Infrared Chemiluminescence Study of CO_2 Formation in CO + NO Reaction on Pd(110) and Pd(111) Surfaces

Kenji Nakao, Shin-ichi Ito, Keiichi Tomishige,* and Kimio Kunimori*

Institute of Materials Science, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan Received: June 1, 2005; In Final Form: July 29, 2005

Infrared (IR) chemiluminescence studies of CO_2 formed during steady-state CO + NO reaction over Pd(110) and Pd(111) surfaces were carried out. Kinetics of the CO + NO reaction were studied over Pd(110)using a molecular-beam reaction system in the pressure range of $10^{-2}-10^{-1}$ Torr. The activity of the CO + NO reaction on Pd(110) was much higher than that of Pd(111), which was quite different from the result of other experiments under a higher pressure range. On the basis of the experimental data on the dependence of the reaction rate on CO and NO pressures and the reaction rate constants obtained by using a reaction model, the coverage of NO, CO, N, and O was calculated under various flux conditions. From the analysis of IR emission spectra in the $CO + O_2$ reaction on Pd(110) and Pd(111), the antisymmetric vibrational temperature (T_V^{AS}) was seen to be higher than the bending vibrational temperature (T_V^B) on Pd(110). In contrast, T_V^B was higher than T_V^{AS} on Pd(111). These behaviors suggest that the activated complex for CO₂ formation is more bent on Pd(111) than that on Pd(110), which is reflected by the surface structure. Both $T_{\rm V}^{\rm B}$ and $T_{\rm V}^{\rm AS}$ for the CO + O₂ reaction on Pd(110) and Pd(111) increased gradually with increasing surface temperature ($T_{\rm S}$). On the other hand, in the case of the CO + NO reaction on Pd(110) and Pd(111), $T_{\rm V}^{\rm AS}$ decreased and T_V^B increased significantly with increasing T_S . T_V^B was lower than T_V^{AS} at lower T_S , while T_V^B was higher than T_V^{AS} at higher T_S . Comparison of the data obtained for the two reactions indicates that T_V^{B} in the CO + NO reaction on Pd(110) at $T_{\rm S} = 800$ and 850 K is much higher than that in the CO + O₂ reaction on Pd(110).

1. Introduction

The reaction of CO and NO to form CO₂ and N₂ 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 ultrahigh 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.⁶⁻¹³ The utilization of single-crystal surfaces can be useful for the elucidation of the reaction mechanism over heterogeneous catalysts. To obtain the information on the reaction mechanism, an effective method is spectroscopic observations of reaction intermediates.8 Another method is an investigation of internal (vibrational and rotational) energy and translational energy of product molecules desorbed from the catalyst surface.9-26 This is because the energy states of the desorbed molecules can reflect the dynamics of catalytic reaction, which can correspond to a transition state (i.e., structure of activated complex). The infrared chemiluminescence (IR emission) of the product molecules from catalytic reaction enables one to analyze the vibrationally excited states.¹⁸⁻²⁵ Analysis of the vibrational states can give information on the structure of the activated CO₂ complex (i.e., the dynamics of CO oxidation)

from which the gas-phase molecules were desorbed.^{16,18–25} Furthermore, the vibrational energy state of the product CO_2 has been found to depend on the surface structure.^{13–16} So, information about the active sites can be obtained in situ from the IR emission spectra of CO_2 under steady-state catalytic reactions.

Our group has reported IR chemiluminescence of CO₂ from the steady-state $CO + O_2$ and CO + NO reactions on singlecrystal Pd surfaces combined with kinetic results.¹³⁻¹⁶ It has been suggested that the activated complex of CO₂ formation (i.e., the transition state of CO_2 formation from CO(a) + O(a)) had a more bent structure on Pd(111) and a relatively linear structure on Pd(110) because CO₂ from Pd(111) was more vibrationally excited than CO₂ from Pd(110).^{13–16} The results indicated that the IR chemiluminescence method can provide direct energetic evidence of the reaction mechanism and the activated complex of CO₂ formation. Almost no work on the vibrational energy of CO_2 produced from the CO + NO reaction on Pt and Pd surfaces has been performed, although Bald and Bernasek¹⁷ found a rough similarity in the vibrational excitation between CO + NO and $CO + O_2$ reactions on a polycrystalline Pt surface.

In this work, we have studied dynamics and kinetics of CO_2 formation during the CO + NO reaction over single-crystal Pd(110) and Pd(111) surfaces. Almost no study has been done on the comparison of the CO + NO activity on single-crystal Pd surfaces with different planes. Goodman et al.^{6–8} have reported that Pd(111) is more active than Pd(100) and Pd(110) at the reactant pressure of 2–17 Torr. First, we elucidate the kinetics of the CO + NO reaction on Pd(110) compared with

^{*}Authors to whom correspondence should be addressed. E-mail: kunimori@ims.tsukuba.ac.jp (K.K.); tomi@tulip.sannet.ne.jp (K.T.). Telephone: +81-29-853-5026. Fax: +81-29-855-7440.

Pd(111). Second, we elucidate partial pressure ($P_{\rm CO}$, $P_{\rm NO}$) and surface temperature ($T_{\rm S}$) dependence on the dynamics of the reaction, and the results are compared with those of CO + O₂ reactions on Pd(110) and Pd(111).

2. Experimental Section

A molecular-beam reaction system in combination with a FT-IR spectrometer (Thermo Electron, Nexus670; an InSb detector) was used to measure IR emission of product CO₂ molecules just desorbed during catalytic reaction on the metal surfaces.^{13–16} A UHV chamber (base pressure $< 1.0 \times 10^{-9}$ Torr) was equipped with an Ar⁺ ion gun for sample cleaning and a quadrupole 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 (total flux was 2.1 \times 10^{18} -2.1 × 10^{19} cm⁻² s⁻¹, CO/NO = 0.25-4) or the CO and O_2 gases (total flux was 8.2×10^{18} cm⁻² s⁻¹, CO/ $O_2 = 1$) were exposed to single-crystal Pd surfaces (Pd(110) and Pd(111)). Steady-state CO + NO and $CO + O_2$ reactions (the pressure range at the flux conditions = $10^{-2} - 10^{-1}$ Torr) were performed in the temperature range of 500-900 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 (O2 treatment, Ar⁺ bombardment, and annealing).¹³⁻¹⁶ After cleaning, the sharp (1×1) LEED pattern was observed, and the reaction occurs on the (1 \times 1) structure under steady-state conditions.¹²

The IR emission spectra of the CO₂ molecules desorbed from the surface were measured with 4 cm⁻¹ resolution. Because of the low resolution (4 cm⁻¹ resolution), no individual vibrationrotation lines were 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 the 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).^{18,19} Although the IR emission observed here is the antisymmetric stretch (AS) vibrational region, i.e., $(n_{SS},$ $n_{\rm B}{}^l, n_{\rm AS}) \rightarrow (n_{\rm SS}, n_{\rm B}{}^l, n_{\rm AS} - 1)$, vibrational excitation levels of symmetric stretch (n_{SS}) and bending (n_B) also affect this region.^{16,18} 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 CO₂ production. Thus, the emission intensity is related to the extent of excitation in the antisymmetric stretch of CO₂, 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 CO₂ yield, ΔE_V is the energy spacing, k_B is Boltzmann constant, and T_V^{AS} is the antisymmetric vibrational temperature. From the steadystate results at high resolution (0.06 cm⁻¹),¹⁸ it was possible to deduce the energy distribution 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, the steady-state CO + O₂ reaction on polycrystalline Pt foil was performed under the same conditions as reported previously¹⁸



Figure 1. The formation rate of CO_2 during the CO + NO reaction on Pd(110). (a) CO/NO ratio = 0.25-2.0 at the fixed CO flux and (b) CO/NO ratio = 0.5-3.0 at the fixed NO flux.

(CO = $O_2 = 4.1 \times 10^{18} \text{ cm}^{-2} \text{ s}^{-1}$), and the IR emission spectra of CO₂ molecules were measured with 4 cm⁻¹ resolution at surface temperature (T_S) of 900 K. This obtained spectrum was compared with the previous results ($T_V^{AS} = 1600 \text{ K}$),¹⁸ and the emission intensity normalized by the rate of CO₂ production was defined as $T_V^{AS} = 1600 \text{ K}$. This emission intensity and T_V^{AS} were used as a standard for various conditions on Pd surfaces. On the basis of T_V^{AS} and T_V^{AV} , it is possible to deduce the bending vibrational temperature (T_V^B) approximately. The relation between T_V^{AV} and each vibrational temperature is represented as the equation below.

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

In this equation, $2T_V{}^B$ corresponds to the two degenerate bending vibrational modes. Assuming that $T_V{}^B$ is equal to $T_V{}^{SS}$ because of the Fermi resonance, ${}^{17,20} T_V{}^B$ can be expected to be $(4T_V{}^{AV} - T_V{}^{AS})/3$. This assumption is plausible on the basis of the previous reports.^{18,20} It should be added that $T_V{}^{AV}$, $T_V{}^{AS}$, and $T_V{}^B$ were used here as parameters characterizing the extent of the vibrational excitation of the product CO₂. 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 CO₂ states under steady-state conditions. The production rate of CO₂ was determined using a QMS spectrometer, and the amount of N₂O formation (byproduct) was checked by a gas chromatograph. In our case, the selectivity of N₂O formation (N₂O/(N₂O + N₂)) was usually below a few percent (8% at most¹³).

3. Results and Discussion

3.1. Kinetics of the CO + NO Reaction on Pd(110). Figure 1 shows the rate of CO_2 formation in steady-state CO + NO reactions on Pd(110) as a function of surface temperature under various partial pressure conditions. In particular, Figure 1a and b exhibit the dependence of the reaction rate on NO pressure under the fixed CO flux and on CO pressure under the fixed NO flux, respectively. Under all the partial pressure conditions, the formation rate of CO₂ increased with increasing the surface temperature (T_S) in the lower temperature range, exhibited a maximum, and then decreased with further increasing $T_{\rm S}$. The same behavior has also been observed in the $CO + O_2$ reaction.^{16,27} Here, we call the temperature, where the highest CO_2 rate is observed, as T_S^{max} . From these results, it is found that the reaction order with respect to NO and CO is about zero at surface temperatures (such as 600 K) lower than $T_{\rm S}^{\rm max}$ under all conditions. On the other hand, at surface temperatures (such as 800 K) higher than $T_{\rm S}^{\rm max}$,

TABLE 1: Kinetic Parameters for the CO + NO and CO + O_2 Reactions on Pd(110)

reaction equation	rate constant/s ⁻¹	ν/s^{-1}	$E_{\rm a}/{\rm kcal}~{\rm mol}^{-1}$	ref
(3), (21)	k_{CO}^{des}	1×10^{17}	35.5	2, 3
(4)	$k_{\rm NO}^{\rm des}$	1×10^{17}	36.0	5
(5)	$k_{\rm NO}^{\rm dis}$	2.7×10^{14}	34.2	this work
(6)	$k_{\rm N}^{\rm des}$	6.5×10^{13}	29.0	29, 32
(7), (23)	$k_{\rm r}^{\rm r_2}$	7.1×10^{15}	33.6	this work
reaction		initial sticking		
equation		coefficient		ref
(3), (21)		$s_{\rm CO} = 0.93$		4
(4)		$s_{\rm NO} = 0.9$		4
(22)		$s_{\Omega_2} = 0.86$		34

the reaction order of NO and CO is determined to be approximately 0.5.

To understand the kinetics of the CO + NO reaction on the Pd surface under steady-state conditions, we calculated the coverage of adsorbate species on the basis of a reaction model. One of the most probable model mechanisms of the CO + NO reaction on Pd surface^{28,29} is as follows (for a review of other possible mechanisms, see ref 30):

$$CO(g) + V \leftrightarrow CO(a)$$
 (3)

$$NO(g) + V \leftrightarrow NO(a)$$
 (4)

$$NO(a) + V \rightarrow N(a) + O(a)$$
 (5)

$$2N(a) \rightarrow N_2(g) + 2V \tag{6}$$

$$CO(a) + O(a) \rightarrow CO_2(g) + 2V$$
 (7)

where V is a vacant site. In this model, it is assumed that the rate-determining step is NO dissociation (eq 5), and this is based on the previous report.³¹ Furthermore, the elementary steps (3) and (4) are considered to be more rapid than the reaction rate, and the adsorption of CO and NO reaches equilibrium. Using the steady-state method, we can derive the following equations for adsorbate coverage.

$$d\theta_{\rm CO}/dt = f_{\rm CO}s_{\rm CO}\theta_{\rm V} - k_{\rm CO}^{\rm des}\theta_{\rm CO}$$
(8)

$$d\theta_{\rm NO}/dt = f_{\rm NO}s_{\rm NO}\theta_{\rm V} - k_{\rm NO}^{\rm des}\theta_{\rm NO}$$
(9)

$$d\theta_{\rm N}/dt = k_{\rm NO}^{\rm dis}\theta_{\rm NO}\theta_{\rm V} - k_{\rm N_2}^{\rm des}\theta_{\rm N^2}$$
(10)

$$\mathrm{d}\theta_{\mathrm{O}}/\mathrm{d}t = k_{\mathrm{NO}}^{\mathrm{dis}}\theta_{\mathrm{NO}}\theta_{\mathrm{V}} - k_{\mathrm{r}}\theta_{\mathrm{CO}}\theta_{\mathrm{O}} \tag{11}$$

where *f* and *s* are the flux of reactants to the surface and the initial sticking coefficients, respectively. The k^{des} , k^{dis} , and k_r are the rate constants for CO, NO, and N₂ desorption, NO dissociation, and the reaction of CO with the oxygen atom to form CO₂, respectively. The fraction of vacant sites is denoted as $\theta_{\rm V} = (1 - \theta_{\rm CO} - \theta_{\rm NO} - \theta_{\rm N} - \theta_{\rm O})$. Here, we adopted the reported rate constants for $k_{\rm CO}^{\text{des}}$, $k_{\rm NO}^{\text{des}}$, and $k_{\rm N_2}^{\text{des}}$ (Table 1). In addition, the rate constant k_r can be determined on the basis of a similar calculation for the CO + O₂ reaction on Pd(110), as will be shown in section 3.2. The initial sticking coefficients of CO and NO are also listed in Table 1. On the basis of the above equations and the steady-state method $(d\theta_{\rm CO}/dt = d\theta_{\rm NO}/dt = d\theta_{\rm O}/dt = d\theta_{\rm O}/dt = 0)$, the coverage of each ad-

sorbed species during the reaction can be calculated as follows. At lower surface temperature range:

$$\theta_{\rm CO} = \frac{f_{\rm CO} s_{\rm CO} k_{\rm NO}^{\rm des} (1 - \theta_{\rm N})}{f_{\rm CO} s_{\rm CO} k_{\rm NO}^{\rm des} + f_{\rm NO} s_{\rm NO} k_{\rm CO}^{\rm des} + k_{\rm CO}^{\rm des} k_{\rm NO}^{\rm des}}$$
(12)

$$\theta_{\rm NO} = \frac{f_{\rm NO} s_{\rm NO} k_{\rm CO}^{\rm des} (1 - \theta_{\rm N})}{f_{\rm CO} s_{\rm CO} k_{\rm NO}^{\rm des} + f_{\rm NO} s_{\rm NO} k_{\rm CO}^{\rm des} + k_{\rm CO}^{\rm des} k_{\rm NO}^{\rm des}}$$
(13)

$$\theta_{\rm N} = \sqrt{r_{\rm CO_2}/k_{\rm N_2}^{\rm des}} \tag{14}$$

$$\theta_{\rm O} = \frac{\gamma_{\rm CO_2}}{k_{\rm r}\theta_{\rm CO}} \tag{15}$$

At higher surface temperature range:

$$\theta_{\rm CO} = \frac{f_{\rm CO} s_{\rm CO} k_{\rm r} + \sqrt{(f_{\rm CO} s_{\rm CO} k_{\rm r})^2 - 4 f_{\rm CO} s_{\rm CO} k_{\rm CO}^{\rm des} k_{\rm r} r_{\rm CO_2}}{2 k_{\rm CO}^{\rm des} k_{\rm r}}$$
(16)

 $\theta_{\rm NO} =$

$$\frac{f_{\rm CO}s_{\rm CO}f_{\rm NO}s_{\rm NO}k_{\rm r} + f_{\rm NO}s_{\rm NO}\sqrt{\left(f_{\rm CO}s_{\rm CO}k_{\rm r}\right)^2 - 4f_{\rm CO}s_{\rm CO}k_{\rm CO}^{\rm des}k_{\rm r}r_{\rm CO_2}}{2f_{\rm NO}s_{\rm NO}k_{\rm NO}^{\rm des}k_{\rm r}}$$
(17)

$$\theta_{\rm N} = \sqrt{r_{\rm CO_2}/k_{\rm N_2}^{\rm des}} \tag{18}$$

$$\theta_{\rm O} = \frac{r_{\rm CO_2}}{k_{\rm r}\theta_{\rm CO}} \tag{19}$$

Here, r_{CO_2} is introduced to the above equations on the basis of $r_{CO_2} = k_r \theta_{CO} \theta_O$, which is the formation rate of CO₂ in CO + NO reactions, and the values as a function of T_S are given from the experimental results shown in Figure 1. In the calculation using θ_V , we have considered the fact that θ_O is negligible in the CO + NO reaction at lower surface temperatures because the O atoms are removed by CO(a) from the surface immediately after the NO dissociation.²⁹ On the other hand, we have considered the fact that θ_{CO} , θ_{NO} , and θ_N are negligible at higher surface temperatures because the desorption rate is much higher than the reaction rate.³³

The calculation results of the coverage of adsorbates under various CO/NO fluxes at $T_{\rm S} = 600, 675$, and 800 K are shown in Figure 2. At $T_{\rm S} = 600$ K, the coverage of NO and CO adsorption is strongly influenced by the flux. When the NO flux increases, θ_{NO} and θ_{O} increase; on the other hand, θ_{CO} decreases and $\theta_{\rm N}$ is almost constant (Figure 2a). In the case of the CO flux dependence at 600 K (Figure 2d), the behavior is similar. When the CO flux decreases, θ_{CO} decreases, and θ_{NO} and θ_0 increase. In contrast, in the NO flux dependence at 800 K (Figure 2c), θ_0 is much higher than θ_{NO} , θ_{CO} , and θ_N . When the NO flux increases, $\theta_{\rm O}$ and $\theta_{\rm NO}$ increase significantly. In contrast, when the CO flux increases, θ_{CO} increases linearly and θ_0 decreases gradually (Figure 2f). At $T_s = 800$ K, the positive order with respect to NO can be explained by the gradual increase of θ_0 , and that with respect to CO can also be explained by the proportional increase of θ_{CO} and gradual decrease of θ_0 . At $T_S = 675$ K, the coverage of adsorbed species can be located between $T_{\rm S} = 600$ and 800 K. Furthermore, from the calculation at each reaction temperature, the temperature



Figure 2. Kinetics of the CO + NO reaction on Pd(110) under various CO/NO fluxes. The adsorbate coverage as a function of NO flux at (a) $T_{\rm S} = 600$ K, (b) $T_{\rm S} = 675$ K, and (c) $T_{\rm S} = 800$ K and as a function of CO flux at (d) $T_{\rm S} = 600$ K, (e) $T_{\rm S} = 675$ K, and (f) $T_{\rm S} = 800$ K.

dependence of the rate constant for NO dissociation can be determined by using eq 20.

$$k_{\rm NO}^{\rm dis} = \frac{r_{\rm CO_2}}{\theta_{\rm NO}\theta_{\rm V}} \tag{20}$$

This gives the preexponential factor $\nu = 2.7 \times 10^{14} \text{ s}^{-1}$ and activation energy $E_a = 34.2 \text{ kcal/mol}$, as listed in Table 1. This activation energy is close to the reported value $E_a = 31.5 \text{ kcal/mol}$.³⁴

3.2. Comparison with Kinetics of the CO + O_2 Reaction on Pd(110). The mechanism of the CO + O_2 reaction on a Pd surface is well-known to be as follows:²⁷

$$CO(g) + V \leftrightarrow CO(a)$$
 (21)

$$O_2(g) + 2V \rightarrow 2O(a)$$
 (22)

$$CO(a) + O(a) \rightarrow CO_2(g) + 2V$$
 (23)

It is possible to write equations regarding the coverage of each intermediate as shown below.^{37,38}

$$d\theta_{\rm CO}/dt = f_{\rm CO}s_{\rm CO} \left(1 - \theta_{\rm CO} - \theta_{\rm O}\right) - k_{\rm CO}^{\rm des}\theta_{\rm CO} - r_{\rm CO_2} \quad (24)$$

$$d\theta_0/dt = 2f_{O_2}s_{O_2}(1 - \theta_{CO} - \theta_0)^2 - r_{CO_2}$$
(25)



Figure 3. Kinetics of the CO + O_2 reaction on Pd(110). The total flux of reactants was 8.2×10^{18} molecules cm⁻² s⁻¹ at the CO/O₂ ratio = 1.

where the rate of O₂ desorption is small enough to be neglected.^{27,37,38} The CO₂ formation rate, r_{CO_2} , was obtained from the experimental results shown in Figure 3. The initial sticking coefficients of CO and O2 and the kinetic parameters used are also listed in Table 1. The results of the coverage calculation in the CO + O_2 reaction on Pd(110) are shown in Figure 3. It is known that, at temperatures lower than $T_{\rm S}^{\rm max}$, 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 $T_{\rm S}^{\rm max}$, the formation rate of CO₂ decreased gradually with increasing surface temperature, and this behavior is due to the drastic decrease of θ_{CO} . Generally, in the CO + O₂ reaction on the Pd surface at lower surface temperatures, the reaction order is -1with respect to CO and ± 1 with respect to O₂.²⁷ On the other hand, at higher temperatures, θ_{CO} can be very small ($\theta_{CO} \ll$ 0.01) and oxygen coverage (θ_0) approaches the saturation level $(\theta_{\rm O} \sim 0.5)$.³⁴ Therefore, it is thought that the reaction order is +1 and 0 with respect to CO and O₂, respectively. The formation rate of CO₂ can be plotted as a function of inverse surface temperature in Arrhenius form, originated from Figure 3. From the temperature range $T_{\rm S} = 500-625$ K, the preexponential factor, ν , and apparent activation energy (E_a) of eq 23 are estimated to be 7.1×10^{15} s⁻¹ and 33.6 kcal/mol, respectively, as listed in Table 1. The rate constant for CO(a) + O(a) reaction in the $CO + O_2$ reaction can be applied to that in the CO +NO reaction (eq 7). Furthermore, the important point is that the CO_2 formation rate for the CO + NO reaction was much lower than that of the CO + O_2 reaction (Figures 1 and 3). Because the CO coverage in both reactions is similar, the difference in reaction rates can be due to that in the oxygen coverage.

3.3. Infrared (IR) Emission Spectra of CO₂ Desorbed by the CO + NO Reaction under Different Partial Pressures. The IR emission spectra of CO_2 formed by the CO + NOreaction were measured at $T_{\rm S} = 675$ K (below $T_{\rm S}^{\rm max}$) and $T_{\rm S} =$ 800 K (above $T_{\rm S}^{\rm max}$) (Figure 1). Figure 4 shows IR emission spectra of CO_2 molecules produced by the CO + NO reaction on Pd(110) for various NO fluxes at a fixed CO flux. The CO₂ emission spectra were observed in the region of 2400-2200 cm^{-1} , while the emission spectrum centered at 2143 cm^{-1} is due to the IR emission of the unreacted CO, which was scattered from the surface. At $T_{\rm S} = 675$ K, the degree of the red-shift from the fundamental band (2349 cm⁻¹) was almost the same under the various NO fluxes; however, the emission intensity became larger with increasing NO flux. On the other hand, at $T_{\rm S} = 800$ K, when the NO flux was decreased in the range of $2.0-8.2 \times 10^{18} \text{ cm}^{-2} \text{ s}^{-1}$, more red-shift from 2349 cm⁻¹ was observed in the emission spectra of CO₂. This degree of red-



Figure 4. IR emission spectra of CO₂ desorbed by the CO + NO reaction on Pd(110). The surface temperature ($T_{\rm S}$) was (a) 675 K and (b) 800 K. The NO flux was 2.0–12.3 × 10¹⁸ molecules cm⁻² s⁻¹ at the fixed CO flux (4.1 × 10¹⁸ molecules cm⁻² s⁻¹). The emission intensity was normalized per unit of CO₂ yield.



Figure 5. IR emission spectra of CO₂ desorbed by the CO + NO reaction on Pd(110). The surface temperature ($T_{\rm S}$) was (a) 675 K and (b) 800 K. The CO flux was 2.0–12.3 × 10¹⁸ molecules cm⁻² s⁻¹ at the fixed NO flux (4.1 × 10¹⁸ molecules cm⁻² s⁻¹). The emission intensity was normalized per unit of CO₂ yield.

shift was almost constant for the higher NO flux (above $8.2 \times 10^{18} \text{ cm}^{-2} \text{ s}^{-1}$). The emission intensity increased monotonically with increasing NO flux. Figure 5a and b show IR emission spectra of the CO flux dependence in the CO + NO reaction on Pd(110) at $T_{\rm S} = 675$ and 800 K. At both reaction temperatures, the degree of the red-shift from the fundamental band was almost constant under the various CO fluxes. The emission intensity became larger with increasing CO flux. From the analysis of the CO₂ emission spectra, information on the vibrational states of desorbed CO₂ can be obtained as shown below.

At first, the average vibrational temperature (T_V^{AV}) obtained from the red-shift in IR emission spectra of CO₂ at $T_S = 675$ and 800 K as a function of (a) NO flux and (b) CO flux is shown in Figure 6. Each T_V^{AV} value was much higher than T_S , and this indicates that the CO₂ formed is vibrationally excited. The T_V^{AV} value was not so changed under various flux conditions and surface temperatures. Next, T_V^{AS} and T_V^B obtained from the IR emission intensity of CO₂ as a function of NO flux at (a) $T_S = 675$ K and (b) $T_S = 800$ K are shown in Figure 7. At both surface temperatures, as the NO flux increased, T_V^{AS} increased and T_V^B decreased. T_V^{AS} at $T_S = 675$ K was higher than that at $T_S = 800$ K; on the other hand, T_V^B at $T_S = 675$ K was lower than that at $T_S = 800$ K. Although the average vibrational temperature was rather similar, it is found



Figure 6. (a) NO flux and (b) CO flux dependence of average vibrational temperature (T_V^{AV}) of CO₂ formed in the CO + NO reaction on Pd(110). The surface temperature (T_S) was 675 and 800 K. The flux conditions are as described in Figures 4 and 5.



Figure 7. NO flux dependence of antisymmetric vibrational temperature (T_V^{AS}) and bending vibrational temperature (T_V^B) in the CO + NO reaction on Pd(110). The surface temperature (T_S) was (a) 675 K and (b) 800 K. The flux conditions are as described in Figure 4.



Figure 8. CO flux dependence of antisymmetric vibrational temperature (T_V^{AS}) and bending vibrational temperature (T_V^B) in the CO + NO reaction on Pd(110). The surface temperature (T_S) was (a) 675 K and (b) 800 K. The flux conditions are as described in Figure 5.

that the vibrational states of desorbed CO₂ were very dependent on the NO flux conditions. At $T_{\rm S} = 675$ K, $T_{\rm V}^{\rm AS}$ is higher than $T_{\rm V}^{\rm B}$, and this means that the internal energy is distributed mainly in the antisymmetric vibrational mode. On the other hand, at $T_{\rm S} = 800$ K, $T_{\rm V}^{\rm AS}$ was lower than $T_{\rm V}^{\rm B}$, suggesting that the energy is distributed mainly to the bending vibrational modes.

Figure 8a and b show T_V^{AS} and T_V^B obtained from IR emission intensity of CO_2 as a function of CO flux at (a) $T_S =$ 675 K and (b) $T_{\rm S}$ = 800 K. At $T_{\rm S}$ = 675 K, the CO flux dependence of T_V^{AS} and T_V^B was similar to the NO flux dependence. However, at $T_{\rm S} = 800$ K, $T_{\rm V}^{\rm AS}$ and $T_{\rm V}^{\rm B}$ were almost constant under various flux conditions, although the tendency that T_V^B was higher than T_V^{AS} was common in both NO and CO flux dependences at $T_{\rm S} = 800$ K. This common phenomenon at $T_{\rm S} = 800$ K can be reflected by the coverage of adsorbed oxygen because the coverage of other adsorbed species was much lower than that of oxygen (Figure 2c and f). On the other hand, at $T_{\rm S} = 675$ K, the coverage of NO, CO, and the nitrogen atom was not low (Figure 2b and e), and this can make the excitation of the vibrational modes more complex. Zhdanov³⁵ has shown that the change in the energy distribution of the reaction products with increasing coverage can be related to lateral adsorbate-adsorbate interactions in the activated state for reaction.



Figure 9. The formation rate of CO₂ during the CO + NO reaction (CO/NO ratio = 1) on Pd(110) and Pd(111). The total flux of reactants (CO + NO) was 4.1×10^{18} molecules cm⁻² s⁻¹.

3.4. Structure-Sensitivity of the CO + NO Reaction on Pd(110) and Pd(111). Figure 9 shows the rate of CO_2 formed in the steady-state CO + NO reaction on Pd(110) and Pd(111) surfaces as a function of $T_{\rm S}$. The CO + NO reaction proceeded above 550 K, and the temperature dependence of the formation rate had maxima on both Pd surfaces, and the observed behavior on the $T_{\rm S}$ dependence was similar to that of Figure 1. It is found that Pd(110) exhibited much higher activity than Pd(111). This indicates that the CO + NO reaction on Pd surfaces is structuresensitive under the steady-state reaction condition with the total pressure of 10⁻² Torr. Generally, the NO dissociation proceeds on step sites, and it is difficult to proceed on the sites on the terrace plane surface, such as on Pd(111).^{5,36} Therefore, the result in Figure 9 reflects the activity for NO dissociation. The turnover frequency of CO₂ formation rate at 625 K was determined to be 1.7 s^{-1} and 0.43 s^{-1} on Pd(110) and Pd(111), respectively. Furthermore, the activation energy of the CO + NO reaction in the temperature range $T_{\rm S} = 550-650$ K was determined to be 45.6 and 24.8 kcal/mol on Pd(110) and Pd(111), respectively. Goodman et al. $^{6-8}$ have reported the results of CO + NO reactions on Pd surfaces, and TOF on Pd(110) and Pd(111) at 625 K was determined to be 5 s^{-1} and 20 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 on the order of 10^{-2} Torr, and in Goodman's study, it was in the range of 2–17 Torr.^{6–8} They have reported that NO dissociates immediately on more open surfaces (Pd(110) and Pd(100)) to form atomic nitrogen (N(a)).⁶⁻⁸ The N(a) species are bound strongly to 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. In particular, they have shown that 80% of the surface sites were covered by nitrogen species during the reaction on Pd(100), while only 20% on Pd(111).⁶ In our case, the coverage of nitrogen was very low ($\theta_N \ll 0.1$) at higher temperatures (800 K), and the rate-determining step is the NO dissociation, which means that the oxygen atom supplied from the NO dissociation can react with CO immediately.

3.5. Dynamics of CO + NO and CO + O₂ Reactions on Pd(110) and Pd(111): Surface Temperature (T_S) Dependence. Figure 10 shows the IR emission spectra for CO₂ molecules produced by the CO + NO reaction on Pd(110) and Pd(111) surfaces as a function of T_S . The higher the surface temperature, the more the red-shift from the antisymmetric stretch fundamental band (2349 cm⁻¹) was observed in the emission spectra of CO₂. Especially, more red-shift was

observed at $T_{\rm S} > 750$ K ($T_{\rm S} > T_{\rm S}^{\rm max}$) on Pd(110). Figure 11 shows the IR emission spectra of CO₂ molecules produced by the CO + O_2 reaction on Pd(110) and Pd(111) surfaces at various surface temperatures. The higher the surface temperature, the more the red-shift from 2349 cm⁻¹ was observed in the emission spectra of CO₂. The emission of the unreacted CO in the $CO + O_2$ reaction was much lower than that in the CO + NO reaction, and this is influenced by the difference of CO₂ formation rate. Because the formation rate of the $CO + O_2$ reaction was much higher than that of the CO + NO reaction as described above, the intensity of the emission spectra of CO normalized by the CO₂ formation rate can be much smaller in the case of the $CO + O_2$ reaction. The average vibrational temperature (T_V^{AV}) from the analysis of CO₂ emission spectra in Figures 10 and 11 is plotted as a function of $T_{\rm S}$ in Figure 12. T_V^{AV} increased with increasing T_S for both reactions on Pd(110) and Pd(111). T_V^{AV} on Pd(111) in both reactions is higher than that on Pd(110), which is in good agreement with the previous results.^{13–16} Especially, in the $T_{\rm S}$ range of 600-725 K, T_V^{AV} was dependent on the surface structure, and it was not dependent on the CO + NO and $CO + O_2$ reactions. However, in the higher temperature range above 750 K on Pd(110), T_V^{AV} of the CO + NO reaction was higher than that of the $CO + O_2$ reaction.

Figures 13 and 14 show T_V^{AS} and T_V^B 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 $T_{\rm V}{}^{\rm B}$ under all the surface temperatures in the CO + O₂ reaction on Pd(110) (Figure 13a). Overall, T_V^B was higher than T_V^{AS} in the CO + O_2 reaction on Pd(111) at all surface temperatures (Figure 13b). This suggests that the structure of the activated complex for CO_2 formation in the $CO + O_2$ reaction on Pd(111) is more bent than that on Pd(110), as reported previously.14-16 This can be reflected by the surface plane structure of Pd(111). As also shown in Figure 13, both T_V^{AS} and $T_{\rm V}^{\rm B}$ increased gradually with increasing $T_{\rm S}$ on Pd(110) and Pd(111), which is a general trend in the case of the $CO + O_2$ reaction.16,18,20 So far, almost no discussion on surface temperature dependence of the product vibrational energy was made.³⁹ Experimental results on the $CO + O_2$ reaction on Pt and Pd showed that the increase in vibrational temperature was higher than that of surface temperature.^{16,18,20} Theoretical works will be needed on the temperature dependence of the internal energy.

The $T_{\rm S}$ dependences in the CO + NO reaction are more complex than those in the CO + O_2 reaction. T_V^{AS} decreased and $T_{\rm V}{}^{\rm B}$ increased significantly with increasing $T_{\rm S}$ in the CO + NO reaction on Pd(110) (Figure 14a). At lower surface temperatures, T_V^{AS} was higher than T_V^B . Above 700 K, T_V^B became higher than T_V^{AS} , which means that the more excited mode changed from the antisymmetric to the bending vibrational modes. This temperature (700 K) corresponds to $T_{\rm S}^{\rm max}$ (Figure 9). This behavior was also observed in the CO + NO reaction on Pd(111) (Figure 14b). These results indicate that the structure of the activated complex for CO₂ formation can be very dependent on $T_{\rm S}$. At temperatures lower than $T_{\rm S}^{\rm max}$, the structure of the activated complex is less bent. Furthermore, it should be noted that the bending vibration is highly excited at higher $T_{\rm S}$. It is characteristic that the $T_{\rm V}^{\rm B}$ in the CO + NO reaction over Pd(110) above 800 K is much higher than other cases. Although the $T_{\rm V}{}^{\rm B}$ in the CO + NO reaction over Pd(111) at high temperaturse cannot be obtained because of the low CO₂ formation rate and low IR emission, the bending vibration can be highly excited, which is suggested from the data obtained.



Figure 10. IR emission spectra of CO₂ desorbed by the CO + NO reaction on (a) Pd(110) and (b) Pd(111). The surface temperature (T_S) was 625–850 K. The total flux of reactants was 8.2×10^{18} molecules cm⁻² s⁻¹ for Pd(110) and 2.1 × 10¹⁹ molecules cm⁻² s⁻¹ for Pd(111) at the CO/NO ratio = 1. The emission intensity was normalized per unit of CO₂ yield.



Figure 11. 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 600–850 K. The total flux of reactants was 8.2×10^{18} molecules cm⁻² s⁻¹ at the CO/O₂ ratio = 1. The emission intensity was normalized per unit of CO₂ yield.



Figure 12. Surface temperature dependence of average vibrational temperature (T_V^{AV}) of CO₂ formed in CO + NO and CO + O₂ reactions on Pd(110) and Pd(111). The reaction conditions are as described in Figures 10 and 11.

3.6. Effect of Oxygen Coverage on the Vibrational Excitation of CO₂. The effect of coverage on T_V^{AS} and T_V^B seems to be more complex at lower temperatures because the coverage of the adsorbed species is rather high (Figure 2). At a higher temperature (800 K), however, the oxygen coverage becomes higher, and the other coverage is very low (Figure 2c and f). The data at 800 K in Figure 7b suggest that T_V^B decreases with



Figure 13. Surface temperature dependence of antisymmetric vibrational temperature (T_V^{AS}) and bending vibrational temperature (T_V^B) in the CO + O₂ reaction on (a) Pd(110) and (b) Pd(111). The reaction conditions are as described in Figure 11.



Figure 14. Surface temperature dependence of antisymmetric vibrational temperature (T_V^{AS}) and bending vibrational temperature (T_V^B) in the CO + NO reaction on (a) Pd(110) and (b) Pd(111). The reaction conditions are as described in Figure 10.

increasing θ_0 (judging from the result in Figure 2c), while T_V^{AS} increased with increasing θ_0 . However, the results seem to be different from those of Bald and Bernasek,¹⁷ who reported that both T_V^B and T_V^{AS} increased with increasing NO/CO ratio for the CO + NO reaction over a polycrystalline Pt surface. Their results indicate that the vibrational excitation became higher with increasing θ_0 .¹⁷ On the other hand, the data at 800 K in Figure 8b show that both T_V^B and T_V^{AS} are almost constant, although θ_0 decreases with increasing CO flux (Figure 2f). Therefore, no clear conclusion on the θ_0 effect in the CO + NO reaction on Pd(110) can be done in this work.

At $T_{\rm S} = 800, 850$ K on Pd(110), $T_{\rm V}^{\rm B}$ in the CO + NO reaction (Figure 14a) is much higher than that in the $CO + O_2$ reaction (Figure 13a). As suggested in Figures 2 and 3, at $T_{\rm S} =$ 800 K, θ_0 was 0.39 and 0.10 for CO + O₂ and CO + NO reactions, respectively. The coverage of other species is negligible. Such a large difference in the oxygen coverage can be observed between the different reactions. In the CO + NOreaction, θ_0 can be small because the rate-determining step is the NO dissociation. One possible explanation is that the large difference in θ_0 affects the dynamics of CO₂ formation. According to the reports on surface diffusion of oxygen, the activation energy for surface diffusion of oxygen atoms over Rh(111) and Pt(111) is very dependent on the coverage of oxygen. At $\theta_0 = 0.25$ and 0.5 on Rh(111), the activation energies are calculated to be $E_a = 10.8$ and 13.1 kcal/mol, respectively.⁴⁰ At $\theta_0 = 0.03$ and 0.25 on Pt(111), E_a is calculated to be 11.3 and 25 kcal/mol, respectively.^{41,42} This suggests that the oxygen atom has a higher mobility under lower oxygen coverage. When the energy of surface diffusion can be added to the formation of the activated CO₂ complex, it is expected that its vibrational mode becomes more excited. Furthermore, in this case, because the energy of surface diffusion is along the surface, this can be distributed to the bending vibrational modes in the activated CO₂ complex rather than the asymmetric stretching vibrational mode. Although this is one explanation, it should be pointed out that this view is not reconciled with the results of the previous reports,^{19,20} where the vibrational

excitation became higher with increasing θ_0 in CO + O₂ reaction on polycrystalline Pt and Pd surfaces.

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 kinetic equations (7 and 23) are used to describe the CO₂ formation. In fact, the T_V^B and $T_{\rm V}^{\rm AS}$ values were different at the high temperatures (800 K and 850 K) on Pd(110) (Figure 13a and 14a). In the CO + O₂ reaction, adsorbed oxygen is accommodated to the surface, while the surface residence time of CO(a) is very short at higher surface temperatures.¹⁶ However, the oxygen atom from NO dissociation, which reacts with CO immediately after the formation, may not be accommodated to the surface, and such a 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.^{43–46} In this case, the rate constant k_r in the CO + NO reaction (eq 7) may be larger than that in the CO + O₂ reaction (eq 23), which results in lower $\theta_{\rm O}$ values in Figure 2c and f. Further investigation is necessary for the elucidation of the mechanism for the excitation of the vibrational modes of the activated complex.

4. Conclusions

(1) Rates of CO₂ formation during steady-state CO + NO reactions were measured over Pd(110) and Pd(111) in the pressure range of $10^{-2}-10^{-1}$ Torr. The activity of Pd(110) was much higher than that of Pd(111) in the low-pressure condition, which means that the rate-determining step is NO dissociation on step sites.

(2) On the basis of kinetic experimental results on the partial pressure dependence of NO and CO, and the reported rate constants using the reaction model, the coverage of NO, CO, N, and O was calculated under various flux conditions, and the results are compared with those of the $CO + O_2$ reaction.

(3) In the IR emission spectra of CO₂ during the CO + O₂ reaction on Pd(110) and Pd(111) in the entire $T_{\rm S}$ range, the antisymmetric vibrational temperature ($T_{\rm V}^{\rm AS}$) was higher than the bending vibrational one ($T_{\rm V}^{\rm B}$) on Pd(110). In contrast, $T_{\rm V}^{\rm B}$ was higher than $T_{\rm V}^{\rm AS}$ on Pd(111). These behaviors suggest that the activated complex for CO₂ formation is more bent on Pd-(111) than that on Pd(110), which is reflected by the surface smoothness. Both $T_{\rm V}^{\rm B}$ and $T_{\rm V}^{\rm AS}$ increased gradually with increasing surface temperature ($T_{\rm S}$).

(4) From the IR emission spectra of CO₂ during the CO + NO reaction over both Pd surfaces, T_V^{AS} decreased and T_V^B increased significantly with increasing T_S . T_V^B was higher than T_V^{AS} at higher temperatures (above 700 K). T_V^B in CO + NO reactions on Pd(110) at 800 and 850 K was much higher than that in CO + O₂ reactions, which was discussed in terms of the large difference in the oxygen coverage and the difference in the dynamics of both reactions.

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

References and Notes

(1) Taylor, K. C. Catal. Rev.-Sci. Eng. 1993, 35, 457.

- (2) Behm, R. J.; Christmann, K.; Ertl, G.; Van Hove, M. A. J. Chem. Phys. 1980, 73, 2984.
 - (3) Guo, X.; Yates, J. T., Jr. J. Chem. Phys. 1989, 90, 6761.
 - (4) Hirsimäki, M.; Valden, M. J. Chem. Phys. 2001, 114, 2345.
- (5) Ramsier, R. D.; Gao, Q.; Waltenburg, H. N.; Lee, K.-W.; Nooij,
 O. W.; Lefferts, L.; Yates, J. T., Jr. Surf. Sci. 1994, 320, 209.
- (6) Vesecky, S. M.; Rainer, D. R.; Goodman, D. W. J. Vac. Sci. Technol., A 1996, 14, 1457.
- (7) Rainer, D. R.; Vesecky, S. M.; Koranne, M.; Oh, W. S.; Goodman,D. W. J. Catal. 1997, 167, 234.
- (8) Ozensoy, E.; Goodman, D. W. Phys. Chem. Chem. Phys. 2004, 6, 3765.
- (9) Kobal, I.; Kimura, K.; Ohno, Y.; Matsushima, T. Surf. Sci. 2000, 445, 472.
- (10) Ma, Y.; Rzeźnicka, I.; Matsushima, T. Chem. Phys. Lett. 2004, 388, 201.
- (11) Rzeźnicka, I.; Ma, Y.; Cao, G.; Matsushima, T. J. Phys. Chem. B 2004, 108, 14232.
 - (12) Matsushima, T. Surf. Sci. Rep. 2003, 52, 1.
- (13) Nakao, K.; Hayashi, H.; Uetsuka, H.; Ito, S.; Onishi, H.; Tomishige, K.; Kunimori, K. *Catal. Lett.* **2003**, *85*, 213.
- (14) Uetsuka, H.; Watanabe, K.; Ohnuma, H.; Kunimori, K. Chem. Lett. 1996, 227.
- (15) Watanabe, K.; Ohnuma, H.; Kimpara, H.; Uetsuka, H.; Kunimori, K. Surf. Sci. 1998, 402–404, 100.
- (16) Uetsuka, H.; Watanabe, K.; Kimpara, H.; Kunimori, K. *Langmuir* **1999**, *15*, 5795.
 - (17) Bald, D. J.; Bernasek, S. L. J. Chem. Phys. 1998, 109, 746.
- (18) Mantell, D. A.; Kunimori, K.; Ryali, S. B.; Haller, G. L.; Fenn, J.
 B. Surf. Sci. 1986, 172, 281.
 - (19) Kunimori, K.; Haller, G. L. Bull. Chem. Soc. Jpn. 1992, 65, 2450.
 (20) Coulston, S. W.; Haller, G. L. J. Chem. Phys. 1991, 95, 6932.
- (21) Mantell, D. A.; Ryali, S. B.; Halpern, B. L.; Haller, G. L.; Fenn, J.
 B. Chem. Phys. Lett. 1981, 81, 185.
- (22) Bernasek, S. L.; Leone, S. R. Chem. Phys. Lett. 1981, 84, 401.
 (23) Mantell, D. A.; Ryali, S. B.; Haller, G. L. Chem. Phys. Lett. 1983,
- 102, 37.(24) Kori, M.; Halpern, B. L. Chem. Phys. Lett. 1984, 110, 223.
 - (24) Koli, M., Haipelli, B. L. Chem. 1 hys. Lett. **1964**, 110, 225.
- (25) Brown, L. S.; Bernasek, S. L. J. Chem. Phys. 1985, 82, 2110.
- (26) Bald, D. J.; Kunkel, R.; Bernasek, S. L. J. Chem. Phys. 1996, 104, 7719.
 - (27) Engel, T.; Ertl, G. Adv. Catal. 1979, 28, 1.
 - (28) Hammer, B. J. Catal. 2001, 199, 171.
 - (29) Olsson, L.; Zhdanov, V. P.; Kasemo, B. Surf. Sci. 2003, 529, 338.
 - (30) Zhdanov, V. P.; Kasemo, B. Surf. Sci. Rep. 1997, 29, 31.
 - (31) Garin, F. Appl. Catal., A 2001, 222, 183.
 - (32) Sellers, H.; Anderson, J. Surf. Sci. 2001, 475, 11.
 - (33) Lombardo, S. L.; Bell, A. T. Surf. Sci. Rep. 1991, 13, 1.
 - (34) Goschnick, J.; Wolf, M.; Grunze, M.; Unertl, W. N.; Block, J. H.;
- Loboda-Cackovic, J. Surf. Sci. 1986, 178, 831.
 - (35) Zhdanov, V. P. Surf. Sci. 1986, 165, L31.
 - (36) Loffreda, D.; Simon, D.; Sautet, P. J. Catal. 2003, 213, 211.
 - (37) Krischer, K.; Eiswirth, M.; Ertl, G. J. Chem. Phys. 1992, 96, 9161.
- (38) Watanabe, K.; Uetsuka, H.; Ohnuma, H.; Kunimori, K. Catal. Lett. 1997, 47, 17.

(39) Mantell, D. A.; Kunimori, K.; Ryali, S. B.; Haller, G. L.; Fenn, J. B. J. Vac. Sci. Technol., A 1985, 3, 1663.

- (40) Inderwildi, O. R.; Lebiedz, D.; Deutschmann, O.; Warnatz, J. J. Chem. Phys. 2005, 122, 034710.
 - (41) Verheij, L. K.; Hugenschmidt, M. B. Surf. Sci. 1998, 416, 37.
 - (42) Zhdanov, V. P.; Kasemo, B. J. Catal. 1997, 170, 377.
- (43) Carley, A. F.; Davies, P. R.; Roberts, M. W. Catal. Lett. 2002, 80, 25 and references therein.
- (44) Tanaka, S.; Yuzaki, K.; Ito, S.; Kameoka, S.; Kunimori, K. J. Catal. 2001, 200, 203.
- (45) Kameoka, S.; Nobukawa, T.; Tanaka, S.; Ito, S.; Tomishige, K.; Kunimori, K. Phys. Chem. Chem. Phys. 2003, 5, 3328.
- (46) Nobukawa, T.; Yoshida, M.; Kameoka, S.; Ito, S.; Tomishige, K.; Kunimori, K. *Catal. Today* **2004**, *93*, 791.