

## Angular Dependence of Rotational and Vibrational Energy of Desorbing CO<sub>2</sub> in CO Oxidation on Pd Polycrystalline and Pd(111) Surfaces

Toshiro Yamanaka

Catalysis Research Center, Hokkaido University, Sapporo 001-0021

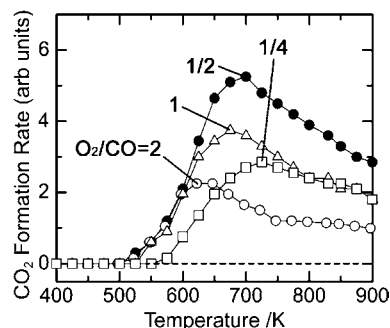
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Angular dependence of rotational and vibrational temperatures of product CO<sub>2</sub> were studied in CO oxidation on a Pd polycrystalline surface by means of chemiluminescence measurements. Rotational temperature ( $T_{\text{rot}}$ ) and vibrational temperature ( $T_{\text{vib}}$ ) showed minimum values at the surface normal and significantly increased as the desorption angle increased.  $T_{\text{rot}}$  and  $T_{\text{vib}}$  became higher when the ratio of exposure of O<sub>2</sub> to that of CO increased. These angular dependences are quite different from those on Pd(111).

Catalytic oxidation of carbon monoxide over noble metal surfaces is one of the prototype reactions in surface chemistry,<sup>1</sup> which is of practical and scientific importance. To elucidate dynamics of this reaction, angular dependence of flux and translational energy of product CO<sub>2</sub> has been studied in detail.<sup>2</sup> Angular distribution of CO<sub>2</sub> is sharply collimated in the direction normal to the reaction site where the translational temperature is also maximized. Also, rotational and vibrational temperatures ( $T_{\text{rot}}$  and  $T_{\text{vib}}$ ) of product CO<sub>2</sub> have been extensively studied in non-angle-resolved ways by means of infrared emission<sup>3–11</sup> and absorption<sup>12</sup> on both polycrystalline and single-crystal surfaces of Pd and Pt. It was found that  $T_{\text{rot}}$  and  $T_{\text{vib}}$  are highly excited depending on surface structures.<sup>7–11</sup> However, until recently the angular dependence of  $T_{\text{rot}}$  and  $T_{\text{vib}}$  has not been studied because the intensity of chemiluminescence is lowered by three orders in angle-resolved (AR) measurements.<sup>13</sup> For a full understanding of reaction dynamics, AR measurements of these energies are required. In this paper, desorption-angle dependences of  $T_{\text{rot}}$  and  $T_{\text{vib}}$  of the product CO<sub>2</sub> in CO oxidation on Pd polycrystalline are described. It was found that  $T_{\text{rot}}$  and  $T_{\text{vib}}$  change with increases in the desorption angle and that results on polycrystalline are quite different from those on Pd(111).<sup>14</sup> Although the structures of polycrystalline have not been elucidated, studies on polycrystalline are important since its structures are thought to be close to those of real catalysts compared with that of single-crystal surfaces.

The design of a new apparatus for analysis of extremely weak infrared emission from AR CO<sub>2</sub> and the difficulty of measurements have recently been described in detail.<sup>13</sup> Infrared light emitted in the relaxation of the antisymmetric stretch mode of product CO<sub>2</sub> after passing through two slits for angle selection, ( $n_s, n_b, n_a$ ) → ( $n_s, n_b, n_a - 1$ ), where  $n_s$ ,  $n_b$ , and  $n_a$  are the quantum numbers of the symmetric stretch, bending, and antisymmetric stretch modes, respectively, is analyzed by an FT-IR spectrometer.

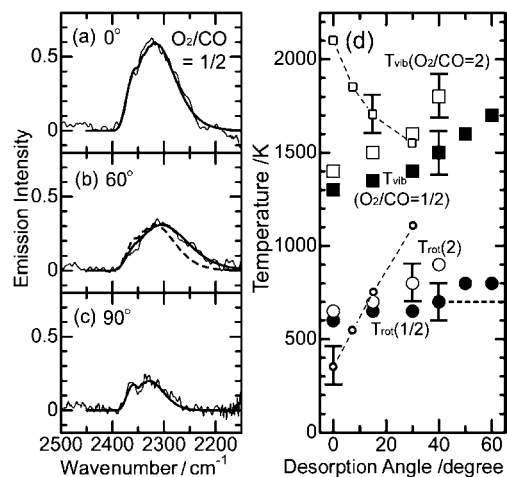
Figure 1 shows the rate of CO<sub>2</sub> formation as a function of the surface temperature ( $T_{\text{surf}}$ ) at the total exposure of  $4.5 \times 10^{17}$  molecules/cm<sup>2</sup> s. With an increase in  $T_{\text{surf}}$ , CO<sub>2</sub> formation started to occur above 500 K and showed a maximum at  $T_{\text{max}}$ . The  $T_{\text{max}}$  value shifted to higher temperatures as the ratio of ex-



**Figure 1.** Rate of CO<sub>2</sub> formation on polycrystalline Pd as a function of sample temperature,  $T_{\text{surf}}$ . Rate of total exposure of CO and O<sub>2</sub> was  $4.5 \times 10^{17}$  molecules/cm<sup>2</sup> s. The ratio of exposure, O<sub>2</sub>/CO, was changed.

posure of O<sub>2</sub> to that of CO (O<sub>2</sub>/CO) decreased. It is well known that dissociative O<sub>2</sub> adsorption is the rate-determining step below  $T_{\text{max}}$ , i.e., CO(a) ≫ O(a).<sup>2</sup> Below  $T_{\text{max}}$ , O<sub>2</sub> dissociation increased with increasing  $T_{\text{surf}}$ , resulting in enhanced CO<sub>2</sub> formation. On the other hand, above  $T_{\text{max}}$ , CO<sub>2</sub> formation decreased owing to reduced CO coverage with increasing  $T_{\text{surf}}$ . These features are consistent with the results of previous works.<sup>7,9–11</sup> The following AR measurements were conducted at  $T_{\text{surf}} = 700$  K and at O<sub>2</sub>/CO = 1/2 and O<sub>2</sub>/CO = 2.

The thin lines in Figures 2a–2c show infrared emission spectra from the product CO<sub>2</sub> at a ratio of O<sub>2</sub>/CO = 1/2 and at desorption angles of 0, 60, and 90°, respectively. In the spectra in (a) and (b), a single broad peak appears in a range from 2400 to 2200 cm<sup>-1</sup>, which consists of contributions from various transition lines from different initial vibrational states. Previous measurements showed that the populations of vibrational and rotational states of product CO<sub>2</sub> were well expressed by rotational and vibrational temperatures,  $T_{\text{rot}}$  and  $T_{\text{vib}}$ , respectively, with corresponding Boltzmann distributions.<sup>13,14</sup> It is possible to determine the values of  $T_{\text{rot}}$  and  $T_{\text{vib}}$  by fitting of experimentally obtained spectra with simulated spectra. The spectrum is more red-shifted owing to the unharmonic nature of vibration when each vibrational temperature for the symmetric stretch, bending and antisymmetric stretch modes increases. Since each vibrational temperature could not be separately estimated only from the degree of redshift,  $T_{\text{vib}}$  averaged over the three modes (i.e., assuming the three vibrational temperatures are equal) and  $T_{\text{rot}}$  were estimated. This method is essentially the same as that used in previous works,<sup>3,7–11</sup> although numbers of vibrational bands (1487) and initial rotational states ( $0 \leq J \leq 270$ ) taken into account in the present simulation may be different. Thick solid lines in Figures 2a–2c show results with optimized values for  $T_{\text{rot}}$  and  $T_{\text{vib}}$ ,  $T_{\text{vib}} = 1300$  K (0°) and  $T_{\text{rot}} = 600$  K (0°),  $T_{\text{vib}} = 1700$  K (60°) and  $T_{\text{rot}} = 800$  K (60°),  $T_{\text{vib}} = 900$  K (90°) and  $T_{\text{rot}} = 450$  K (90°). The simulated results for  $T_{\text{vib}} = 1300$  K



**Figure 2.** Fine lines in a–c show infrared emission spectra from product CO<sub>2</sub> on polycrystalline Pd measured with resolution of wave number of 4 cm<sup>-1</sup> at desorption angles of 0, 60, and 90°, respectively. Black thick lines in a–c show the optimum simulated results. For comparison, the best fit obtained for the spectrum at 0° is also shown in b as a dashed line. d shows  $T_{\text{rot}}$  (closed (O<sub>2</sub>/CO = 1/2) and open (O<sub>2</sub>/CO = 2) circles) and  $T_{\text{vib}}$  (closed (O<sub>2</sub>/CO = 1/2) and open (O<sub>2</sub>/CO = 2) squares) on polycrystalline Pd as a function of desorption angle. Results on Pd(111) at O<sub>2</sub>/CO = 1/2 are also shown by small squares ( $T_{\text{vib}}$ ) and circles ( $T_{\text{rot}}$ ).

and  $T_{\text{rot}} = 600$  K are also presented in Figure 2b by a dashed line, showing that the spectrum at 60° is more red-shifted compared to the dashed line because  $T_{\text{vib}}$  is higher at 60°. The values at 90° are low since this chemiluminescence is from CO<sub>2</sub> scattered on the wall of the apparatus before it passes the first slit, of which the contribution is negligible at small desorption angles. Figure 2d summarizes the optimized values for  $T_{\text{vib}}$  and  $T_{\text{rot}}$  at O<sub>2</sub>/CO = 1/2 (closed squares and circles) and at O<sub>2</sub>/CO = 2 (open squares and circles) as a function of the desorption angle. It can be seen that both  $T_{\text{vib}}$  and  $T_{\text{rot}}$  increase as the desorption angle increases. It can also be seen that  $T_{\text{vib}}$  and  $T_{\text{rot}}$  at O<sub>2</sub>/CO = 2 are higher than those at O<sub>2</sub>/CO = 1/2. For comparison, results on Pd(111) are shown, as indicated by small squares and circles, in Figure 2d (O<sub>2</sub>/CO = 1/2 and  $T_{\text{surf}} = 700$  K).  $T_{\text{rot}}$  increased but  $T_{\text{vib}}$  decreased as the desorption angle increased.<sup>14</sup> It should be mentioned that the temperature of the antisymmetric mode can be separately determined if the chemiluminescence intensity is properly analyzed,<sup>9–11</sup> although the chemiluminescence intensity was not accurately analyzed in the present study owing to insufficient stability of measurement at this stage. However, on the polycrystalline surface, chemiluminescence intensities normalized by the amount of CO<sub>2</sub> increased with increases in desorption angle, indicating increased temperatures of the antisymmetric mode.

On a polycrystalline surface,  $T_{\text{vib}}$  and  $T_{\text{rot}}$  have been expected to be independent of the desorption angle due to disordered orientation of grains. Nevertheless, the present work shows a remarkable increase in  $T_{\text{vib}}$  and  $T_{\text{rot}}$  with increase in the desorption angle, which is quite different from those on Pd(111). This indicates the importance of AR measurements for a full understanding of energy partition in surface reactions. The enhanced  $T_{\text{vib}}$  at large desorption angles is probably due to contribution from CO<sub>2</sub>

formed on inclined formation sites. On Pd polycrystalline, CO<sub>2</sub> molecules are thought to be formed on several kinds of different sites with different inclinations, and CO<sub>2</sub> is desorbed in the direction normal to each formation site. This implies that it is possible to study internal energies of CO<sub>2</sub> formed on each site with different inclinations on stepped or reconstructed single crystal surfaces. For example,  $T_{\text{vib}}$  and  $T_{\text{rot}}$  of CO<sub>2</sub> formed on (111) and (001) facets on Pd(113) or Pt(113) may be separately studied.

In the present study,  $T_{\text{vib}}$  on polycrystalline was about 200 K lower than that on Pd(111), though the difference between  $T_{\text{rot}}$  on a polycrystalline surface and that on a Pd(111) surface was less significant. These features are consistent with the results of previous works.<sup>7,9</sup> This indicates that  $T_{\text{vib}}$  and  $T_{\text{rot}}$  are sensitive to surface structures, as previously found by Kunimori's group in studies on various polycrystalline and single-crystal surfaces.<sup>7–11</sup> The present results indicate that angular dependences of  $T_{\text{vib}}$  and  $T_{\text{rot}}$  are also sensitive to surface structures. The values of  $T_{\text{rot}}$  at 0 and 7.5° are lower than those of  $T_{\text{surf}}$  probably owing to rotational cooling.  $T_{\text{rot}}$  on Pd(111) observed in the present study seems lower than that observed in previous works (950 K)<sup>9</sup> partly because in the present study  $T_{\text{rot}}$  above 30° is not presented and also the method of simulation is not exactly the same as that in previous works.

$T_{\text{vib}}$  and  $T_{\text{rot}}$  at O<sub>2</sub>/CO = 2 are higher than those at O<sub>2</sub>/CO = 1/2 as shown in Figure 2d. This agrees with previous results on a Pd polycrystalline showing that both temperatures increased with increase in oxygen coverage, which was attributed to increased energy of the transition state due to repulsion between adsorbates.<sup>4</sup> It should be noted that  $T_{\text{rot}}$  is not changed with change in the O<sub>2</sub>/CO ratio on Pd(110).<sup>9</sup>

Different angular dependence of  $T_{\text{vib}}$  and  $T_{\text{rot}}$  between Pd polycrystalline and Pd(111) surfaces indicates that angular dependence of  $T_{\text{vib}}$  and  $T_{\text{rot}}$  is sensitive to surface structures. The present results emphasize the importance of AR measurements of energies of products for a full understanding of surface reaction dynamics.

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