared chemiluminescence (IR emission) of the product $CO_2$ molecules from CO oxidation enables to analyze the vibrationally excited states [13–15]. 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 are desorbed [11,13–15]. Furthermore, the vibrational energy state of the product $CO_2$ has been found to depend on the surface structure [10,11]. So, information about the active sites can be obtained *in situ* from the IR emission spectra of $CO_2$ under steady-state catalytic reaction. Almost no work on the vibrational energy of $CO_2$ produced from CO + NO reaction on Pd and Pt surfaces has been performed, although Bald and Bernasek [12] found a rough similarity in the vibrational excitation between CO + NO and $CO + O_2$ reactions on a polycrystalline Pt surface.

Our group has reported IR chemiluminescence of $CO_2$ from the steady-state $CO + O_2$ and CO + NO reactions on single crystal Pd surfaces combined with kinetic results [10,11]. In the temperature range of 620–720 K, the average vibrational temperature of $CO_2$ from CO + NO reaction was almost the same as that from $CO + O_2$ reaction on both Pd(110) and Pd(111), and the vibrational temperature on Pd(111) was higher than that on Pd(110). Since the emission intensity analysis of the spectra can give the antisymmetric vibrational temperature and it is possible to estimate the bending vibrational temperature at the same time, we can discuss the structure of activated complex of $CO_2$ formation from the comparison between these two vibrational temperatures, although the details were not reported in our previous paper [10].

In this letter, the vibrational states of $CO_2$ from CO + NO reaction on Pd(110) are compared to those from $CO + O_2$ reaction at high temperature range ($>750$ K), which was not included in our previous paper [10]. This is because more vibrationally excited $CO_2$ from CO + NO reaction was significantly observed than that from $CO + O_2$ reaction in this high temperature range. The detailed analysis was carried out here, and we attempt to interpret this phenomenon in terms of the structure of the activated complex and the reaction mechanism. In addition, the activities are

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compared again between Pd(110) and Pd(111) [10], which will be useful to elucidate the mechanism of CO + NO reaction.

## 2. Experimental

A molecular-beam reaction system in combination with an FT-IR spectrometer (Thermo Electron, Nexus670; an InSb detector) was used to measure IR emission of product $CO_2$ molecules just desorbed during catalytic reaction on the metal surfaces [10,11]. The UHV chamber (base pressure $< 1.0 \times 10^{-9}$ Torr) was equipped with an $Ar^+$ ion gun for sample cleaning and a quadruple mass spectrometer (QMS, Pfeiffer Vacuum, QME200). Two free jet molecular-beam nozzles (0.1 mm diameter orifice) were used for the supply of reactant gases. The fluxes of the reactants were controlled by mass flow controllers. The CO and NO gases (the total flux was $8.2 \times 10^{18}$ $cm^{-2}$ $s^{-1}$: CO/NO ratio = 1) or the CO and $O_2$ gases (the total flux was $8.2 \times 10^{18}$ $cm^{-2}$ $s^{-1}$: $CO/O_2$ ratio = 1) were exposed to single crystal Pd surfaces (Pd(110) and Pd(111)). Steady-state CO + NO and $CO + O_2$ reactions were performed in the temperature range of 600–850 K. Another UHV chamber (base pressure $< 2.0 \times 10^{-10}$ Torr) equipped with the same molecular-beam reaction system, an $Ar^+$ ion gun, low energy electron diffraction (LEED) and a QMS was used to prepare the samples and to characterize Pd(110) and Pd(111) surfaces. Before the molecular-beam reaction, Pd(110) and Pd(111) were cleaned by a standard procedure ($O_2$ treatment, $Ar^+$ bombardment and annealing) [10,11].

The IR emission spectra of the $CO_2$ molecules desorbed from the surface were measured with 4 $cm^{-1}$ resolution. Because of the low resolution, no individual vibration–rotation lines are resolved. The IR emission spectra were analyzed on the basis of simulation of model spectra, yielding an average vibrational Boltzmann temperature ($T_V^{AV}$, i.e., an average temperature of antisymmetric stretch, symmetric stretch and bending modes), which could be estimated from analysis of the degree of the red-shift from the fundamental band (2349 $cm^{-1}$) [13,14]. Although the IR emission observed here is the antisymmetric stretch (AS) vibrational region, i.e., $(n_{SS}, n_B^l, n_{AS}) \rightarrow (n_{SS}, n_B^l, n_{AS} - 1)$, vibrational excitation levels of symmetric stretch ($n_{SS}$) and bending ($n_B$) also affect this region [11,13]. Here, $n_{SS}$, $n_B$ and $n_{AS}$ are the vibrational quantum number of each mode, and $l$ is the quantum number of vibrational angular momentum in linear molecules. Note that the emission intensity is normalized by the rate of $CO_2$ production. Thus, the emission intensity is related to extent of excitation in the antisymmetric stretch of $CO_2$, which is given by following equation [11]:

$$f \propto \exp(-\Delta E_V / k_B T_V^{AS}) \qquad (1)$$

Here, $f$ is the emission intensity normalized per unit $CO_2$ yield, $\Delta E_V$ is the energy spacing, $k_B$ is Boltzmann constant, and $T_V^{AS}$ is the antisymmetric vibrational temperature. From the steady-state results at high resolution (0.06 $cm^{-1}$) [13], it was able to deduce the vibrational temperature in each vibrational mode ($T_V^{SS}$, $T_V^B$, $T_V^{AS}$), where the superscripts, respectively, indicate symmetric stretch, bending and antisymmetric stretch. Here, steady-state $CO + O_2$ reaction on polycrystalline Pt foil was performed under the same conditions as reported previously [13] ($CO = O_2 = 4.1 \times 10^{18}$ $cm^{-2}$ $s^{-1}$), and the IR emission spectra of $CO_2$ molecules were measured with 4 $cm^{-1}$ resolution at surface temperature ($T_S$) of 900 K. This obtained spectrum was compared with the previous result ($T_V^{AS} = 1600$ K) [13], and the emission intensity normalized by the rate of $CO_2$ production is defined as $T_V^{AS}$ = 1600 K. The emission intensity and $T^{AS}$ were used as a standard for various conditions on Pd surfaces. On the basis of $T_V^{AS}$ and $T_V$, it is possible to deduce the bending vibrational temperature ($T_V^B$) approximately. The relation between $T^{AV}$ and each vibrational temperature is represented by the equation below.

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

In this equation, 2 $T_V^B$ 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 [12,15], $T_V^B$ can be expected to be $(4T_V^{AV} - T_V^{AS})/3$. This assumption is plausible on the basis of the previous reports [12,13]. It should be added that $T_V^{AV}$, $T^{AS}$ and $T_V^B$ were used here as parameters characterizing the extent of the vibrational excitation of the product $CO_2$. It took about 30–90 min to measure the IR spectra with 2000–6000 scans. During the measurement, the activity was stable and therefore the results reflected the $CO_2$ states under steady-state conditions. The production rate of $CO_2$ was determined using the QMS spectrometer, and the amount of $N_2O$ formation (by-product) was checked by a gas chromatograph. In our case, the selectivity of $N_2O$ formation ($N_2O/(N_2O + N_2)$) was usually below a few percent (8% at most [10]).

## 3. Results and discussion

The turnover frequencies of $CO_2$ formation in CO + NO and $CO + O_2$ reactions over Pd(110) and Pd(111) surfaces are listed in table 1. Regarding CO + NO reaction, Pd(110) exhibited much higher TOF than Pd(111). This indicates that the CO + NO reaction on Pd surfaces is structure-sensitive under the steady-state reaction condition with the total pressure of $10^{-3}$ to $10^{-2}$ Torr. In the case of $CO + O_2$ reaction, Pd(110)

Table 1
Turnover frequencies (TOF in $s^{-1}$) of CO + NO and CO + $O_2$ reactions on Pd(110) and Pd(111)

| Surface temperature ($T_S$)/K | CO + NO | | CO + $O_2$ | |
|---|---|---|---|---|
| | Pd(110) | Pd(111) | Pd(110) | Pd(111) |
| 650 | 40 | 3 | 775 | 260 |
| 700 | 135 | 3 | 650 | 220 |
| 750 | 160 | 2 | 490 | 160 |
| 800 | 100 | 1 | 400 | 130 |
| 850 | 50 | 1 | 340 | 100 |

TOFs were obtained from the activity data in Ref. [10].

also showed higher TOF than Pd(111). From the comparison between Pd(110) and Pd(111), the difference of TOF in CO + NO reaction was much larger than that in CO + $O_2$ reaction. Although CO + $O_2$ reaction is also structure-sensitive, the level of structure sensitivity of CO + NO reaction is much more remarkable than that of CO + $O_2$ reaction. This is because the rate determining step of CO + NO reaction is NO dissociation [16], which can proceed on the stepped Pd(110) surface. On Pd(111) surface, the number of the NO dissociation sites, which can correspond to the step sites or defect sites, is too small, and this can explain very low TOF of CO + NO reaction. The activation energy of CO + NO reaction in the surface temperature range $T_S = 600$–650 K was determined to be 42.4 and 24.8 kcal/mol on Pd(110) and Pd(111), respectively. Goodman *et al.* [6,7] have reported that TOF of CO + NO reaction on Pd(110) and Pd(111) at 650 K was determined to be 9 and 35 $s^{-1}$, respectively. In addition, the activation energy on Pd(110) and Pd(111) was estimated to be 17.0 and 16.2 kcal/mol, respectively. The difference from our results is due to the difference in the reactant pressure. In our case, it was in the range of $10^{-3}$ to $10^{-2}$ Torr, and on the other hand, it was 2–17 Torr in the reported results [6,7]. They have reported that NO molecule dissociates immediately on more open surfaces (Pd(110) and Pd(100)) to form atomic nitrogen (N(a)). The N(a) species are bounded strongly on the surface, and inhibit the adsorption of NO and CO. Therefore, the activity (TOF) on Pd(110) and Pd(100) was lower than that on Pd(111), and the rate-determining step is the nitrogen desorption under the pressure condition reported. In particular, they have shown that 80% of the surface sites were covered by N(a) species during the reaction on Pd(100), while only 20% on Pd(111) [6]. Under our reaction conditions, the coverage of N(a) was very low ($\theta_N < 0.1$) above 650 K, and the rate-determining step is the NO dissociation, which means that oxygen atom supplied from the NO dissociation can react with CO immediately.

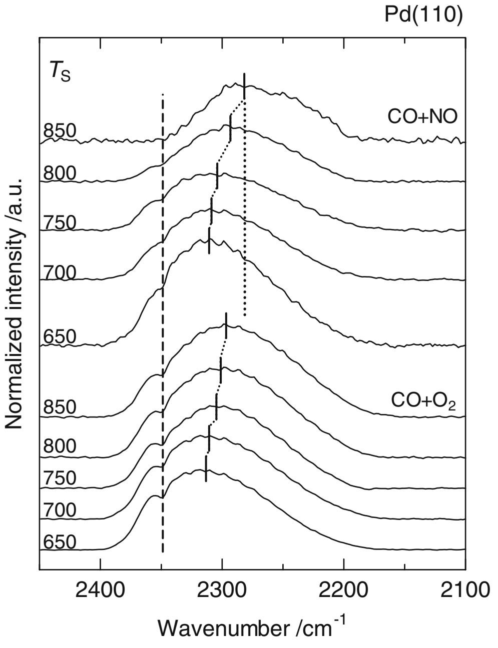

Figure 1. IR emission spectra of $CO_2$ desorbed by CO + NO and CO + $O_2$ reactions on Pd(110). The surface temperature ($T_S$) was 650–850 K. The IR emission spectrum centered at 2143 $cm^{-1}$ of the unreacted CO was subtracted [10]. The emission intensity was normalized per unit $CO_2$ yield.

Figure 1 shows the IR emission spectra of $CO_2$ molecules produced by CO + NO and CO + $O_2$ reactions on Pd(110) surface as a function of surface temperature ($T_S$). When $T_S$ became higher, more red-shift from the antisymmetric stretch fundamental band (2349 $cm^{-1}$) was observed in the emission spectra of $CO_2$. Especially, more red-shift was observed in CO + NO reaction at $T_S > 750$ K. The average vibrational temperature ($T_V^{AV}$) estimated from the red-shift is plotted as a function of the surface temperature in figure 2(a). $T_V^{AV}$ increased with increasing $T_S$ in both reactions on Pd(110). In the $T_S$ range of 650–750 K, $T_V^{AV}$ was almost the same in the CO + NO and CO + $O_2$ reactions, which is in good agreement with the previous result [10]. In higher temperature range above 750 K, however, $T_V^{AV}$ of CO + NO reaction was significantly higher than that of CO + $O_2$ reaction. The increase of $T_V^{AV}$ with increasing $T_S$ is related to the distribution of the excess energy [13–15], which is caused by the reaction of $CO(a) + O(a) \rightarrow CO_2(g)$, to the desorbed $CO_2$ molecules. The energy can also be distributed to the surface. In the case of higher surface temperature, it is interpreted that the distribution to the surface becomes smaller, and the distribution to desorbed $CO_2$ becomes larger. The agreement in $T_V^{AV}$ of CO + NO and CO + $O_2$ reactions in the range of 650–750 K means that the energy distribution is similar. On the other hand, at the higher reaction temperatures, vibrational energy of $CO_2$ in CO + NO reaction was higher than that in CO + $O_2$ reaction. This represents that $CO_2$ from CO + NO reaction is more vibrationally excited than that from CO + $O_2$ reaction. As discussed later, this is probably reflected by the energy states of adsorption species. In order to understand the vibrational energy distribution in more detail, we analyzed the distribution to each vibrational mode.

Figure 2(b) and (c) shows $T_V^{AS}$ and $T_V$ derived from IR emission intensity of $CO_2$ as a function of $T_S$ in CO + $O_2$ and CO + NO reactions, respectively. $T_V^{AS}$ was always higher than $T_V^B$ under all the surface temperatures in CO + $O_2$ reaction (figure 2(b)). This represents that the antisymmetric vibrational mode is more excited than the bending vibrational mode. This behavior can be explained by the structure of activated complex of $CO_2$ formation over Pd(110) [11]. In contrast, in the case of CO + NO reaction, $T_V^{AS}$ was higher than $T_V^B$ at $T_S = 650$ K, however, in higher surface temperature range, $T_V^{AS}$ decreased and $T_V^B$ increased drastically with increasing $T_S$ (figure 2(c)). These behaviors are much different from the case of CO + $O_2$ reaction, which means that the more excited mode changed from antisymmetric to bending vibrational mode at the higher surface temperatures. The change of the excited vibrational mode occurred at 750 K, where the TOF of CO + NO reaction was maximum (table 1). These results suggest that the structure of activated complex of $CO_2$ formation is much dependent on $T_S$.

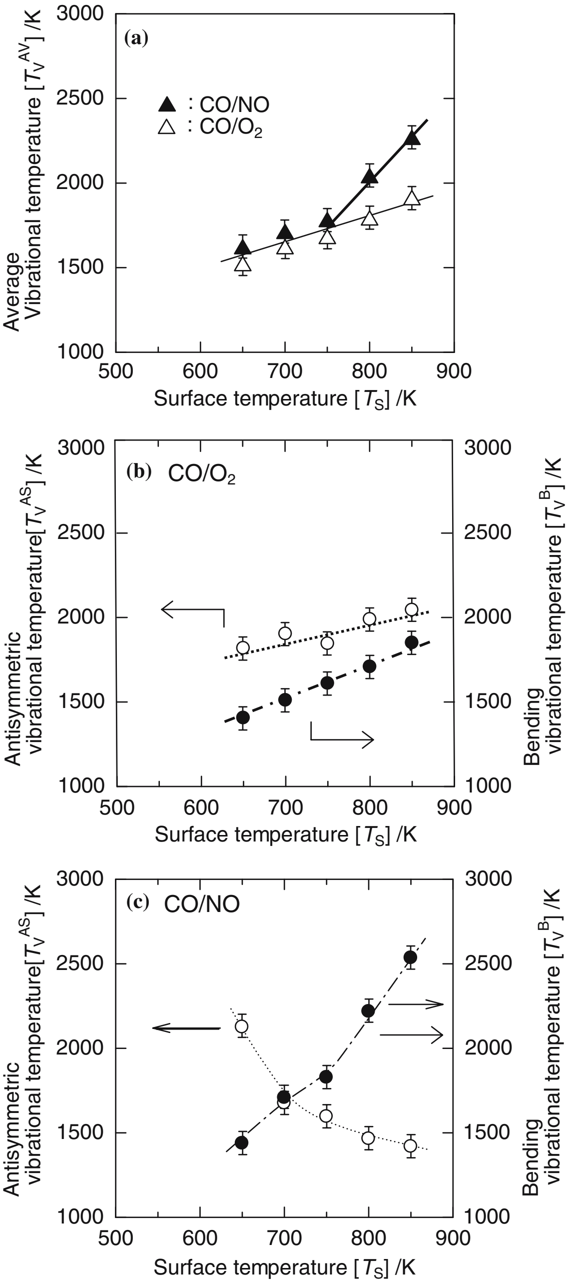

Figure 2. Surface temperature dependence of (a) average vibrational temperature ($T_V^{AV}$) of $CO_2$ formed in CO + NO and CO + $O_2$ reactions, antisymmetric vibrational temperature ($T_V^{AS}$) and bending vibrational temperature ($T_V^B$) in (b) CO + $O_2$ and (c) CO + NO reactions on Pd(110).

From the comparison between CO + NO and CO + $O_2$ reactions in terms of $T_V^{AV}$, it was found that $CO_2$ in CO + NO reaction was more vibrationally excited than that in CO + $O_2$ reaction at the higher reaction temperatures (800–850 K). At these surface temperatures, CO coverage ($\theta_{CO}$) can be very small ($\theta_{CO} \ll 0.01$) in both reactions, and oxygen coverage ($\theta_O$) in CO + $O_2$ reaction is approaching almost saturation level ($\theta_O \sim 0.5$) [17]. On the other hand, $\theta_O$ in CO + NO reaction can be very small, because the rate-determining step is NO dissociation [16]. Generally, it has been reported that the vibrational excitation became higher with increasing $\theta_O$ in CO + $O_2$ reaction on a polycrystalline Pd surface [15] and in CO + NO reaction on a polycrystalline Pt surface [12]. However, $T^{AV}$ in CO + NO reaction is higher than that in CO + $O_2$ reaction in the high temperature range (figure 2(a)), although $\theta_O$ is higher in CO + $O_2$ reaction. Therefore, no clear conclusion on the $\theta_O$ effect on Pd(110) can be done at the present stage.

The further analysis of $CO_2$ emission spectra indicated that bending vibrational mode was more excited than antisymmetric vibrational mode (figure 2(c)). This means that the activated complex of $CO_2$ formation in CO + NO reaction has more bent form than that in CO + $O_2$ reaction. The structure of activated complex can be strongly influenced by the adsorption sites of CO and O. The adsorption site of CO on Pd(110) at higher temperature is thought to be bridge site of the row in the first layer [2]. In contrast, the most stable adsorption site for atomic oxygen is threefold hollow site [18] as shown in figure 3. Since the angle $\theta_{CO+O2}$ described in figure 3(a) is much higher than 90°, it is expected that the activated complex formed from the reaction between the adsorbed CO and O can have a little bent structure. Judging from very high bending vibrational temperature of CO + NO reaction, the activated complex should have more bent structure. One possible interpretation is the activated complex formed from the reaction of the adsorbed CO with oxygen atom located on the first layer (figure 3(b)). On the basis of the report on the adsorption energy of oxygen atom on the various sites over Pd(110) [18], bridged oxygen atom on the first layer has

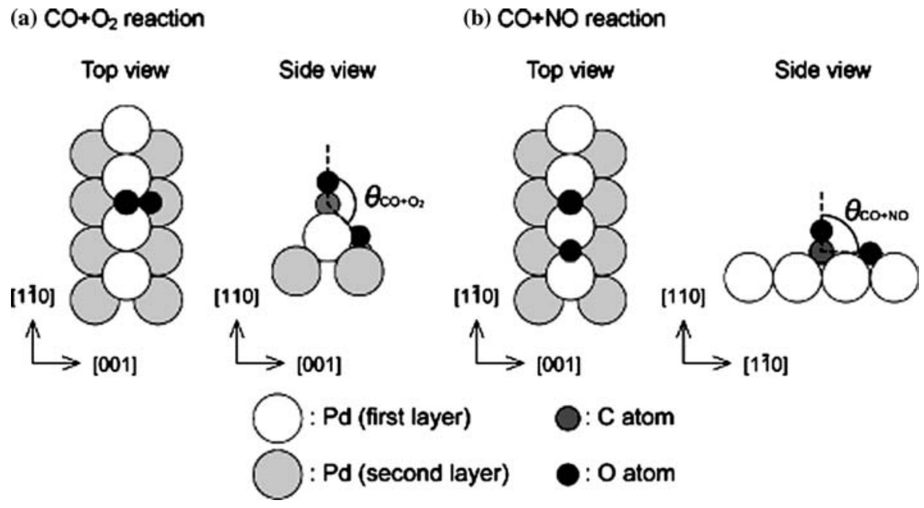

Figure 3. Models of adsorption sites of CO and O in (a) CO + $O_2$ and (b) CO + NO reactions high surface temperature range over Pd(110).

1.1 eV higher energy than that on threefold hollow site described in figure 3(a). This means that the energy state of adsorbed CO and O in CO + NO reaction is higher than that in CO + $O_2$ reaction, which can be related to the result that $T_V^{AV}$ of CO + NO was higher than that of CO + $O_2$ in the high surface temperatures.

Another possible explanation is that the dynamics of $CO_2$ formation can be different between the CO + NO and CO + $O_2$ reactions, although the same equation (CO(a) + O(a) → $CO_2$) is used in the kinetics of $CO_2$ formation. In fact, the $T_V^B$ and $T_V^{AS}$ values were different at the high surface temperatures (800 and 850 K) (figure 2(b) and (c)). In CO + $O_2$ reaction, adsorbed oxygen is accommodated to the surface, while the surface residence time of CO(a) is very short at higher surface temperatures [11]. In CO + NO reaction, however, oxygen atom from NO dissociation, which reacts with CO immediately after the formation, may not be accommodated to the surface, and such hot O atom can affect the extent of the vibrational excitation. Such dynamic roles of nascent hot oxygen have also been observed in other reaction systems [19–22]. Further investigation is necessary for the elucidation of mechanism for the excitation of the vibrational modes of the activated complex.

## 4. Conclusions

Turnover frequencies (TOF) of $CO_2$ formation during steady-state CO + NO reaction were measured over Pd(110) and Pd(111) in the pressure range of $10^{-3}$ to $10^{-2}$ Torr. The activity of Pd(110) was much higher than that of Pd(111) at the low pressure condition, which means that the rate-determining step is NO dissociation on the stepped Pd(110). The difference of TOF between both Pd surfaces in CO + NO reaction was much larger than that in CO + $O_2$ reaction.

From the analysis of the IR emission spectra of $CO_2$ on Pd(110), $T_V^{AV}$ of CO + NO reaction was higher than $T_V^{AV}$ of CO + $O_2$ reaction in high reaction temperature range, and $T_V^{AS}$ was higher than $T_V^B$ in CO + $O_2$ reaction at all the surface temperatures. In contrast, $T_V^B$ was much higher than $T_V^{AS}$ in CO + NO reaction at higher surface temperatures (800 and 850 K). This indicates that the structure of the activated complex of $CO_2$ formation in CO + NO reaction is more bent than that in CO + $O_2$ reaction, and the reaction dynamics of $CO_2$ formation are different between both reactions at the higher surface temperatures.

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