Active Sites in a Two-Step Catalytic Bimolecular Reaction on a Reconstructed Platinum Surface

Toshiro Yamanaka*
Catalysis Research Center, Hokkaido University, Sapporo 001-0021, Japan

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Active sites for a thermally induced bimolecular two-step catalytic reaction ($O_2 \rightarrow 2O$, $O + CO \rightarrow CO_2$) that occurs on a Pt(113)(1 × 2) structure at around 160 K were studied by angular distribution measurements of desorbing product CO_2. It was found that the intrinsic activity level of two-atom-wide (001) facets is significantly higher than that of two-atom-wide (111) facets, while the activity of (111) facets was also significant when this reaction was induced by irradiation of 193 nm photons. Possible mechanisms for the difference in activities of the two facets are discussed.

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Elucidation of active sites in surface reactions is an important subject since such a microscopic understanding of surface processes is required to develop superior catalysts, electrodes, and material growth processes. It has been believed for a long time that catalytic reactions proceed at specific active sites such as steps and defects [1]. Results of studies using scanning tunneling microscopy (STM) [2,3] and theoretical works [4] over the past decade have provided evidence of higher levels of activity of local microstructures (monoatomic steps and defects) than that of flat terraces for simple association and dissociation processes. The mechanism for the enhanced activity on step sites is thought to be a local rise in energy level of a *d* band at these narrow protruding sites. Activity on monoatomic steps versus wide terraces has been extensively studied, but experimental studies on activity on two different local microstructures that have similar geometries, for example, two-atom-wide (111) and two-atom-wide (001) microfacets with similar inclinations in a Pt(113)(1 × 2) structure (Fig. 1), are still lacking. Studying activities of these facets with the next smallest width to monoatomic steps is important for designing and controlling reactions at an atomic level.

Activity on different sites has so far been studied for single step processes, such as activity for dissociation of a molecule on step versus terrace sites. However, in many cases catalytic reactions proceed through two or more elementary processes.

In this study, active sites for a thermally induced two-step bimolecular reaction, $O_2 \rightarrow 2O$ and $O + CO \rightarrow CO_2$, on a Pt(113)(1 × 2) reconstructed structure that has two-atom-wide (111) and two-atom-wide (001) facets with similar inclination angles were investigated. Active sites were determined by measurements of angular distribution of desorbing product CO_2 since STM observation of these facets inside deep ditches is difficult. It was found that the intrinsic activity level is higher on two-atom-wide (001) facets than on two-atom-wide (111) facets in this (1 × 2) structure. The results indicate that activity is different even between atomic facets with very similar sizes and shapes. In addition, the activity of these sites is controllable by selection of the excitation method, since activity of (111) facets was also significant when this reaction was induced by irradiation of photons.

CO oxidation on platinum surfaces is one of the most extensively studied catalytic reactions. At temperatures above 200 K, this reaction proceeds through association of CO admolecules and oxygen adatoms that results from dissociative adsorption of O_2, known as "the Langmuir Hinshelwood (LH) mechanism" [5]. At lower temperatures, another type of CO oxidation occurs between O_2 and CO. Oxygen is adsorbed on platinum surfaces as O_2 admolecules at temperatures below 150 K [6]. During heating of the surface, some O_2 molecules are desorbed around 150 K, while the other O_2 molecules dissociate. The dissociation products, O atoms, initially have high translational energies of about 1 eV and are known as

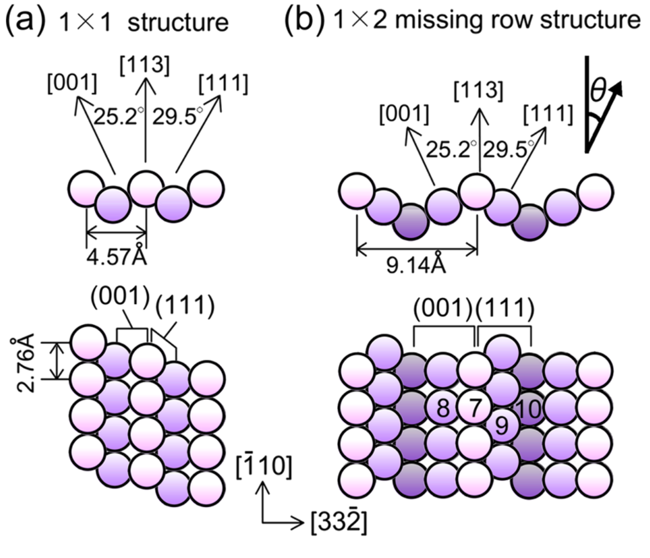

FIG. 1 (color online). Top and side views of Pt(113) surface structures. (a) An ideal (1 × 1) structure. (b) A (1 × 2) missing row structure. The actual clean surface reconstructs into this structure. (111) and (001) facets are declined by 29.5° and 25.2° from the (113) macroscopic plane, respectively. Coordination numbers of Pt atoms are also shown in the top view.

"hot atoms" [7]. Hot atoms migrate on the surface for a short time before their energy is dissipated into the bulk. CO oxidation occurs if a hot atom collides with a coadsorbed CO molecule [6,8]. This CO_2 formation is observed at the same temperature as that of O_2 desorption (about 150 K) [6]. Similar CO oxidation by the hot-atom (HA) mechanism is also induced by irradiation of ultraviolet photons, that is, by collision between CO and hot-oxygen atoms emitted by photodissociation of oxygen admolecules [9,10].

In CO oxidation on platinum surfaces, nascent CO_2 receives strong repulsion perpendicular to its formation site [11], resulting in CO_2 desorption in the perpendicular direction. Thus, the formation sites can be identified from angular distribution of desorbing CO_2 [12]. An ideal Pt (113) surface consists of (111) and (001) facets, and the actual clean surface is reconstructed into a (1×2) missing row structure [13,14], as shown in Fig. 1. This surface was successively exposed to 1.2 Langmuir (L) of $^{18}O_2$ and 2.5 L of $^{12}C^{16}O$ at 110 K so that both (111) and (001) facets on the surface were saturated by $^{18}O_2$ [0.67 monolayer (ML)] and $^{12}C^{16}O$ (0.50 ML). CO-induced reconstruction of this surface into the 1×1 structure [13] should be negligibly slow in the present study conducted at a low temperature. CO oxidation was induced by heating of the sample or irradiation of ArF excimer laser pulses (193 nm, 16 ns in duration) at 110 K. Desorbing $^{12}C^{16}O^{18}O$ and $^{18}O_2$ passed through two slits being collimated and were detected at specific desorption angles (angle-resolved signals) by a quadrapole mass spectrometer (QMS) [6]. In addition, desorbing $^{12}C^{16}O^{18}O$ and $^{18}O_2$ were also detected by another QMS without passing through slits (angle-integrated signals).

Figure 2 shows angle-integrated signals of O_2 desorption and CO_2 formation obtained during heating of the Pt(113)(1×2) surface saturated by O_2 and CO at 110 K. The O_2 signals show a sharp peak at 160 K and small shoulders at 225 K. These are due to direct thermal desorption of O_2 admolecules [15]. Simultaneously, some of the O_2 dissociates at these temperatures. Another O_2 desorption peak was observed at 650 K–1000 K (not shown), which is due to recombinative desorption of the resultant oxygen adatoms [15]. The CO_2 formation signals show four peaks, as can be seen in Fig. 2. The position of the peak at the lowest temperature (P1) is almost the same as that of the main O_2 desorption peak, and this P1-CO_2 formation is observed only when the surface is covered by O_2. Therefore, this peak is assigned to CO_2 generated by the HA mechanism. The CO_2 formation peak at 225 K (P2) may also be CO_2 generated by the HA mechanism, but the contribution of CO_2 generated by the LH mechanism may also be significant at this temperature. Thus, only P1-CO_2 will be discussed below.

Angular distribution of P1-CO_2 desorption in the $[3\ 3\ \bar{2}]$ direction is shown in Fig. 3(a). This distribution has a maximum at $-16°$. This distribution can be fitted by a linear combination of cosine power functions, $2\cos^{25}(\theta + 16) + 0.75\cos^{25}(\theta - 16)$ (normalized so that the value at zero degrees is one), as indicated by the solid and dashed lines. The collimation angles of these components (-16 and $+16$) are close to the angles of inclination of (001) and (111) facets, respectively. Therefore, these two components are assigned to CO_2 formed on (001) and (111) facets, respectively. This result indicates that CO_2 is formed mainly on (001) facets.

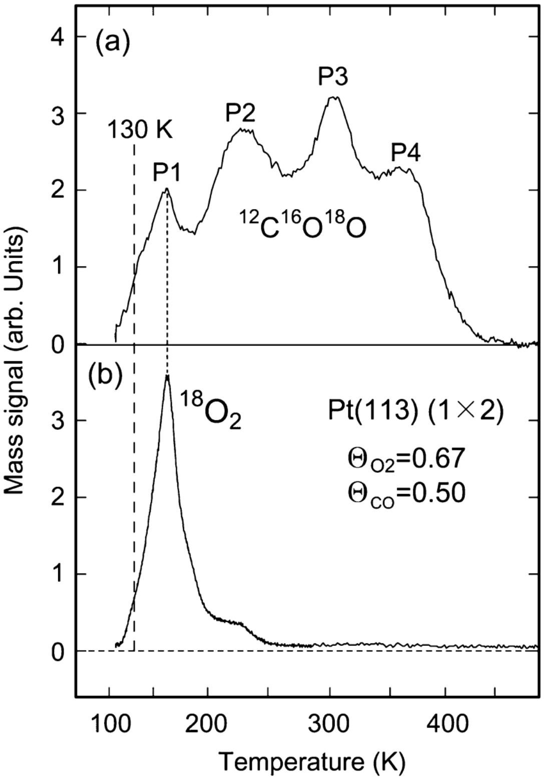

FIG. 2. Angle-integrated thermal desorption spectra of (a) $^{12}C^{16}O^{18}O$ and (b) $^{18}O_2$ from a Pt(113)(1×2) surface covered by a 0.67 monolayer of $^{18}O_2$ and 0.50 monolayer of $^{12}C^{16}O$. The Pt(113)(1×2) surface was successively exposed to 1.2 L of $^{18}O_2$ and 1.5 L of $^{12}C^{16}O$ at 110 K. The vertical dashed and dotted lines indicate a temperature of 130 K and the temperature at the peak of desorption of $^{18}O_2$, respectively. At 130 K the decreases of $^{18}O_2$ and $^{12}C^{16}O$ compared with the initial coverage are negligibly small.

The purpose of these experiments was to identify reaction sites of CO oxidation by the HA mechanism at the surface saturated by O_2 and CO. However, when the sample was heated to 160 K (the maximum of P1-CO_2), about 27% of O_2 and 9% of CO were reduced from the surface due to desorption of O_2 and CO oxidation, and oxygen adatoms should have been created by O_2 dissociation. After these changes, the adsorption sites of O_2 and CO might have changed and CO oxidation by the LH mechanism might have started. To eliminate these effects, angular distribution of CO_2 was studied at a lower temperature of 130 K (indicated by a vertical dashed line in Fig. 2), a temperature at which the decrease in O_2 and CO coverages

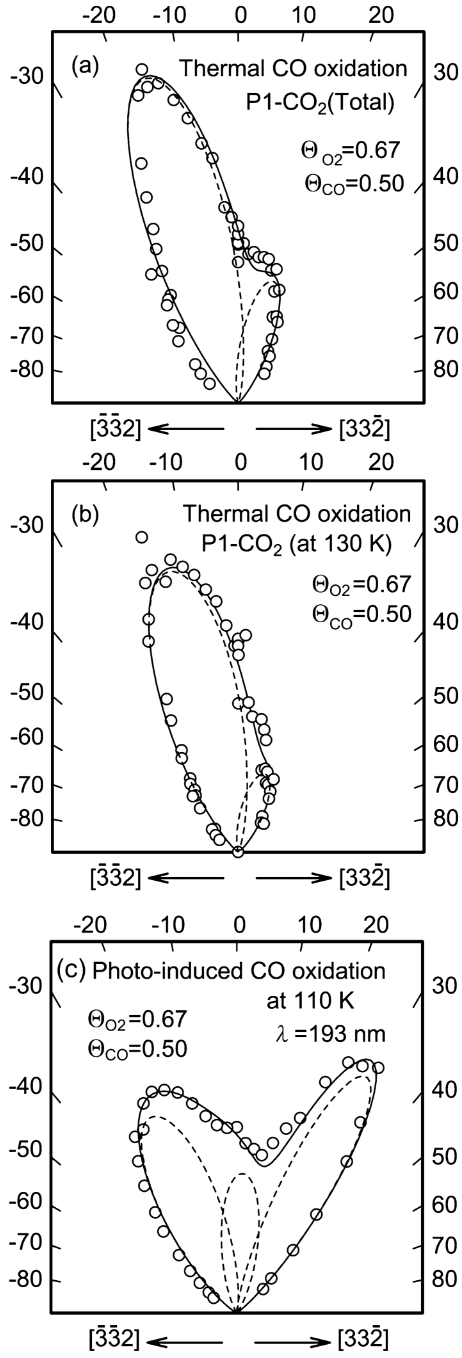

FIG. 3. (a),(b) Angular distribution of product $^{12}C^{16}O^{18}O$ desorption in thermal CO oxidation from a Pt(113)(1 × 2) surface saturated by a 0.67 ML of $^{18}O_2$ and 0.50 ML of $^{12}C^{16}O$. (a) Total yields of P1-CO$_2$ desorption in thermal reaction. (b) CO$_2$ desorption yields in thermal reaction at 130 K. (c) Angular distribution of product $^{12}C^{16}O^{18}O$ desorption during irradiation of 193 nm photons on a Pt(113)(1 × 2) surface saturated by a 0.67 ML of $^{18}O_2$ and 0.50 ML of $^{12}C^{16}O$ at 110 K.

(about 2.3% and 1%, respectively) is negligible. The results are shown in Fig. 3(b). The distribution is explained well by $1.4\cos^{20}(\theta + 15) + 0.4\cos^{18}(\theta - 19)$, indicating again a higher reaction rate on the (001) facets.

For comparison, angular distribution of CO$_2$ during photoinduced HA CO oxidation on the same surface saturated by O$_2$ and CO at 110 K is shown in Fig. 3(c). The decrease of total reactants after photoirradiation is less than 10%. This distribution shows two maxima, one at 30° and one at 21°, quite different from the results obtained for thermal reaction. This distribution is explained well by $1.15\cos^{19}(\theta + 23.7) + 1.45\cos^{43}(\theta - 28.7) + 0.75\cos^{20}(\theta - 2.3)$, as indicated by the solid and dashed lines. The angles $-23.7°$ and $+28.7°$ are very close to the inclination angles of (001) and (111) facets on this surface, and the two components are assigned to CO$_2$ formed on (001) and (111) facets, respectively. The new component collimated at around 2° may be assigned to CO$_2$ formed at the top or bottom of the (1 × 2) structure. This result indicates that CO$_2$ formation on the (111) facets is also significant in contrast to the thermal reaction. In both thermal- and photoinduced CO oxidation, angular distributions of CO$_2$ in a plane along the edges (in the [$\bar{1}$ 1 0] direction) had a maximum at the surface normal (not shown). The collimation angles in thermal reactions at 160 and 130 K [Figs. 3(a) and 3(b)] are smaller than the expected values (29.5° and 25.2°) because the corrugation of the repulsive potential (density of metal electrons) is less than that of atomic arrangements [12]. The collimation angles may also be changed by difference in repulsion from neighboring reactants between 130 and 160 K. In photoreaction, the product CO$_2$ has greater translational energy [16], suggesting that CO$_2$ receives repulsion at a deep position where the corrugation of the potential is close to that of the atomic arrangement, resulting in collimation angles close to the expected values [Fig. 3(c)].

CO$_2$ formation sites in LH reactions have been analyzed in previous works by angular distribution measurements of product CO$_2$ [6,17]. In these works, the site of CO oxidation was determined by the locations of O atoms and CO, and it was found to change depending on coverages of CO and O atoms and temperature since the location of CO and O atoms changed depending on these coverages and temperature. Therefore, the intrinsic activity of each reaction site remains ambiguous. On the other hand, in the present work, the surface was initially saturated by O$_2$ and CO so that both (111) and (001) facets were occupied by both O$_2$ and CO, and the change in adsorption sites due to diffusion of reactants was suppressed at a low temperature. The fact that CO photo-oxidation occurred on both (111) and (001) facets indicates the existence of O$_2$ and CO on both facets. Nevertheless, thermal CO oxidation occurred mostly on (001) facets. This indicates that the intrinsic activity level of (001) facets in a thermal CO oxidation is significantly higher than that of (111) facets and that the activity of sites can be controlled by selection of the excitation method (heat and photoirradiation). On the present surface, O$_2$ admolecules are aligned parallel to the edges of this surface [15], and hot atoms are emitted parallel to the edges [10,16]. In addition, the diffusion lengths of hot atoms are only one or two lattice constants [7,18]. Therefore, most of the CO_2 formation is expected to occur by collision between CO and a hot atom emitted from the nearest O_2 on the same facet.

In LH CO oxidation, the main origin of the activation barrier is the energy to weaken O-metal [5,19] and CO-metal [20] bonds to create a O-CO transition state, since the energy cost due to repulsion between O and CO in the transition state, i.e., competition between CO and O to bind to the same Pt atom and Pauli repulsion between CO and O, is not large [21]. Thus, the activation barrier will increase with increases in O-Pt and CO-Pt bonding energies in the initial adsorbed states. Applying the criteria of binding energy of an O atom on a Pt surface proposed by Feibelman *et al.* [22], binding energy of O on the Pt(113) × (1 × 2) surface is expected to be higher in the vicinity of low-coordinated Pt atoms on (001) facets than in the vicinity of those on (111) facets (the coordination numbers are shown in Fig. 1). The binding energy of CO is also expected to be higher on (001) facets since the binding energy of CO is calculated to be higher on a Pt(001) surface than on a Pt(111) surface [23,24]. Therefore, on a Pt(113)(1 × 2) surface, the activation barrier for LH CO oxidation on (001) facets is expected to be higher. It was also theoretically predicted that the reaction rate of LH CO oxidation on Pt(111) is higher than that on Pt(001) [25]. This is opposite to the present results showing that thermal CO oxidation occurs mainly on (001) facets, suggesting that the thermal CO oxidation in the present study did not occur by the LH mechanism.

The rate of HA reaction, which is a two-step reaction, should be high when the barrier of the first dissociation step of O_2 is low and binding between intermediate hot-oxygen atoms and the substrate is weak [26]. Since bonding of a hot O atom to the substrate is naturally expected to be weak, the hot O atom should be quite reactive toward CO. In this case, O_2 dissociation is the rate-limiting step. Generally, the energy levels of transition states for dissociation of admolecules (E_{TS}) decrease with increases in bonding energies between dissociation products and substrates [27–29]. In the case of O_2 dissociation on platinum surfaces, E_{TS} is considered to be an important parameter rather than the local dissociation barrier from the molecular precursor state, E_{TS}-E_{MPS}, where E_{MPS} is the energy level of an O_2 molecular precursor (energy levels given with respect to gas-phase O_2) [30]. That is, the dissociation rate increases when E_{TS} becomes low, regardless of E_{TS}-E_{MPS}. On a Pt(113)(1 × 2) surface, E_{TS} for O_2 dissociation should be lower on the (001) facets, where the adsorption energy of O atoms is higher, resulting in an enhanced reactivity for HA CO oxidation on the (001) facets. This explains the higher rate for thermal CO oxidation on the (001) facets observed in the present study. For the HA CO oxidation photoinduced by 193 nm irradiation, the reactivity on the (111) facets was found to be as high as that on the (001) facets, since the energy of 193 nm photons is thought to be sufficiently high for excitation of O_2 dissociation at any sites. These results demonstrate a new possibility for selection of reactants to induce catalytic reactions.

In summary, intrinsic activities of two-atom-wide facets for bimolecular two-step catalytic reaction on a Pt(113) × (1 × 2) structure have been distinguished by angular distribution measurements of desorbing product CO_2, which would be difficult to study by other experimental methods. This distinction has become possible by comparing angular distributions in thermal reaction and photoreaction at a low temperature. The present results suggest that the notion of active sites can be extended to multistep reactions on surfaces with micro facet structures.

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*yama@cat.hokudai.ac.jp

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