Infrared Chemiluminescence Study of Excited CO_2 Produced by Molecular-Beam CO Oxidation on Pt(111)

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The infrared emission spectra of CO_2 molecules produced by CO oxidation on Pt(111) single crystal surface have for the first time been measured by molecular-beam/infrared chemiluminescence technique. The CO_2 molecules were vibrationally excited (especially, antisymmetric stretch mode) compared with those desorbed from a polycrystalline Pt foil. This is the first information on the internal energy distribution from the steady state surface reaction on a well-defined single crystal surface.

To elucidate the dynamics of surface chemical reaction, it is important to measure the internal energy (vibration and rotation) and the translational energy of product molecules desorbed from catalyst surfaces.[1-7] Catalytic oxidation of CO on Pt and Pd surfaces is one of the prototype reactions for dynamic studies, and the information on the translational and internal states of the CO_2 product has been obtained by means of time-of-flight (TOF)[6,7] and infrared chemiluminescence (IR)[1-5] techniques, respectively. The TOF experiments have been performed in UHV conditions with well-defined single crystal surfaces.[6,7] However, the IR measurements have been performed during steady-state reaction ($\sim 10^{-3}$ Torr) on polycrystalline Pt and Pd foils.[1-5] So far, no work has been done on a well-defined single crystal surface to obtain the information on the internal energy.

In the present work, for the first time, we measured the IR emission spectra of the CO_2 product from Pt(111) single crystal surface, and the degrees of the vibrational and rotational excitation have been compared with those from a polycrystalline Pt surface.

A supersonic molecular-beam reaction system with an FT-IR spectrometer was used to measure IR emission of product molecules just desorbed from the metal surface.[3,4] Sample preparation and characterization were performed in a UHV chamber (base pressure < 2×10^{-10} Torr) equipped with Ar ion gun, LEED, AES, XPS and QMS, and the reaction chamber with the molecular-beam system was attached to the UHV chamber through a gate valve.[5] The Pt(111) single crystal (1.1 cm^2) was spotwelded to tantalum wires. The sample was resistively heated and the temperature was monitored with chromel-alumel thermocouple that was spotwelded to edge of the crystal. Before the reaction rate and IR measurements, the Pt(111) was cleaned by heating in O_2 (1×10^{-7} Torr O_2, 1000 K), followed by cycle Ar^+ bombardment and annealing at 1200 K. After cleaning, the sharp hex (1x1) LEED pattern was observed and no contamination was detected by AES and XPS. The reactant CO and O_2 gases (30 cm^3/min [STP]) were exposed from the supersonic molecular-beam nozzles, and the steady-state CO oxidation was performed in the temperature range of 500~1000 K. A polycrystalline Pt foil (2.0 cm^2) was also used in the same experiment.

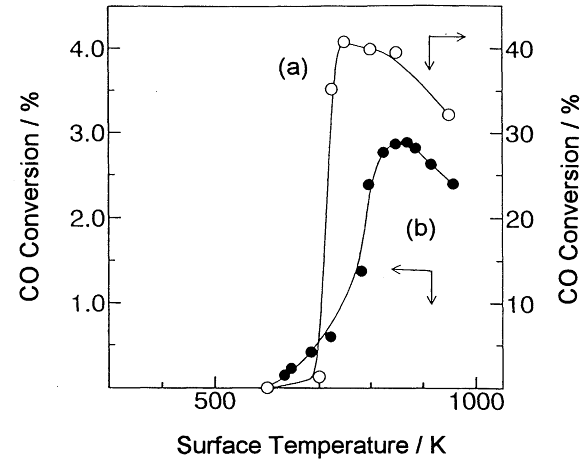

Figure 1. The conversions of CO oxidation as a function of surface temperature: (a) on polycrystalline Pt, (b) on Pt(111).

Figure 1 shows the CO conversion on Pt(111) as a function of surface temperature. The curve (a) is the CO conversion on polycrystalline Pt for comparison. The CO oxidation started at about 600 K on Pt(111), and reached the maximum conversion at about 850 K, followed by the decrease with increasing surface temperature. The conversion profile appears to be similar in shape to that of polycrystalline Pt, and these results are in good agreement with the general characteristics of CO oxidation on Pt and Pd.[1-3] The maximum value of CO conversion on Pt(111) was about one order of magnitude smaller (2.9%) than that on polycrystalline Pt (40.8%). The large difference in the reaction rate may be due to the difference in the sticking provability of O_2 on the Pt surface. The PEEM observations[8] demonstrate that a polycrystalline Pt surface consists of three low-index planes:

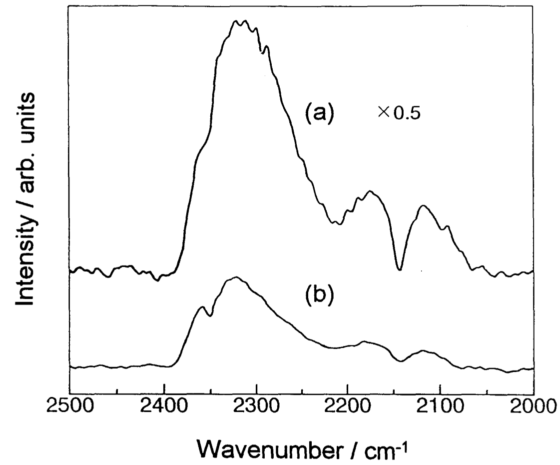

Figure 2. Infrared emission spectra of CO_2 desorbed by the CO oxidation on (a) Pt(111) and (b) polycrystalline Pt. The Surface temperature (Ts) was (a) 870 K and (b) 750 K. The spectral intensity was normalized by the CO_2 production rate.

Table 1. Vibrational and rotational temperatures (K) of the product CO_2

	T_S	T_V	T_R
Pt(111)	870	1580	700
Polycrystalline Pt	750	1360	1200

Pt(111), Pt(110) and Pt(100). The initial sticking coefficient S_0 is quite high on Pt(110), 0.4 to 0.6,[9] about one order of magnitude smaller ($S_0 = 0.046$) on Pt(111),[10] and only of the order of 10^{-4} on hex-Pt(100).[11] Therefore, the Pt(110)-oriented surface would be the most active for CO oxidation. The experiments on the other planes, Pt(110) and Pt(100), will be the subject of future investigation to confirm this suggestion.

In order to obtain information on the surface state after the molecular-beam reaction, the XPS and LEED measurements were performed on Pt(111). The reaction was started on a clean surface, but after the reaction, oxygen remained on the surface (θ ~0.4 on Pt(111), θ~0.2 on polycrystalline Pt: here, the θ is the surface coverage in O atoms per surface Pt atom). No C_{1s} peak was observed. The (1x1) LEED pattern was remained unchanged after the reaction in this study. On the other hand, the (2x2) LEED pattern was observed with the coverage of 0.25 on Pt(111).[12] These results show no long range order exists in the O atoms on the Pt(111) surface under our reaction condition.

Figure 2 shows the infrared emission spectra of CO_2 molecules produced by CO oxidation on Pt(111) and polycrystalline Pt. The emission spectra of the product CO_2 were significantly red-shifted from 2349 cm^{-1} (fundamental band). In the low-resolution (4 cm^{-1}) spectra, no individual rotational lines were resolved, but the average vibrational temperature T_V and the rotational temperature T_R can be estimated from the red-shift and the band width.[13] As shown in Table 1, T_V is a little higher but T_R is significantly lower on Pt(111) than on polycrystalline Pt. As shown in Figure 2, the spectral intensity normalized by the CO_2 production rate was much higher on Pt(111) than on polycrystalline Pt. This result shows that antisymmetric-stretch temperature (T_{AS}) of CO_2 desorbed from Pt(111) may be much higher than from polycrystalline Pt, since we have measured the CO_2 emission intensity in the antisymmetric-stretch region and the spectral intensity should be proportional to a Boltzmann factor $\exp(-\Delta E/kT_{AS})$ if we assume a Boltzmann distribution.[4] On the other hand, there is no large change in the average T_V in Table 1. Our interpretation would be that the antisymmetric-stretch mode is excited selectively, while symmetric stretch and bending modes have cooled, i.e., the transition state comprises an almost linear activated CO_2 molecule on the Pt(111) surface. The present result clearly shows that it is important to study the dynamics on well-defined surfaces, and such experiments are now in progress in this laboratory.

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