Tunneling Effect in Dissociative Adsorption of O₂ on Pt(001) SurfaceKoji SHIMIZU^{*1}, Wilson Agerico DIÑO^{*1,*2} and Hideaki KASAI^{*1,*2}^{*1}*Department of Applied Physics, Osaka University, 2-1 Yamadaoka, Suita-shi, Osaka 565-0871, Japan*^{*2}*Center for Atomic and Molecular Technologies, Osaka University, 2-1 Yamadaoka, Suita-shi, Osaka 565-0871, Japan*

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Dissociative adsorption process of O₂ molecule on Pt(001) surface are explored using quantum dynamical calculations based on coupled-channel method. The explored adsorption sites are the direct dissociative adsorption channels, where the molecularly adsorption or precursor state for O₂ sticking are absent, with certain amount of activation barrier. We find that the dissociative sticking probability of O₂ depicts the sigmoidal (S-shaped) curve in all cases which is a manifestation of the tunneling effect. Moreover, the sticking curve is sensitively dependent on the shape of the activation barrier which affects the width of the transition region. Finally, the tunneling effect can be clearly acknowledged from the wave function of O₂.

One of the main goals of surface science is to get a detailed description of different catalytic reactions. This topic has garnered remarkable interests from both experimental and theoretical researchers as evidenced by large number of studies conducted related to this subject^{1,2)}. Among these catalytic reactions, oxygen reduction reaction (ORR) has been a subject of extensive scientific scrutiny due to its practical importance and industrial applications. Currently, the predominantly used ORR catalyst is platinum (Pt) because of its impeccable ability to effectively facilitate cathodic reactions in fuel cells. However, since it is a precious metal and considering its scarcity, Pt offers a huge challenge for industrial use and mass production. To reduce Pt loading, studies related to design alternative catalysts have been widely performed (e.g., organic catalyst or platinum alloy, PtM (M=Cr, Mn, Co, Ni and Fe), catalyst³⁻⁵⁾).

Dissociative adsorption of O₂ molecule on the surfaces, which may be a rate-limiting step in many complex reactions, has been continually examined in terms of energetics by the aid of first principles calculations⁵⁾. In these studies, stability in terms of binding energy and transition states are discussed from the picture of electronic state. However, we stress that the motion of atoms and molecules should be considered to obtain constitutive understanding of the reactions.

According to six-dimensional potential energy surfaces (PESs) of O₂/Pt system, the manner by which the reaction proceeds is different for the entrance channels and for the surface facets (e.g., direct dissociation, precursor-mediated dissociation^{2,5,6)}). In this paper, we focus on the direct dissociative adsorption channels, where the precursor state is absent, to clarify the reaction processes with the existence of activation barrier.

To our knowledge, light molecules, such as H₂/D₂, show the tunneling effect clearly when they undergo the dissociative adsorption with certain amount of activation barrier^{7,8)}. Conversely, due to the idea of the absence of tunneling effect, the other molecules with relatively large mass have been dealt with classically.

However, as suggested in the case of N₂⁹⁾, we will present the tunneling effect of O₂ when it undergoes dissociative adsorption in the following discussion.

We model the dissociative adsorption of O₂ interacting with rigid surface, and then perform quantum dynamical calculations for the dissociative adsorption probability by solving the time-independent Schrödinger equation for O₂ moving along the reaction path, using the coupled-channel method¹⁰⁻¹⁶⁾. We neglect the energy dissipation of the molecule because the direct dissociation is not strongly affected by such phenomenon⁷⁾. The dynamical variables we considered include the O₂ center-of-mass (CM) distance Z from the surface, and the O₂ bond-length r . To solve the corresponding time-independent Schrödinger equation, which describes dissociative adsorption, it is convenient to make the coordinate transformation $(r, Z) \rightarrow (s, \rho)$, where (s, ρ) are the reaction path coordinates¹⁷⁻¹⁹⁾. s gives the position of the O₂ CM along the reaction path, and ρ is a coordinate orthogonal to s , at all points along the reaction path. Although it is possible to carry out fully quantum mechanical calculations, in this study we take into account only translational motion of the molecule to observe the tunneling effect in the dissociative adsorption reaction.

While it is widely known that O₂ sometimes undergoes molecular adsorption or precursor-mediated dissociation⁶⁾, we investigate the direct dissociative adsorption of O₂ on Pt(001) surface. Adsorption sites explored in this study are labeled hollow-bridge-hollow (H-B-H) and bridge-hollow-bridge (B-H-B) as shown in Fig. 1, where the open and filled circles depict Pt atoms of the surface and O atoms, respectively. The polar orientation of O₂ is fixed parallel to the surface, with $\theta = \pi/2$.

The potential energy curves (PECs) of the O₂ dissociative adsorption for the corresponding systems are extracted from previous studies^{5,20,21)}, and are shown in Fig. 2, wherein solid and dotted lines are PECs for H-B-H and B-H-B adsorption sites, respectively. Ener-

Fig. 1 Dissociative adsorption sites of O_2 on Pt(001) surface explored in this study. Open and filled circles show the Pt atoms of the surface and oxygen atoms, respectively. Description of O_2 is given in terms of the direction of the molecular axis and the position of the center-of-mass (CM) of the molecule. H and B specify the hollow and bridge sites.

Fig. 2 Potential energy curves (PEC) corresponding to O_2 dissociative adsorption on Pt(001) surface as a function of reaction coordinate, determined from previous studies^{5,20,21}. Solid line and dotted line depict the PEC for H-B-H and B-H-B configuration, respectively. Energies are given in eV relative to the value at $(r, Z) = (1.2 \text{ \AA}, 5.0 \text{ \AA})$.

gies are given in electronvolts (eV) relative to the value at $(r, Z) = (1.2 \text{ \AA}, 5.0 \text{ \AA})$, where the O_2 is sufficiently far and does not interact with the surface. At the middle of the PECs, where the reaction coordinate is around 0 (cf., Fig. 2), O_2 encounters an activation barrier, which is ca. 1.2 eV and ca. 0.16 eV for H-B-H and B-H-B, respectively. After O_2 overcomes the activation barrier, the distance between atoms exceeds ca. $2.8 \text{ \AA}$ which means that the molecule dissociates at these points. The adsorption energies are ca. 0.54 eV and ca. 2.40 eV at H-B-H and B-H-B, respectively. This discrepancy of the magnitude of binding energy is explained by site dependence of hybridization of p -orbital of O atom and d -orbital of Pt atoms⁵.

The calculated incident translational energy dependent sticking probabilities of O_2 , corresponding to the PECs of Fig. 2, are shown in Fig. 3. In both cases, the sticking probabilities depict sigmoidal (S-shaped) curves against incident translational energy. This is clearly due to the tunneling effect of O_2 revealed by quantum dynamical

Fig. 3 Calculated incident translational energy dependent one-dimensional sticking probabilities of O_2 at (a) H-B-H and (b) B-H-B adsorption sites, respectively.

calculations. Moreover for H-B-H in Fig. 3 (a), the threshold of the sticking probability is ca. 1.16 eV which is lower than the activation barrier with a value of 1.20 eV. The dissociative adsorption can proceed at incident translational energy which is 40 meV smaller than the activation barrier. On the other hand, if the incident translational energy is larger than the activation barrier ($E_t > 1.20 \text{ eV}$), the sticking probability does not reach unity immediately. Furthermore, the sticking probability finally becomes unity at $E_t \sim 1.23 \text{ eV}$, which again represents the tunneling effect of O_2 . In the case of B-H-B in Fig. 3 (b), the same effects can be seen as well with energy values of ca. 0.16 eV and ca. 0.145 eV for the activation barrier and the initial rise for the sticking probability, respectively. During the O_2 dissociation, the incident translational energy is ca. 15 meV smaller than the activation barrier and the sticking probability reaches unity at $E_t \sim 0.173 \text{ eV}$. The inflection points are just the middle of the transition region (where the sticking probability increase from 0 to 1) for both cases.

As can be seen in Fig. 3, the transition regions are ca. 70 meV and ca. 28 meV for H-B-H and B-H-B, respectively, and the size of the tunneling effect on H-B-H is larger than that of B-H-B. This is due to the width of the barrier, and independent of the height of the barrier. The width of the barrier, through which the molecules tunnel for dissociation, is defined by the distance between intersections of PEC and the translational energy of the molecule. When the translational energies are, for instance, 1.19 eV and 0.15 eV for H-B-H and B-H-B respectively, which are both 10 meV below from the activation barriers, the barrier width of H-B-H is one third of that of B-H-B. Thus, the incident molecule can easily tunnel through the activation barrier for the former than the latter and the slope of the curve has a considerable dependence on the barrier width. This trend continues throughout the transition regions.

For the purpose of visualization of the tunneling

Fig. 4 The absolute value of O_2 wave functions along the reaction coordinate when the translational energies of O_2 are 1.19 eV on H-B-H (solid line) and 0.15 eV on B-H-B (dotted line), respectively.

effect, the wave functions of O_2 along the reaction coordinate are represented in **Fig. 4**. When the translational energies of the molecule are 10 meV below from the activation barriers (i.e., 1.19 eV and 0.15 eV for H-B-H and B-H-B sites respectively), the wave function exists over the barrier; we can again acknowledge the tunneling effect of O_2 . Furthermore, the amplitude of the wave function of dissociated molecule for H-B-H is larger than that of B-H-B. This is equivalent to the size of the tunneling effect discussed above.

In summary, we investigate the dissociative adsorption probability of O_2 on Pt(001) surface using quantum dynamical calculations. The potential energy used in the calculations are built at the entrance channels with direct dissociative adsorption path. We find that the incident translational energy dependent sticking probability depicts the sigmoidal (*S*-shaped) curve which represents the tunneling effect of O_2 . This sticking curve is sensitive to the shape of the activation barrier which affects the width of transition region. Finally, we can clearly recognize the tunneling effect of O_2 from its wave function. Since we exclude several degrees-of-freedom of the system, these calculations may be insufficient for the quantitative comparison with experiment. We emphasize, however, the necessity of quantum dynamical calculations for detailed description of the reactions.

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