Structure-sensitivity of the Dynamics of CO Oxidation on Pd(111), Pd(110) and Polycrystalline Pd Surfaces: Infrared Chemiluminescence Study of the Product CO_2

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The infrared chemiluminescence technique has been applied to the catalytic oxidation of CO on Pd(111), Pd(110) and polycrystalline Pd surfaces. The product CO_2 molecules were vibrationally and rotationally excited in all cases. However, the vibrational energy states of CO_2 were different among these three surfaces. This result means that the structure of the activated CO_2 complex (i.e., the dynamics of CO oxidation) depends on the surface structures. In addition, the steady-state reaction rates of CO oxidation as a function of surface temperature were also different among the Pd surfaces. These results show that the CO oxidation on Pd is structure-sensitive not only in the kinetics but also in the dynamics.

A great number of investigations about CO oxidation on Pt and Pd have been performed to understand the elemental steps of the surface catalyzed reaction.[1-3] Furthermore, the CO oxidation is one of the prototype reactions for the studies of the dynamics, and measurements of the internal energy states of the product CO_2 molecules have been performed by IR emission (chemiluminescence) technique.[4-9] Analysis of the vibrational and rotational 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 molecule desorbed.[4-8] However, the infrared (IR) emission spectra of the product CO_2 have been measured on polycrystalline Pt and Pd foils.[4-7] We have recently obtained the IR emission spectra of the product CO_2 from CO oxidation on well-defined single crystal surfaces such as Pt(111),[8,9] and found that the CO_2 molecules from Pt(111) were excited more vibrationally than those from a polycrystalline Pt foil.[8] Few works on the steady-state activities of CO oxidation on well-defined Pd surfaces have been reported.[10,11] According to the earlier work by Ertl and Koch,[11] CO oxidation on Pd surfaces appeared to be structure-insensitive; i.e., the reaction rates were identical between the single crystal Pd planes and a polycrystalline Pd wire. In the present work, we have studied steady-state CO oxidation on Pd(111), Pd(110) and polycrystalline Pd surfaces, and found that both the kinetics and the dynamics of CO oxidation are structure-sensitive under a molecular-beam condition ($\sim 10^{-2}$ Torr).[12]

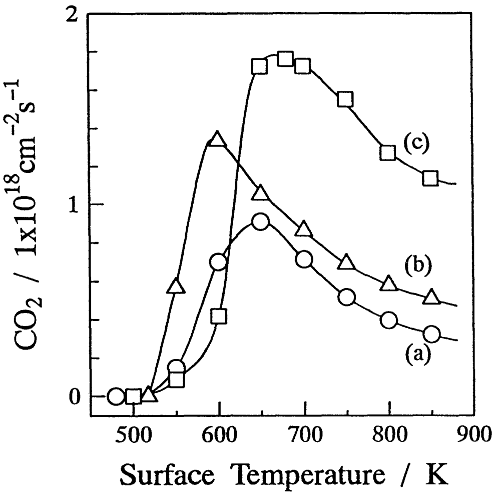

Figure 1. The production rate of CO_2 during CO oxidation (O_2/CO ratio = 1/1) on (a) Pd(111), (b) Pd(110) and (c) polycrystalline Pd foil.

A supersonic molecular-beam reaction system (base pressure < 1.5×10^{-9} Torr) combined with an FT-IR spectrometer was used to measure IR emission of nascent product CO_2 molecules just desorbed from the metal surface.[5,8] Another UHV system (base pressure < 2×10^{-10} Torr) equipped with molecular-beam reaction chamber had Ar^+ ion gun, LEED, AES, XPS and QMS. This UHV system was used to prepare samples and to characterize the surfaces.[13] Before the molecular-beam reaction, the Pd(111) and Pd(110) single crystals and a polycrystalline Pd foil (1.1 cm^2; the same area as the single crystal surfaces) were cleaned by O_2 treatment, short time Ar^+ bombardment and annealing. After cleaning, the sharp (1x1) LEED pattern was observed for Pd(111) and Pd(110), and no contamination was detected by AES and XPS for all the samples. The reactant CO and O_2 gases (the flux was 6×10^{18} cm^{-2}s^{-1}, respectively: O_2/CO ratio was unity) were exposed from the supersonic molecular-beam nozzles, and the steady-state CO oxidation was performed in the temperature range of 400 ~ 1000 K.

Figure 1 shows the production rate of CO_2 on Pd (111), Pd(110) and polycrystalline Pd surfaces as a function of surface temperature. The CO oxidation started above 500 K and the reaction rate profiles showed the maxima on these Pd surfaces. These max. temperatures were lower than those for Pt surfaces.[9] These behaviors are in good agreement with the general kinetics of CO oxidation on Pt and Pd surfaces. The max. temperature (T_{max}) and the production rate of CO_2 were, however, different among these surfaces. The (1x1) LEED patterns remained unchanged after the molecular-beam CO oxidation on Pd(111) and Pd(110). Generally, a polycrystalline surface consists of low index planes: (111), (110) and (100). The difference in the activity of CO oxidation may be related to the difference in the sticking probabilities of oxygen on three low-index surfaces. Indeed, the initial sticking probability S_0 is high (0.86) on Pd (110),[14] 0.14[15] or 0.5[16] on Pd(111) and 0.1 on Pd(100).[17] In addition, the contribution from higher index planes might be important in the case of the polycrystalline surface.[18]

Kinetics of CO oxidation on single crystal metal surfaces and supported metal catalysts have been extensively studied, and the reaction appears to be structure-insensitive.[10,19] However, the experiments have been done at relatively higher pressure range (0.1 ~ 600 Torr), in which the surface is covered with CO and the reaction rate is controlled by the desorption of CO.[19] In addition, Ertl and Koch[11] reported that CO oxidation appeared to be structure-insensitive (in the kinetics) on Pd surfaces under a UHV condition (~ 10^{-7} Torr), but they reported only relative reaction rates.[11] The present results show that the kinetics of CO

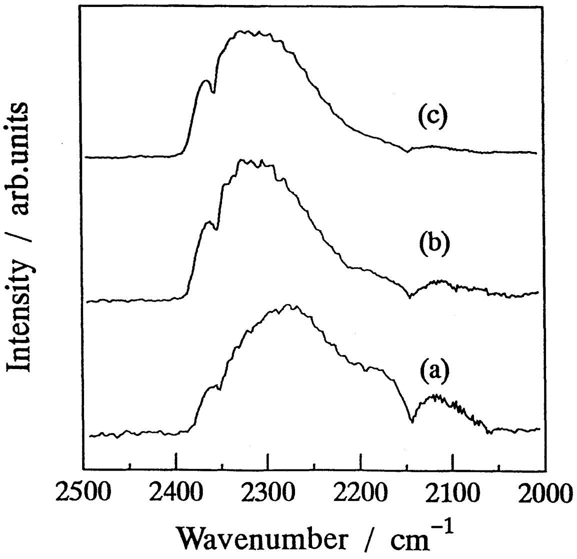

Figure 2. IR emission spectra of CO_2 desorbed by the CO oxidation on (a) Pd(111), (b) Pd(110) and (c) polycrystalline Pd. The surface temperature (T_S) was 850K. The spectral intensity was normalized by the CO_2 production rate.

oxidation is structure-sensitive under our steady-state molecular-beam condition (~10^{-2} Torr). As far as the authors know, no detailed work (except the ref. 11) on the structure-sensitivity of the overall rates of CO oxidation on Pd (or Pt) surfaces has been published in the *steady-state* reaction conditions ($P \leq 10^{-1}$ Torr, $T_S \geq T_{max}$). However, it is reasonable that the CO oxidation in the lower-pressure and higher-temperature conditions is structure-sensitive if the chemisorption of oxygen is rate-limiting,[1] because the sticking probability (S_0) of O_2 is different among the Pd surfaces.[14-17]

Figure 2 shows the IR emission spectra of CO_2 molecules produced by CO oxidation on Pd(111), Pd(110) and polycrystalline Pd surfaces at 850 K. The CO_2 emission spectra observed in the region of 2400 ~ 2150 cm^{-1} were significantly red-shifted from 2349 cm^{-1} (fundamental band of antisymmetric stretch), while the emission spectra centered at 2143 cm^{-1} are due to the IR emission of unreacted CO which was scattered from the surface. The degree of red-shift from fundamental band and the width of spectra reflects vibrational and rotational states of excited molecules.[5,7] In particular, the spectrum from Pd(111) is more red-shifted than those from the other surfaces. Table 1 shows the vibrational temperature (T_V) and rotational temperature (T_R) derived from IR emission spectra of CO_2 (figure 2). In the case of CO_2, T_V is the average of three vibrational modes (symmetric stretch, bending and antisymmetric stretch).[7,13] As shown in Table 1, T_V and T_R are much higher than the surface temperature (T_S). Furthermore, the CO_2 from Pd(111) is more excited than those from Pd(110) and polycrystalline Pd. Although the vibrational states of CO_2 from Pd(110) and polycrystalline Pd are at the same level, the T_R from Pd(110) is lower than that from polycrystalline Pd. These results show that the internal energy states of the product CO_2 molecules desorbed from the three surfaces are much different.

Because we have observed the antisymmetric stretch region of CO_2 emission spectra, the emission intensity normalized by CO_2 production rate is related to the antisymmetric temperature (T_{AS}),[13] if we assume a Boltzmann distribution.

$$f \propto \exp(-\Delta E_V/kT_{AS}) \quad (1)$$

Here, f is normalized emission intensity and ΔE_V is the energy spacing. As shown in figure 2, the normalized emission intensity is almost the same, indicating that there is no big change in T_{AS}. Therefore, it is suggested that the symmetric stretching and/or bending modes are more highly excited on Pd(111) than on Pd(110) and polycrystalline Pd. The difference in the internal energy states of product CO_2 from CO oxidation on Pd(111), Pd(110) and polycrystalline Pd surfaces may reflect the difference of structure of activated CO_2 complex. Therefore, the transition state of CO oxidation is strongly affected by the structure of reaction sites; i.e., the reaction dynamics of CO oxidation are structure-sensitive.

Table 1. The vibrational and rotational temperatures (T_V, T_R) of the product CO_2 desorbed from CO oxidation on Pd surfaces[a)]

Surface	T_S(K)	T_V(K)	T_R(K)
Pd(111)	650	1600	1130
Pd(110)	650	1300	960
Polycrystalline Pd	650	1340	1050
Pd(111)	850	2340	1400
Pd(110)	850	1650	1220
Polycrystalline Pd	850	1660	1450

a The uncertainty in T_V and T_R is ± 30 K and ± 50 K, respectively.

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12 The terminology "structure-sensitive (or insensitive)" has usually been used when the overall reaction rates (i.e., the kinetics) depend (or not depend) upon the structures of catalyst surfaces. In this paper, however, the term "structure-sensitive" is also used when the difference is observed in the internal energy of the product molecules, which is concerned with the CO_2 formation process (i.e., the dynamics of CO oxidation).
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