Steric Effect in O_2 Sticking on Al(111): Preference for Parallel Geometry

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We present experimental evidence that the sticking probability of O_2 on Al(111) depends strongly on the alignment of an O_2 molecule relative to the surface. The steric effect was measured with an aligned O_2 beam prepared by a hexapole magnet. It has been found that, at translational energies <0.2 eV, O_2 sticking occurs predominantly when the molecular axis is *parallel* to the surface, and that the dissociation barrier at the perpendicular geometry is ~0.1 eV higher than at the parallel geometry. The present results indicate that the abstraction process, which would occur at the perpendicular geometry, is a *minor* event at low translational energies.

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Oxygen adsorption on metallic surfaces is of great technological importance as the initial step of catalytic oxidation, oxide formation, and corrosion. Especially, oxidation of an Al(111) surface has been investigated intensively as the most representative system of surface oxidation. Its initial reaction mechanism, however, has not been well understood and is still under debate regarding the following two points. The first is that, despite the enormous exothermicity, the dissociative sticking probability of thermal O_2 on Al(111) is very low (< 0.01) [1,2]. A finite energy barrier causing the inefficient sticking has been derived theoretically by explicitly considering the spin selection rule [3,4], nonlocal exchange effects [5] or short-ranged correlation effects [6]. The second concerns the dynamical process of the initial oxidation. A scanning tunneling microscopy (STM) study has shown widely separated atomic oxygen species after O_2 adsorption [2,7]. In early discussions this has been attributed to the transient mobility driven by the chemisorption energy [2,7], but this "hot adatom" model has been found to be unlikely [8,9]. The abstraction mechanism, in which one oxygen atom is bound to the surface while the other is ejected toward the vacuum, has been proposed alternatively [10–13]. This mechanism is supported by a resonance enhanced multiphoton ionization (REMPI) measurement, which has detected the atomic oxygen ejected by O_2 dissociation [10–13] and shown that its yield changes similarly with the O_2 sticking probability when the O_2 translational energy (E_0) is varied [11–13]. This proves that the abstraction process is happening. It is, however, not evident whether or not the abstraction process is the dominant event at low E_0. In addition, this mechanism seems not fully consistent with recent theoretical calculations. Previous studies agree that the abstraction process occurs when the O_2 molecular axis is perpendicular to the surface [6,10–16]. The computed dissociation barrier for the perpendicular geometry is, however, higher than [4] or comparable to that for the parallel geometry [6]. Furthermore, an STM study by Schmid *et al.* [17], which has suggested that the adsorbate formed after exposure to thermal O_2 consists of two oxygen atoms locating at nearby sites, has not been disproved. To settle the controversy, it is essential to get another new experimental evidence which enables us to discuss the validity of the abstraction mechanism.

In this Letter, we present alignment-resolved O_2 chemisorption measurements showing that O_2 molecules parallel to an Al(111) surface have much higher sticking probabilities than those perpendicular to the surface at $E_0 < 0.2$ eV. The E_0 dependence of the sticking probability indicates that the dissociation barrier at the perpendicular geometry is ~0.1 eV higher than at the parallel geometry. The present results reveal that the abstraction process, which occurs at the perpendicular geometry, is a *minor* event at low E_0.

The details about the experimental method were described in our previous papers [18,19]. In brief, a single spin-rotational state-selected $[(J, M) = (2, 2)]$ O_2 beam prepared with a hexapole magnet was used for the O_2 sticking experiment. Since the rotational quantum numbers are nearly specified to be $(K, M_K) = (1, 1)$ for this quantum state, the angular distribution function for the molecular axis is approximately equal to the spherical harmonic function $|Y_1^1|^2$ ($\propto \sin^2\theta$), where θ is the polar angle relative to the defining magnetic field (H) direction. Therefore, by directing H perpendicular (parallel) to the surface, we can realize the so-called helicopter (cartwheel) geometry (see the inset of Fig. 1). The O_2 axis is mainly parallel to the surface for the helicopter geometry while parallel and perpendicular configurations coexist in the cartwheel geometry. The sticking probabilities for the helicopter $[S_0(H)]$ and cartwheel $[S_0(C)]$ geometries are given by

$$S_0(H) = \frac{3}{4\pi}\int_0^{2\pi} d\phi \int_0^{\pi/2} R_{\rm av}(\theta, \phi)\sin\theta^3 d\theta. \quad (1)$$

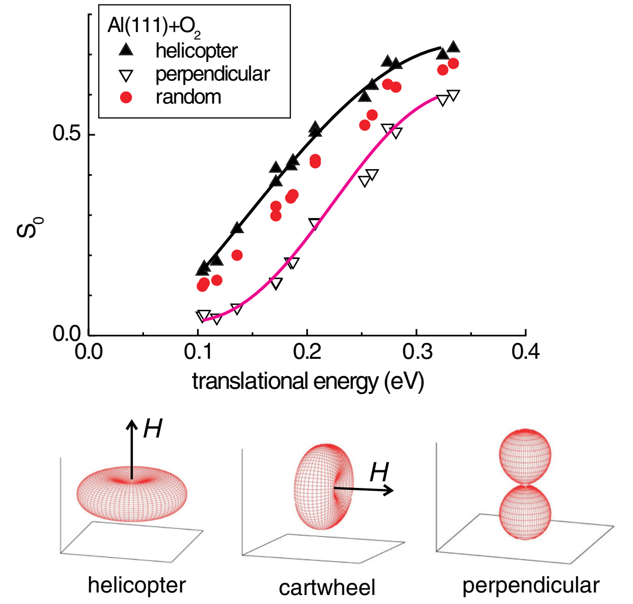

FIG. 1 (color online). The translational energy dependence of the O_2 sticking probability on Al(111) measured at 300–310 K for the geometries shown. Solid lines are guides to the eye. The O_2 axis angular distribution functions for helicopter, cartwheel, and perpendicular geometries are depicted at the bottom.

$$S_0(C) = \frac{3}{4\pi}\int_0^{2\pi} d\phi \int_0^{\pi/2} R_{\mathrm{av}}(\theta, \phi) \times [1 - \sin^2\theta \sin^2\phi] \sin\theta d\theta. \tag{2}$$

Here, $R_{\mathrm{av}}(\theta, \phi)$ is the reaction rate of an O_2 molecule, the molecular axis of which had initially been at polar and azimuthal angles of θ, ϕ relative to the surface before approaching the surface. The suffix "av" means that the reaction rate is the average over the adsorption sites. If we have a condition $R_{\mathrm{av}}(\theta, \phi) = R_{\mathrm{av}}(\theta, \phi + \pi/n)$ $(n \geq 2)$ due to the surface crystallographic symmetry, $S_0(C)$ is reduced as follows:

$$S_0(C) = \frac{3}{4\pi}\int_0^{2\pi} d\phi \int_0^{\pi/2} R_{\mathrm{av}}(\theta, \phi)\left[1 - \frac{1}{2}\sin^2\theta\right]\sin\theta d\theta. \tag{3}$$

This condition is satisfied when O_2 is incident perpendicularly to an Al(111) surface having a sixfold symmetry. Using Eqs. (1) and (3), we can derive the sticking probabilities for random [$S_0(R)$] and perpendicular distributions [$S_0(P)$; see the inset of Fig. 1] as follows.

$$\begin{aligned} S_0(R) &= \frac{1}{3}S_0(H) + \frac{2}{3}S_0(C) \\ &= \frac{1}{2\pi}\int_0^{2\pi} d\phi \int_0^{\pi/2} R_{\mathrm{av}}(\theta, \phi) \sin\theta d\theta. \end{aligned} \tag{4}$$

$$\begin{aligned} S_0(P) &= 2S_0(C) - S_0(H) \\ &= \frac{3}{2\pi}\int_0^{2\pi} d\phi \int_0^{\pi/2} R_{\mathrm{av}}(\theta, \phi)\cos^2\theta \sin\theta d\theta. \end{aligned} \tag{5}$$

The sticking probability was measured at the sample temperature of 300–310 K with the King and Wells method [20] using an ion gauge [19]. To clarify the difference in S_0 between different geometries, we monitored the sticking probability while alternating the O_2 geometry at a frequency of 0.5 Hz. The magnetic field direction ($|H| = 1$ G) was controlled by three pairs of Helmholz coils. The H direction was calibrated with a 3-axis magnetic field sensor before installing the sample manipulator. The O_2 beam flux was adjusted so that the adsorption rate is around 0.01 monolayers/sec. A clean Al(111) surface was prepared by repeating 500 eV Ne^+ bombardment and annealing at around 773 K. This procedure was repeated until no contaminants were detected by Auger electron spectroscopy and a sharp low energy electron diffraction pattern was observed.

Figure 1 shows the E_0 dependence of the O_2 sticking probability for helicopter [$S_0(H)$], perpendicular [$S_0(P)$], and random [$S_0(R)$] geometries at normal incidence. $S_0(R)$ and $S_0(P)$ were derived from the measured $S_0(H)$ and $S_0(C)$ using Eqs. (4) and (5), respectively. The sticking probabilities at these three geometries increase steeply with E_0 at 0.1–0.3 eV, and $S_0(R)$ agrees well with the reported values obtained with a randomly oriented O_2 beam [1]. It is clearly shown that $S_0(H)$ is much higher than $S_0(P)$ at $E_0 < 0.2$ eV. This unambiguously proves that O_2 molecules parallel to the surface have much higher sticking probabilities than those perpendicular to the surface at $E_0 < 0.2$ eV. The molecules at the perpendicular geometry also react at higher E_0, but the dissociation barrier is about 0.1 eV higher than that at the parallel geometry. The present result indicates that the abstraction process, which would occur at the perpendicular geometry, is a minor event at $E_0 < 0.2$ eV.

Figure 2(a) shows the incidence angle (α) dependence of $S_0(H)$ and $S_0(C)$ measured at two different translational energies. The α dependence curves were taken along the $[1\bar{1}0]$ azimuth. Although an anomalous angular dependence showing a peak at $\alpha = \sim 25°$ has been reported by Österlund *et al.* [1], we observed the monotonic decrease of S_0 with increasing α. The α dependence of $S_0(H)$ and $S_0(C)$ at $E_0 = 0.18$ eV agrees well with the sticking probability curve scaled with the translational energy normal to the surface (E_n), which was derived from the E_0 dependence of S_0 at normal incidence. Figure 2(b) shows that the sticking probability ratio between the helicopter and cartwheel geometries [$S_0(H)/S_0(C)$] increases with α at $E_0 = 0.18$ eV. This is consistent with the fact that $S_0(P)$ decays more steeply than $S_0(H)$ with decreasing E_0 at 0.1–0.2 eV. $S_0(H)/S_0(C)$ is larger at $E_0 = 0.1$ eV, indicating the smaller contribution of endon collisions to the sticking. $S_0(H)/S_0(C)$ tends to decay slightly with α at $E_0 = 0.1$ eV. This might be due to the steering effect [21], which redirects incoming molecules to favorable orientations and becomes efficient at lower E_0. This tendency is seen also in

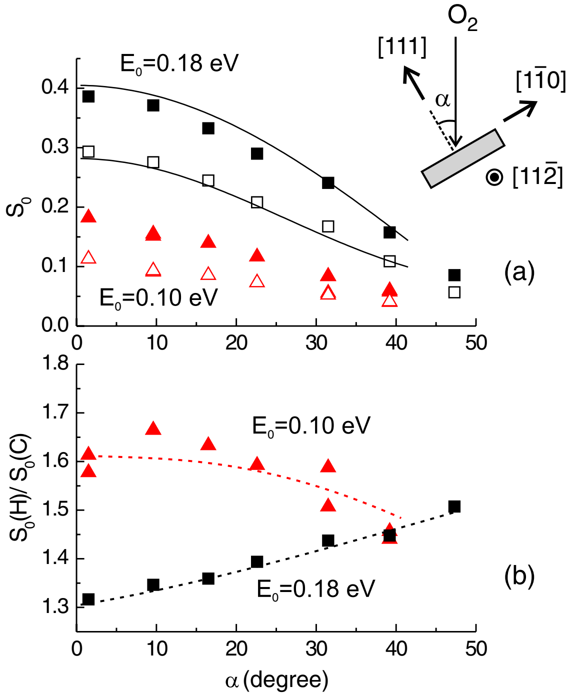

FIG. 2 (color online). (a) The incidence angle dependence of the O_2 sticking probability measured for helicopter (filled) and cartwheel (open) geometries at $E_0 = 0.18$ eV (black squares) and at 0.1 eV (red triangles). The defining magnetic field was directed to [111] ([11$\bar{2}$]) direction of the Al(111) crystal to establish the helicopter (cartwheel) geometry. Solid lines correspond to the normal energy scaling curves derived from the E_0 dependence of the sticking probability. (b) The incidence angle dependence of the sticking probability ratio between the helicopter and cartwheel geometries for $E_0 = 0.18$ eV (black squares) and 0.1 eV (red triangles). Dashed lines are guides for the eye.

Fig. 1 showing that, with decreasing E_0, $S_0(P)$ tends to saturate at $E_0 < 0.15$ eV while $S_0(H)$ continues to decrease. A similar decay of the steric effect has been reported for NO adsorption on Al(111) at $E_0 < 0.1$ eV, and has been ascribed to the steering [22]. By assuming the normal energy scaling at $E_0 = 0.1$ eV, we can estimate the steric effect at $E_n < 0.1$ eV. $S_0(H)/S_0(C)$ at $\alpha = 40°$, which corresponds to $E_n \sim 60$ meV, is around 1.5, indicating that the preference of the parallel geometry is still very strong even if the steering might work.

Previous REMPI measurements have detected the atomic oxygen ejected by O_2 dissociation [10–13], and shown that the E_0 dependence of its yield matches that of the sticking probability for randomly oriented O_2 [11–13]. The observed atomic oxygen ejection would be due to the abstraction process that occurs at the perpendicular geometry. However, as far as the dissociation barrier at the perpendicular geometry is higher than at the parallel geometry (Fig. 1), the abstractive adsorption is a minor process. It would be because the dissociation barriers at these two geometries differ only slightly (0.1 eV) that the E_0 dependence of the abstraction yield apparently looks consistent with that for the sticking probability.

Our result indicates that O_2 dissociation at the parallel geometry is dominant at low E_0. Therefore, the adsorbates formed after exposure to thermal O_2 originate mostly from the molecules parallel to the surface. Since the hot-adatom model [2,7] seems unlikely, the dissociation mechanism [17], in which the two oxygen atoms are placed close to each other after adsorption, is most consistent with the present result. We note that previous theoretical studies have agreed that the oxygen adatoms occupy nearby sites if O_2 dissociation occurs at the parallel geometry [6,12,15].

The STM images taken by Komrowski *et al.* [13] have shown two types of oxygen adsorbates with different sizes. The smaller dot dominates at low E_0 while the number of the larger dot increases with increasing E_0 and plateaus at $E_0 > 0.4$ eV [13]. Following a density functional theory calculation of O/Al(111) [9], a single oxygen adatom on Al(111) is energetically unfavorable and tends to form clusters. Schmid *et al.* [17] have concluded that the atomic species can move to form larger clusters at room temperature while the oxygen pair does not tend to separate into atomic species for diffusion. The computed diffusion barrier, i.e., the energy difference between the energetically favorable fcc hollow site and the bridge site, is 0.75 eV [9]. As has been discussed by Schmid *et al.* [17], this level of barrier allows the diffusion of the atomic species at room temperature. A possible scenario for O_2 dissociation on Al (111) would therefore be as follows. At low E_0, O_2 molecules nearly parallel to the surface dissociate and therefore the adsorbates consist of a pair of O atoms. Since the oxygen pair is already stabilized, the pair breaking and diffusion to form larger clusters would scarcely occur at room temperature. At high E_0, however, O_2 molecules in any orientation can dissociate. The molecules parallel to the surface create oxygen pairs while those in the perpendicular geometry cause the abstractive adsorption. The atomic species formed by the abstraction process move at room temperature to form larger clusters, which has been observed by the previous STM measurement [13]. Since $S_0(P)$ tends to saturate at $E_0 > 0.4$ eV as shown in Fig. 1, the number of the atomic species created by the abstraction process and therefore the number of the larger clusters become saturated at $E_0 > 0.4$ eV.

While the origin of the inefficient sticking at low E_0 has been investigated mostly by theoretical calculations, the present result implies that only molecules with favorable *parallel* geometry contribute to the sticking, resulting in the low S_0 at low E_0. Although the present experiment clarified only the polar angle dependence of S_0 averaged over the surface, the reaction probability would depend on the adsorption site and/or the azimuthal angle of the O_2 axis relative to the surface. These two factors would also limit the phase space leading to dissociation. The present results show that the dissociation barrier at the perpendicular geometry is ~0.1 eV higher than at the parallel geometry. The spin-constrained calculation [4] has predicted the preference of the parallel geometry, but overestimated the barrier for the perpendicular geometry while the correlated wave function calculation has predicted the preference of the perpendicular geometry [6]. The accuracy of these calculations would therefore be still not enough to quantitatively simulate the O_2 dissociation. Our results would provide a firm basis to advance the theoretical treatments.

The incidence angle dependence of Fig. 2 indicates that the normal energy scaling holds well on Al(111). This is consistent with the fact that O_2 dissociation on Al(111) proceeds via the direct mechanism, which has been found from the absence of the temperature dependence in S_0 [1]. The normal energy scaling has been confirmed for O_2 dissociation on metallic surfaces such as Cu(110) [23], W(110) [24], Ru(0001) [25] at the high E_0 range where the direct mechanism dominates. The deviation from it was observed on Si(100) [26] where a large corrugation exists, or on Pt(111) [27] where temperature dependent effects play important roles even at the high E_0 range. An Al(111) surface is known to be very flat in terms of charge density [9,28]. In addition, no temperature dependent process is involved in the sticking [1]. The present result showing the normal energy scaling would therefore be reasonable although the deviation from it was reported previously [1].

In summary, we have presented a firm experimental evidence that, at translational energies <0.2 eV, O_2 sticking occurs predominantly when the molecular axis is *parallel* to the surface. This is consistent with the dissociation mechanism [17] in which the adsorbates formed after exposure to thermal O_2 consist of two oxygen atoms. The present results elucidate that the abstraction process, which occurs at the perpendicular geometry, is a minor event at low translational energies. The alignment-resolved O_2 chemisorption experiment thus proved its high potential for clarifying the stereodynamics in O_2-surface interaction. The single spin-rotational state-selected O_2 beam used here will also enable the spin-resolved experiment, which would unveil the role of electron spins in O_2 chemisorption.

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