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Elucidation of CO_2 formation mechanism in $CO + NO$ reaction on Pd(111) and Pd(110) surfaces using IR chemiluminescence method

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The infrared (IR) chemiluminescence technique was applied to steady-state CO oxidation by NO on Pd(111) and Pd(110). From a comparison of IR emission spectra of CO_2 between the $CO + NO$ and $CO + O_2$ reactions, it was found that the vibrational energy states of CO_2 in the $CO + NO$ reaction were similar to those in the $CO + O_2$ reaction. This indicates that the reaction path of CO_2 formation in $CO + NO$ is the same as that in $CO + O_2$, although the vibrational states are very dependent on the surface structure.

KEY WORDS: mechanism; steady state; carbon dioxide; carbon monoxide; nitric oxide; chemiluminescence; palladium.

1. Introduction

The reaction between nitric oxide and carbon monoxide on palladium has practical importance in the removal of pollutants from combustion exhaust. The overall reaction is

$$NO(g) + CO(g) \rightarrow \tfrac{1}{2}N_2(g) + CO_2(g). \qquad (1)$$

Automobile emissions of nitrogen oxides (NO_x) are controlled by the after treatment of engine exhaust with catalytic converters that contain a mixture of three noble metals: Pt, Rh, and Pd. Recently, there has been considerable interest in using Pd-only catalysts for three-way exhaust gas conversion [1]. Many ultrahigh-vacuum (UHV) studies have focused on the nature of CO and NO chemisorption on single-crystal Pd surfaces. Much work has also been done to identify the $CO + NO$ reaction products and kinetics over polycrystalline Pd surfaces [2–4]. Few studies, however, have examined the steady-state $CO + NO$ reaction on well-defined single-crystal Pd surfaces [5,6].

The reaction between CO and NO is considered to proceed by a Langmuir–Hinshelwood mechanism between two adsorbed species. However, there has not been complete agreement in the literature as to which of the surface species are involved in the CO_2 formation step. Most studies have suggested that NO dissociates to atomic oxygen which is scavenged by CO, similar to the $CO + O_2$ reaction [5–8]. However, several studies have proposed a bimolecular surface reaction between adsorbed NO and CO species to yield directly CO_2 as a product [4,9,10]. The respective CO_2 formation steps for the two mechanisms are

Dissociative:

$$NO(g) \rightarrow N(a) + O(a), \qquad (2)$$

$$CO(a) + O(a) \rightarrow CO_2(g). \qquad (3)$$

Bimolecular:

$$CO(a) + NO(a) \rightarrow CO_2(g) + N(a). \qquad (4)$$

The infrared (IR) chemiluminescence technique has been applied to measure the internal energy of the product CO_2 molecules desorbed during catalytic CO oxidation by O_2 on Pt and Pd surfaces in order to obtain information about the dynamics of CO_2 formation. However, most work has been performed on polycrystalline Pt and Pd surfaces [11,12]. Recently, we have found that the steady-state $CO + O_2$ reaction on a single-crystal Pd surface is structure sensitive with regard to the dynamics [13–15]: the CO_2 molecules from Pd(111) were more vibrationally excited than those from Pd(110). From these results, we have concluded that the activated CO_2 complex (i.e., the transition state of CO_2 formation from $CO(a) + O(a)$) was more bent on flat Pd(111) terraces, and relatively linear on atomically rough Pd(110) [13]. The results indicate that the IR chemiluminescence method can provide direct energetic evidence of the reaction sites for CO_2 formation. If the dissociative mechanism (equations (2) and (3)) prevails, we may find similarities in the vibrational excitation and its dependence on surface temperature. If the bimolecular mechanism (equation (4)) prevails, the vibrational states of CO_2 would be different from those in the $CO + O_2$ reaction,

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or at least have a different dependence on surface temperature [16]. Almost no work on the vibrational energy of CO_2 produced from the CO + NO reaction has been performed. Bald and Bernasek [16] found a rough similarity in the vibrational excitation during the CO + NO reaction on a polycrystalline Pt surface. In this paper, on the basis of the results of CO oxidation by O_2, we elucidate the mechanism of the CO + NO reaction over well-defined Pd(111) and Pd(110) surfaces.

2. Experimental

A molecular-beam reaction system in combination with an FTIR spectrometer (equipped with an InSb detector) was used to measure IR emission of product CO_2 molecules desorbed immediately after catalytic reaction on the metal surface [13–15]. The UHV chamber (base pressure $<1.0 \times 10^{-9}$ torr) was equipped with a CaF_2 lens, which collects IR emission, an Ar^+ ion gun for sample cleaning, and a quadrupole mass spectrometer (QMS) with a differential pumping system. Two supersonic molecular-beam nozzles (0.1 mm diameter orifice) were used for the supply of reactant gases. The CO and NO gases (total flux was 0.4–$2.0 \times 10^{19}\,cm^{-2}\,s^{-1}$; CO/NO ratio = 1/1) or the CO and O_2 gases (total flux was 1.2–$2.0 \times 10^{19}\,cm^{-2}\,s^{-1}$; CO/$O_2$ ratio = 1/1) were exposed to the Pd surface. Steady-state CO + NO and CO + O_2 reactions were performed in the temperature range 400–900 K. Another UHV system (base pressure $<2 \times 10^{-10}$ torr) equipped with a molecular-beam reaction chamber, an Ar^+ ion gun, LEED, and a QMS was used to prepare the sample and to characterize the Pd surface. Before the molecular-beam reaction, Pd(111) and Pd(110) were cleaned by a standard procedure (O_2 treatment, short Ar^+ bombardment and annealing).

The IR emission spectra of the CO_2 molecules desorbed from the surface were measured with 4 cm^{-1} resolution, as reported previously [11,17]. Because of the low resolution, no individual vibration–rotation lines were resolved. However, analysis of the degree of red shift from the fundamental band (2349 cm^{-1}) allowed an estimation of the average vibrational temperature (T_V) of CO_2. Here, T_V was used as a parameter characterizing the extent of the vibrational excitation of the product CO_2 [17,18]. It took about 1–5 h to measure the IR spectra with 2000–10 000 scans. The signal-to-noise ratio has been improved since a more sensitive InSb detector was used instead of using an MCT detector [18]. During the measurement, the activity was stable and therefore the results reflected the CO_2 states under steady-state conditions. The production rate of CO_2 was determined using a mass spectrometer, and the amount of N_2O formation (by-product) was checked by a gas chromatograph.

3. Results and discussion

Figure 1 shows the rate of CO_2 formed in the steady-state CO + NO reaction on Pd(111) and Pd(110) as a function of surface temperature (T_S). The CO + NO reaction proceeded above 550 K, and the CO_2 formation rate increased with surface temperature in the range 550–700 K, while it decreased in the range 700–900 K. In addition, it is found that Pd(110) exhibited much higher activity than Pd(111). This indicates that the CO + NO reaction on Pd surface is structure sensitive. A possible by-product in the CO + NO reaction (equation (1)) is N_2O:

$$2NO + CO \rightarrow N_2O + CO_2. \qquad (5)$$

However, in our case, the contribution of equation (5) is small. The selectivity of N_2O formation ($N_2O/(N_2O + N_2)$) was 8% at most in the result shown in figure 1.

Figure 2 shows the rate of CO_2 formed in the steady-state CO + O_2 reaction on Pd(111) and Pd(110) as a function of surface temperature. The CO oxidation proceeded above 450 K and the profiles of the formation rate had maxima on both Pd surfaces. These behaviors are in good agreement with the general kinetics of CO oxidation on Pd surfaces [11–17,19,20]. The temperature of highest activity (T_{max}) and the formation rate of CO_2 were also different between these surfaces, although the difference in the activity is not so large as in the case of the CO + NO reaction. From the comparison between the results in figures 1 and 2, the formation rate of CO_2 in the CO + NO reaction is much lower than that of CO + O_2 on both surfaces. This difference in the activity can be related to the difference in the reactivity between oxygen and NO.

Regarding the reaction kinetics of the CO + O_2 reaction [19,20], it is known that at lower temperatures than T_{max}, the surface coverage of CO is high, and the rate-determining step is desorption of CO (since CO(a)

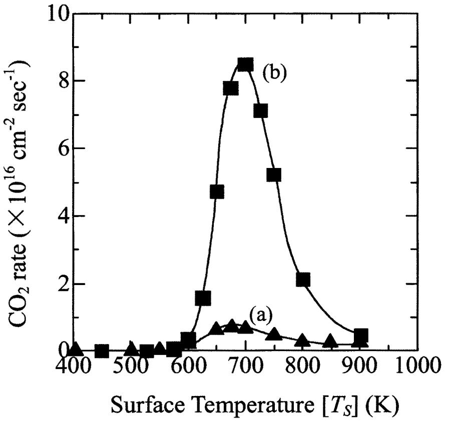

Figure 1. Formation rate of CO_2 during the CO + NO reaction (CO/NO ratio = 1/1) on (a) Pd(111) and (b) Pd(110). The total flux of reactants (CO + NO) was 4.1×10^{18} molecules $cm^{-2}\,s^{-1}$.

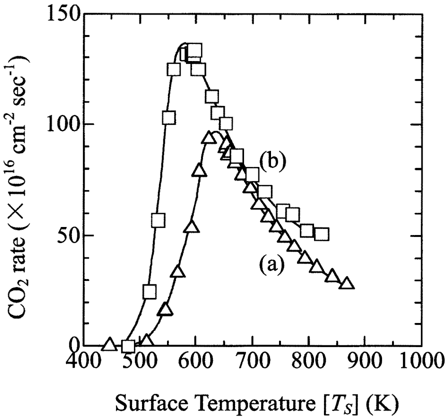

Figure 2. Formation rate of CO_2 during the $CO + O_2$ reaction (CO/O_2 ratio = 1/1) on (a) Pd(111) and (b) Pd(110). The total flux of reactants ($CO + O_2$) was 1.2×10^{19} molecules cm^{-2} s^{-1}.

inhibits chemisorption of oxygen). At higher temperatures than T_{max}, the rate decreases due to a continuous decrease of the stationary CO(a) concentration: the rate is now limited by CO adsorption. Similar kinetics have been proposed for the CO + NO reaction on Pt and Pd surfaces [4,9,16]. Adsorbed CO has been found to inhibit dissociation and adsorption of NO [21], so at lower temperatures the reaction is initially limited by CO desorption. As the CO molecules desorb, sites are open for NO adsorption, and the rate increases with surface temperature. At higher temperatures (above T_{max}), the surface CO coverage is very low, and the rate is limited by CO adsorption.

Figure 3 shows the IR emission spectra of CO_2 molecules produced by the CO + NO and $CO + O_2$ reactions on Pd(111) and Pd(110) at $T_S = 670$ K. The CO_2 emission spectra observed in the region of 2400–2200 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 the unreacted CO, which was scattered from the surface. The degree of red shift from the fundamental band reflects the vibrational state of excited molecules. In particular, the spectra from Pd(111) are more red-shifted than these from Pd(110).

Figure 4 shows the vibrational temperature (T_V) derived from IR emission spectra of CO_2 as a function of surface temperature (T_S). Each T_V value is much higher than T_S, which indicates that the CO_2 formed is vibrationally excited. The T_V values of CO_2 formed in both CO + NO and $CO + O_2$ reactions on Pd(111) are much higher than those of CO_2 on Pd(110). It is surprising that T_V for the CO + NO reaction is almost the same as that for the $CO + O_2$ reaction on each Pd surface, although the formation rate of CO_2 was different in the two reactions, as shown in figures 1 and 2. This indicates that T_V is strongly dependent on the surface structure, not on the reactions.

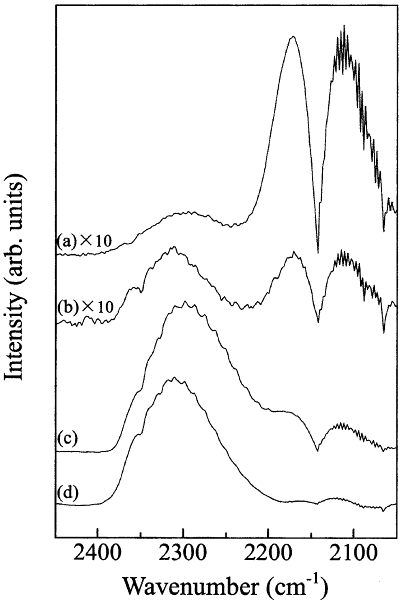

Figure 3. IR emission spectra of CO_2 desorbed by the CO + NO reaction on (a) Pd(111) and (b) Pd(110), and by the $CO + O_2$ reaction on (c) Pd(111) and (d) Pd(110). The surface temperature (T_S) was 670 K. The total flux of reactants was 2.0×10^{19} molecules cm^{-2} s^{-1} at the CO/NO or CO/O_2 ratio = 1 on Pd(111), 1.2×10^{19} molecules cm^{-2} s^{-1} at the CO/NO or CO/O_2 ratio = 1 on Pd(110).

As shown in figure 4, both the vibrational excitation and its dependence upon the surface temperature are similar for the CO + NO and $CO + O_2$ reaction systems on each Pd surface (Pd(111) or Pd(110)). This provides strong evidence that the CO_2 formation steps for the two reaction systems are the same, which suggests that the CO + NO reaction proceeds by the dissociative mechanism (i.e., equations (2) and (3)). According to the literature [22–24], the step sites contribute to the dissociation of NO.

The results of the IR chemiluminescence measurements for the $CO + O_2$ reaction (see figure 4) are in good agreement with previous results [13–15]. The higher T_V values are observed for the CO_2 formation on flat Pd(111) terraces, while the lower T_V values are

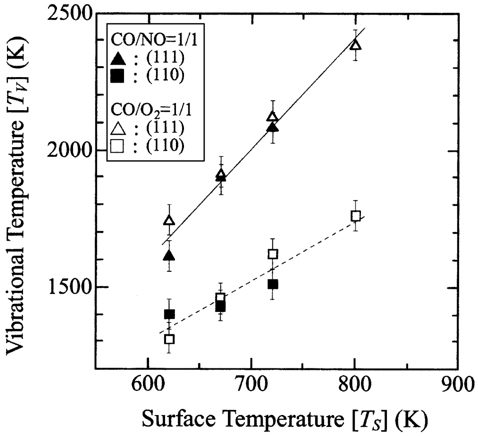

Figure 4. Surface temperature dependence of vibrational temperature (T_V) of CO_2 formed in CO + NO and $CO + O_2$ reactions on Pd(111) and Pd(110). The reaction conditions are as described in figure 3.

observed for the CO_2 formation on stepped (atomically rough) Pd(110). As already mentioned, the CO_2 formation steps for the CO + NO reaction are the same as those for the CO + O_2 reaction (i.e., equation (3)). Therefore, for the CO + NO reaction on Pd(110) the CO_2 formation takes place on the steps, which give the lower T_V values, while on Pd(111) the CO_2 formation takes place on the terraces, which give the higher T_V values.

It is generally thought that the NO dissociation is difficult to proceed on Pd(111). This is supported by the results that the activity of the CO + NO reaction was much lower on Pd(111) than on Pd(110). According to the theoretical calculation by Hammer [25], the step may be about 10^5 times more reactive per site than the other flat Pd surface, and small amounts of Pd steps and defects, which do exist on the surface of flat surfaces such as Pd(111), may therefore completely dominate the kinetics of the CO + NO reaction. NO may dissociate on the steps and defects, and the O(a) produced may diffuse onto the terraces, and react selectively with CO(a) on the terraces. In a temperature-programmed reduction study on Pt(321), Gland *et al.* [26] suggested the preferential reaction of CO(a) with atomic oxygen adsorbed on terrace sites rather than on step sites. As an alternative interpretation, the diffusion of O(a) may be much faster than the rate of CO_2 formation (i.e., the CO(a) + O(a) recombination) at these high temperatures [15]. In this case, the IR emission signals of CO_2 from the terraces should be dominant because of the small number of steps and defects on Pd(111).

4. Conclusions

(1) The activity of the CO + NO reaction on Pd(110) was much higher than that on Pd(111). This can be due to the structure sensitivity of the reaction, especially NO dissociation.

(2) The vibrational temperatures (T_V) of CO_2 formed in both CO + NO and CO + O_2 reactions on Pd(111) were much higher than those of CO_2 on Pd(110).

(3) The T_V values of CO_2 formed in the CO + NO reaction were similar to those in the CO + O_2 reaction on each Pd surface as a function of surface temperature. This indicates the transition state of CO_2 formation is the same for both reactions on each Pd surface.

(4) In the CO + NO reaction, it is concluded that CO_2 is formed in the reaction between CO(a) and O(a), which is supplied by NO dissociation. On Pd(110) the CO_2 formation takes place on the steps, which give the lower T_V values, while on Pd(111) CO_2 is formed on the terraces, which give the higher T_V values.

References

[1] K.C. Tayler, Catal. Rev. Sci. Eng. 35 (1993) 457.
[2] A. Obuchi, S. Naito, T. Ohnishi and K. Tamaru, Surf. Sci. 122 (1982) 235
[3] L.M. Carballo, T. Hahn and H.G. Lintz, Appl. Surf. Sci. 40 (1989) 53.
[4] G. Xi, J. Bao, S. Shao and S. Li, J. Vac. Sci. Technol. A 10 (1992) 2351.
[5] X. Xu, P. Chen and D.W. Goodman, J. Phys. Chem. 98 (1994) 9242.
[6] S.M. Vesecky, P. Chen, X. Xu and D.W. Goodman, J. Vac. Sci. Technol. A 13 (1995) 1539.
[7] M. Daté, H. Okuyama, N. Takagi, M. Nishijima and T. Aruga, Surf. Sci. 350 (1996) 79.
[8] S.M. Vesecky, D.R. Rainer and D.W. Goodman, J. Vac. Sci. Technol. A 14 (1996) 1457.
[9] R.L. Klein, S. Schwartz and L.D. Schmidt, J. Phys. Chem. 89 (1985) 4908.
[10] B.A. Banse, D.T. Wickcham and B.E. Koel, J. Catal. 119 (1989) 238.
[11] D.A. Mantell, K. Kunimori, S.B. Ryali, G.L. Haller and J.B. Fenn, Surf. Sci. 172 (1986) 281.
[12] G.W. Coulston and G.L. Haller, J. Chem. Phys. 95 (1991) 6932.
[13] H. Uetsuka, K. Watanabe, H. Ohnuma and K. Kunimori, Chem. Lett. (1996) 227.
[14] K. Watanabe, H. Ohnuma, H. Kimpara, H. Uetsuka and K. Kunimori, Surf. Sci. 402–404 (1998) 100.
[15] H. Uetsuka, K. Watanabe, H. Kimpara and K. Kunimori, Langmuir 15 (1999) 5795.
[16] D.J. Bald and S.L. Bernasek, J. Chem. Phys. 109 (1998) 746.
[17] K. Kunimori and G.L. Haller, Bull. Chem. Soc. Jpn. 65 (1992) 2450.
[18] K. Kunimori, H. Uetsuka, T. Iwade, T. Watanabe and S. Ito, Surf. Sci. 283 (1993) 58
[19] T. Engel and G. Ertl, Adv. Catal. 28 (1979) 1.
[20] T. Engel and G. Ertl, J. Chem. Phys. 69 (1978) 1267
[21] R.J. Gorte and L.D. Schmidt, Surf. Sci. 111 (1981) 260.
[22] R.D. Ramsier, Q. Gao, H. Neergaard Waltenburg and J.T. Yates Jr., J. Chem. Phys. 100 (1994) 6837
[23] R.D. Ramsier, Q. Gao, H. Neergaard Waltenburg, K.-W. Lee, O.W. Nooij, L. Lefferts and J.T. Yates Jr., Surf. Sci. 320 (1994) 209.
[24] I. Nakamura, T. Fujitani and H. Hamada, Surf. Sci. 514 (2002) 409.
[25] B. Hammer, J. Catal. 199 (2001) 171.
[26] J.L. Gland, M.R. McClellan and F.R. McFeely, J. Vac. Sci. Technol. A 1 (1983) 1070.