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The dynamics of CO oxidation on Pt(110) studied by infrared chemiluminescence of the product CO_2: effect of CO coverage

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The infrared chemiluminescence technique has been applied to the catalytic oxidation of CO on a Pt(110)(1 × 2) surface. The vibrational and the rotational states of CO_2 formed on the reconstructed Pt(110)(1 × 2) surface are more excited than those on the terrace Pt(111) surface. The vibrational state of the product CO_2 strongly depends on the CO coverage: the vibrational temperature (T_V) of the product CO_2 becomes higher, as the coverage of CO increases.

Keywords: infrared chemiluminescence, Pt(110)(1 × 2), dynamics of CO oxidation, internal states of CO_2

1. Introduction

To elucidate the dynamics of a surface-catalyzed reaction, it is important to measure internal (vibrational and rotational) energy and translational energy of product molecules desorbed from the surface [1–15]. The oxidation of CO is one of the prototype reactions for the study of the dynamics, and information on the internal and translational states has been obtained by means of infrared chemiluminescence (emission) [1–13] and time-of-flight (TOF) [14,15] techniques, respectively. We have recently obtained IR emission spectra of vibrationally excited CO_2 molecules produced by the oxidation of CO on single-crystal Pt and Pd surfaces [7–13]. It has been found that the internal energy states of CO_2 depend on the surface structure, which means that the dynamics of CO oxidation is structure-sensitive [10–13].

Pt(110) displays a stable (1 × 2) reconstruction and this structure has been investigated extensively [16–18]. The (1 × 2) reconstruction is explained by the "missing row model", in which every second atomic row in the $[1\bar{1}0]$ azimuth is missing, and there are three-atom-wide terraces of a (111) structure, which incline about ±30° in the [001] direction [16–18].

In the present work, the infrared emission technique has been applied to the steady-state catalytic oxidation of CO on the Pt(110)(1 × 2) surface, and the vibrational and the rotational states of the CO_2 molecules produced are compared with those on Pt(111) reported previously [7–10]. Furthermore, we have studied, for the first time, the effect of the CO coverage (θ_{CO}) on the vibrational state of the product CO_2 molecules. The effect of the oxygen coverage has been studied by increasing the surface temperature (T_S) [3] or by changing the O_2/CO ratio [6,9,19] at a high T_S, where θ_{CO} is very low. Recent results on a polycrystalline Pt or Pd surface [6,19] showed that increasing the oxygen coverage caused an increase in vibrational excitation of the product CO_2. So far, however, no work was done on the effect of θ_{CO} at a relatively lower temperature, at which θ_{CO} is rather high.

2. Experimental

The experiments were performed with a free-jet molecular-beam system (base pressure $< 1 \times 10^{-9}$ Torr) [11] which was equipped with an FTIR spectrometer (using an MCT detector) for measuring infrared emission of CO_2 molecules, a CaF_2 lens for collecting the IR emission, and a differentially pumped QMS for measuring the steady-state reaction rate. Reactant gases (CO and O_2) were introduced through two molecular-beam nozzles (0.1 mm diameter orifice), respectively. The Pt(110) sample was in the form of a disk of 12 mm diameter and 1 mm thickness, and it was spot-welded between two parallel tantalum wires and could be resistively heated. The surface temperature was measured by a chromel–alumel thermocouple which was spot-welded to the side of the sample. Another ultra-high vacuum (UHV) system (base pressure $< 1 \times 10^{-10}$ Torr) [2] equipped with a molecular-beam reaction chamber, LEED, AES, XPS and QMS was used to prepare and characterize the surface of the sample. Before a molecular beam reaction, the surface was cleaned by repeating a cycle of standard Ar^+ ion bombardment and annealing (at 1100–1200 K). After cleaning, no contamination was detected by XPS and AES, and the reconstructed (1 × 2) LEED pattern was observed for Pt(110). The IR emission spectra of the product CO_2 were measured with a low resolution (4 cm^{-1}). Although the individual vibration–rotation lines could not be resolved, the average

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vibrational temperature (T_V, i.e., an average of antisymmetric-stretch, symmetric-stretch and bending) and the rotational temperature (T_R) can be estimated from analysis of the degree of the red-shift from the fundamental band (2349 cm^{-1}) and the width of the spectra [1,4]. Here, the T_V and T_R values should be considered only as characteristic parameters to see the extent of vibrational and rotational excitation of the product CO_2, respectively, assuming a Boltzmann distribution [1,4].

In order to estimate the CO coverage (θ_{CO}) and the oxygen coverage (θ_O) under the steady-state condition, the following differential equations are used [20]:

$$\mathrm{d}\theta_{CO}/\mathrm{d}t = f_{CO}s_{CO}[1-(\theta_{CO}/\theta_{CO,S})^{q}] - k_d\theta_{CO} - r, \qquad (1)$$

$$\mathrm{d}\theta_{O}/\mathrm{d}t = 2f_{O}s_{O}(1-\theta_{CO}/\theta_{CO,S} - \theta_{O}/\theta_{O,S})^{2} - r. \qquad (2)$$

Here, f and s are the flux of reactant gas to the surface and the initial sticking coefficient, respectively. The rate constant k_d for the desorption of CO is used with the pre-exponential factor of 2×10^{16} s^{-1} and the activation energy of 35.3 kcal/mol [20,21]. The rate of O_2 desorption is assumed to be small enough to be neglected. The rate of CO_2 production, r, was obtained in the experiment. The subscripts CO, O and S denote carbon monoxide, oxygen and saturation, respectively. The precursor effect has been observed in the CO adsorption, and the mobility parameter q of 3 has been obtained [20]. Other parameters are taken as follows: $s_{CO} = 1.0$, $\theta_{CO,S} = 1.0$; $s_O = 0.4$, $\theta_{O,S} = 0.35$ [22,23].

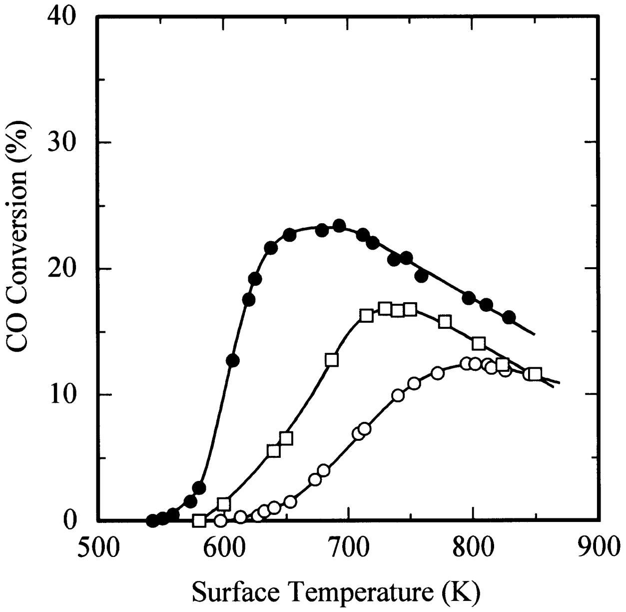

Figure 1. Carbon monoxide conversion on Pt(110). The O_2 : CO ratios were 1 (○), 2 (□), and 4 (●). The total flux of reactants were 32.8 (○), 12.3 (□), and 20.5 (●) × 10^{18} molecules cm^{-2} s^{-1}.

3. Results and discussion

The steady-state conversion of CO to CO_2 was measured at three O_2 : CO ratios, 4 : 1, 2 : 1 and 1 : 1, on Pt(110) at the surface temperature (T_S) of 300–900 K. As shown in figure 1, these results are in agreement with the general kinetics [24], in which T_0 and T_{max} (the surface temperatures at which the catalytic reaction starts and the conversion of CO is maximum, respectively) are shifted to lower temperature with increasing O_2/CO ratio, and the activity is higher with higher O_2/CO ratio. On the other hand, Ertl et al. [20,25] reported that an oscillatory phenomenon was observed in the oxidation of CO on Pt(110) under the condition of ~ 10^{-4} Torr and 300–600 K. In particular, microfacetting ((210), (320)) takes place under the oscillatory conditions, and is accompanied by the formation of defects which yield two additional peaks at 860 and 945 K in TDS of O_2 [26]. However, the oscillation was not observed under our experimental conditions (10^{-2} Torr, 550–900 K), and no additional peak appeared in the O_2 TDS after the molecular-beam reaction. Therefore, the microfacets and defects may not exist during the molecular-beam reaction.

As shown in figure 2, the infrared emission spectra of the product CO_2 were observed in the antisymmetric-stretch region of 2400–2150 cm^{-1}. As shown in table 1, the T_V values are much higher than the surface temperature (T_S), indicating that the CO_2 molecules are vibrationally excited by the catalytic CO oxidation. As compared with Pt(111) at the same T_S of 870 K, the T_V and the T_R values from Pt(110) ($T_V = 1800$ K,

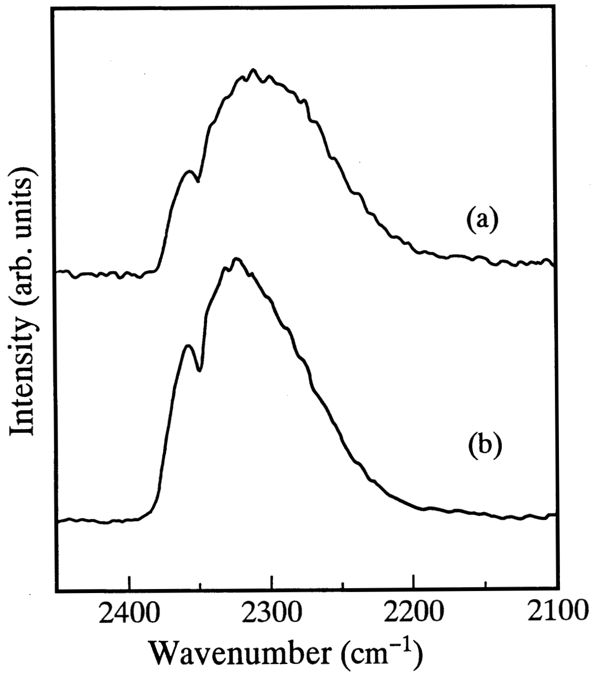

Figure 2. Infrared emission spectra of the CO_2 molecules produced by CO oxidation on Pt(110)(1 × 2) at $T_S = 680$ K. The O_2/CO ratios were 1 (a) and 4 (b). The surface temperature and the flux of O_2 were constant at 680 K and 16.4 × 10^{18} molecules cm^{-2} s^{-1}, respectively. The spectral intensity is normalized by the rate of CO_2 production.

Table 1
The vibrational temperature (T_V) and the rotational temperature (T_R) of the CO_2 produced by CO oxidation on Pt(110) (T_S: surface temperature)

T_S (K)	O_2/CO ratio	θ_{CO} [a]	θ_O [a]	T_V (K) [b]	T_R (K) [b]
680	1	0.19	0.21	1650	950
680	4	3.8×10^{-2}	0.24	1280	830
750	1 [c]	6.5×10^{-3}	0.22	1450	1000
750	4	3.2×10^{-3}	0.26	1400	920
870 [d]	1 [c]	2.5×10^{-4}	0.24	1800	1000

[a] The coverages of CO (θ_{CO}) and oxygen (θ_O) were calculated from eqs. (1) and (2) (see text).

[b] The uncertainty in T_V and T_R was estimated to be 30 and 50 K, respectively. The O_2 flux was constant at 16.4×10^{18} cm^{-2} s^{-1} except for [c] (6.2×10^{18} cm^{-2} s^{-1}).

[d] Ref. [10].

$T_R = 1000$ K) are higher than those from Pt(111) ($T_V = 1580$ K, $T_R = 700$ K) [7,8,10]. A Pt(110) surface is known to be reconstructed to a (1 × 2) structure which consists of three-atom-wide terraces of a (111) structure [16–18]. In practice, the (1 × 2) LEED pattern of the Pt(110) surface remained unchanged after exposing the surface to the molecular-beam conditions ($T_S = 680$–870 K) used in the infrared emission experiment. The different T_V and T_R values between Pt(111) and Pt(110)(1 × 2) may suggest that the reaction sites of the formation of CO_2 on Pt(110)(1 × 2) are not only the terrace of the (111) structure, but also a trough and/or top-most Pt atoms. By means of angular-resolved thermal desorption combined with TOF technique under a transient condition, Ohno et al. [14] have postulated that there are three reaction sites on the Pt(110) surface: two of the reaction sites are terrace sites which incline about ±30°, and the other is the bottom of the trough. These reaction sites may contribute to the overall reaction under our steady-state conditions.

To study the effect of a high CO coverage (θ_{CO}) on the internal states of the CO_2 molecules produced, the infrared emission measurements were performed at a fixed surface temperature ($T_S = 680$ K) with different O_2/CO ratios, 1 and 4. The effect of gas-phase collision on the vibrational temperature is negligible because of a much smaller cross section [1], although a small rotational relaxation due to the collisional effect may occur at the larger flux [3]. As shown in table 1, at $T_S = 680$ K, θ_{CO} is rather high (0.19) at $O_2/CO = 1$ ($T_S < T_{max}$), while θ_{CO} is very low at $O_2/CO = 4$ ($T_S \approx T_{max}$), which is in good agreement with the general kinetics of CO oxidation [24]. As shown in figure 2, the infrared emission spectra of CO_2 at $O_2/CO = 1$ is more red-shifted than at $O_2/CO = 4$, suggesting that CO_2 is more vibrationally excited at the high θ_{CO}. As shown in table 1, the T_V value is much higher at high θ_{CO} than at low θ_{CO}, when compared at the same T_S (680 K). The T_V value at $O_2/CO = 4$ becomes higher with increasing T_S from 680 to 750 K. Mantell et al. [3] also observed the increase in vibrational temperatures with increasing T_S (in the region of $T_S \geqslant T_{max}$, where θ_{CO} is very low). At $T_S = 750$ K, the CO and the oxygen coverages are almost the same in our experimental conditions (table 1) and no difference in the internal states is observed between the different O_2/CO ratios. The results in table 1 indicate that the effect of the CO coverage causes more dramatic change in the vibrational state of CO_2 than that of the surface temperature.

The spectral intensities normalized by the rate of CO_2 production in figure 2 should be proportional to the Boltzmann factor, $\exp(-\Delta E/kT_{AS})$ [2,12]. Here, T_{AS} is the antisymmetric-stretch temperature, and ΔE is the energy spacing. As the normalized intensity is a little smaller at $O_2/CO = 1$ than at $O_2/CO = 4$, T_{AS} may be slightly lower at high θ_{CO}. In contrast, the average vibrational temperature (T_V) is much higher at high θ_{CO}. Therefore, the CO_2 molecules formed at high θ_{CO} may be more excited selectively into the bending and/or the symmetric-stretch modes than into the antisymmetric-stretch mode, as compared with those at low θ_{CO}.

The CO coverage of 0.19 at $O_2/CO = 1$ suggests that the reaction is still proceeding on the (1 × 2) surface because the local (1 × 1) structure starts to grow above θ_{CO} of 0.2. This is in agreement with the (1 × 2) LEED pattern observed after the molecular-beam reaction. On a narrow three-atom-wide terrace, the oxygen or CO domain is compressed easily as the coverage increases [14]. Hence the interaction between the adsorbates is larger with increasing coverages. In addition, Ohno et al. [14] have suggested that the reaction site ratio of the trough to the terrace is higher with increasing CO coverage, when the oxygen coverage is fixed. The present results showed that the vibrational energy distribution of CO_2 was very different between the different θ_{CO}, from the analysis of the infrared emission spectra. Two possibilities may be considered to explain the difference. One is that the lateral interaction is larger at high θ_{CO} than at low θ_{CO}, and the increased CO coverage raises the potential energy of the transition state. This provides additional energy available to the desorbing CO_2 resulting in vibrational excitation. A similar discussion has been made to explain the effect of the oxygen coverage [4,6,19]. The other is that the contribution of the reaction sites of the trough and/or the top-most Pt atoms is larger with increasing θ_{CO}, as suggested by Ohno et al. [14], resulting in different structures of the activated complex.

In summary, the present work shows the first result on the effect of θ_{CO} in the region of lower surface temperature ($T_S < T_{max}$): T_V is much higher at higher θ_{CO}. On the other hand, T_V is higher with increasing T_S ($T_S \geqslant T_{max}$), where θ_{CO} is very small and θ_O is about 0.25. Determining the product energy distribution in more detail, including the effect of T_S, θ_O and θ_{CO}, will allow one to gain more insight into the dynamics of the catalytic reactions.

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References

[1] K. Kunimori, H. Uetsuka, T. Iwade and S. Ito, Surf. Sci. 283 (1993) 58.
[2] H. Uetsuka, K. Watanabe, T. Iwade and K. Kunimori, J. Chem. Soc. Faraday Trans. 91 (1995) 1801.
[3] D.A. Mantell, K. Kunimori, S.B. Ryali, G.L. Haller and J.B. Fenn, Surf. Sci. 172 (1986) 281.
[4] K. Kunimori and G.L. Haller, Bull. Chem. Soc. Jpn. 65 (1992) 2450.
[5] K. Kunimori, T. Iwade and H. Uetsuka, J. Electron Spectrosc. Relat. Phenom. 64/65 (1993) 451.
[6] G.W. Coulston and G.L. Haller, J. Chem. Phys. 95 (1991) 6932.
[7] H. Uetsuka, K. Watanabe and K. Kunimori, Chem. Lett. (1995) 633.
[8] H. Uetsuka, K. Watanabe and K. Kunimori, Surf. Sci. 363 (1996) 73.
[9] K. Watanabe, H. Uetsuka, H. Ohnuma and K. Kunimori, Appl. Surf. Sci. 99 (1996) 411.
[10] K. Watanabe, H. Ohnuma and K. Kunimori, Surf. Sci. 368 (1996) 366.
[11] K. Watanabe, H. Uetsuka, H. Ohnuma and K. Kunimori, Stud. Surf. Sci. Catal. 101 (1996) 891.
[12] H. Uetsuka, K. Watanabe, H. Ohnuma and K. Kunimori, Chem. Lett. (1996) 227.
[13] H. Uetsuka, K. Watanabe, H. Ohnuma and K. Kunimori, Surf. Rev. Lett., in press.
[14] Y. Ohno, T. Matsushima and H. Uetsuka, J. Chem. Phys. 101 (1994) 5319.
[15] K.-H. Allers, H. Pfnür, P. Feulner and D. Menzel, J. Chem. Phys. 100 (1994) 3985.
[16] T. Gritsch, D. Coulman, R.J. Behm and G. Ertl, Appl. Phys. A 49 (1989) 403.
[17] E.C. Sowa, M.A. Van Hove and D.L. Adams, Surf. Sci. 199 (1988) 174.
[18] F. Masson and J.W. Rabalais, Surf. Sci. 253 (1991) 245.
[19] D.J. Bald, R. Kunkel and S.L. Bernasek, J. Chem. Phys. 104 (1996) 7719.
[20] K. Krischer, M. Eiswirth and G. Ertl, J. Chem. Phys. 96 (1992) 9161.
[21] J. Fair and R.J. Madix, J. Chem. Phys. 73 (1980) 3480.
[22] C.M. Comrie and R.M. Lambert, J. Chem. Soc. Faraday I 72 (1976) 1659.
[23] R. Ducros and R.P. Merrill, Surf. Sci. 55 (1976) 227.
[24] C.T. Engel and G. Ertl, Adv. Catal. 28 (1979) 1.
[25] G. Ertl, Adv. Catal. 17 (1990) 213.
[26] R. Imbihl, M. Sander and G. Ertl, Surf. Sci. 204 (1988) L701.