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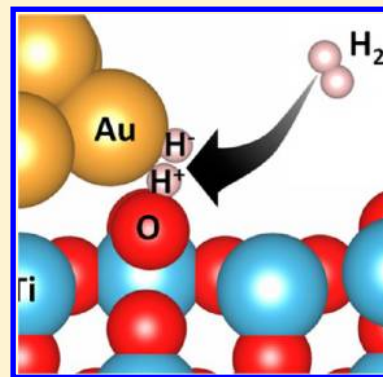
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A Study on the Mechanism for H₂ Dissociation on Au/TiO₂ Catalysts

Keju Sun,^{*,†,‡} Masanori Kohyama,[‡] Shingo Tanaka,[‡] and Seiji Takeda[†][†]The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan[‡]Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31, Midorigaoka, Ikeda, Osaka 563-8577, Japan

ABSTRACT: The mechanism of H₂ dissociation on supported gold catalysts was investigated due to their wide applications in hydrogenation reactions. The analysis of Hückel theory suggests O²⁻–H⁺–H⁻–Au as a transition-state structure for H₂ dissociation on a Au/TiO₂ system because of strong O²⁻–H⁺ interaction. Subsequent density-functional theory (DFT) calculations verified that the O²⁻–H⁺–H⁻–Au structure at the perimeter of Au/TiO₂ displays the lowest reaction barrier for H₂ dissociation among various surface sites of gold, TiO₂, and Au/TiO₂ systems. In addition, the dissociation barrier on this O²⁻–H⁺–H⁻–Au structure is dependent on the charge on oxygen; TiO₂-surface oxygen, not directly connected to gold, with less electrons leads to a lower barrier, compared to perimeter oxygen connected to gold, and a reduced TiO_x/Au system should be less active due to more electrons on oxygen, which can explain recent experimental results.



INTRODUCTION

In recent years, supported gold catalysts have attracted much attention due to their wide applications in oxidation/selective oxidation reactions,^{1–3} water-gas shift reaction,⁴ hydrogenation reactions,^{5–7} etc. Numerous studies have been carried out to identify the active sites of gold catalysts and to elucidate the mechanism of the high catalytic activity especially for the low-temperature CO oxidation reaction. The active site for the low-temperature CO oxidation has been debated for a long time⁸ and was assigned to low-coordinated gold atoms,⁹ the support-induced strain of Au,¹⁰ etc. Until very recently, the viewpoint of the active sites locating at the perimeter interface around gold particles in contact with oxide supports^{11–15} was gradually accepted experimentally.¹⁶

The active site of supported gold catalysts for H₂ dissociation was also investigated, since H₂ dissociation is regarded as the rate determining steps in the selective hydrogenation of unsaturated aldehydes, ketones, and hydrocarbons^{7,17–19} and in the direct formation of hydrogen peroxide from H₂ and O₂ mixtures.^{16,20} Bus et al. investigated the hydrogen dissociative adsorption on Au/Al₂O₃ catalysts by using in situ X-ray absorption spectroscopy and concluded the corner or edge atoms of gold particles as active sites.²¹ However, this conclusion was challenged by the experimental results of Fujitani et al.²² They studied the hydrogen dissociation by the H₂–D₂ exchange reaction on Au(111), Au(311), and TiO₂(111) surfaces, and Au/TiO₂(110) systems with size-controlled gold particles. They observed the HD formation only for Au/TiO₂(110) systems and suggested that the perimeter interfaces of Au/TiO₂ are the active sites for H₂ dissociation, based on the fact that the turnover frequencies (TOFs) normalized by the total number of gold atoms at the perimeter interfaces are almost constant among the Au/TiO₂ systems with different Au-particle sizes.²² Subsequently,

Nakamura et al.¹⁶ studied the H₂–D₂ exchange reaction over Au(111) surfaces with TiO_x-layer islands formed by the oxidation of deposited Ti. They observed no HD formation over Au(111) surfaces bearing reduced TiO_x (Ti, TiO, Ti₂O₃, and Ti₃O₅) layers. Instead, HD is produced over the Au(111) surface with stoichiometric TiO₂-layer islands. Furthermore, the activation energy and the TOFs for HD formation on the TiO₂-layer/Au(111) system agrees well with those on the Au/TiO₂(110) system.²² Therefore, they concluded the active sites for H₂ dissociation to be local Au^{δ+}–O^{δ-}–Ti sites at the perimeter interface between stoichiometric TiO₂ and Au. Theoretically, Lyalin and Taketsugu²³ investigated H₂ adsorption and dissociation on Au nanoparticles supported on the TiO₂ surface and demonstrated that the active sites are located at corners and edges on the surface of the gold nanoparticle in the vicinity of the support. Yang et al.²⁴ calculated H₂ dissociation at the perimeter sites of Au/TiO₂ by density-functional theory (DFT) calculations and found that the heterolytic dissociation is favored over the homolytic dissociation.

Although the experimental and theoretical results^{16,22,24} clearly showed the active sites for H₂ dissociation located at the perimeter interface between TiO₂ and Au, several puzzles still remain as follows. Why is the perimeter site of Au/TiO₂ active for H₂ dissociation? What is the mechanism for H₂ dissociation on Au/TiO₂? Why is the reduced TiO_x inactive compared to the stoichiometric TiO₂? In this work, we aim to answer these questions. Previously, we have investigated O₂ dissociation on Au/metal oxide catalysts by a combination of Hückel theory and DFT calculations.²⁵ DFT calculations with

Received: October 7, 2013

Revised: November 25, 2013

Published: January 1, 2014



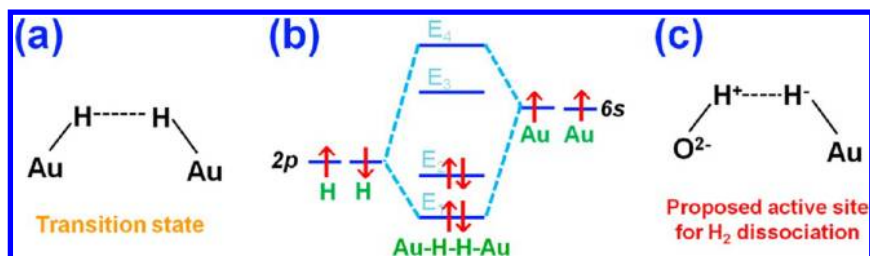


Figure 1. Models of orbital interactions in a Au–H–H–Au configuration (a), the electron distribution in Au–H–H–Au molecular orbitals (b), and proposed model of a transition state for H₂ dissociation on a Au/TiO₂ system (c).

sufficient accuracy comparable to the experimental data, combined with Hückel theory as a powerful tool in grasping the essence and tendency of chemical phenomena, could provide interesting and valuable insights into catalytic mechanisms.^{26,27} Here, we apply the same scheme to the active site for H₂ dissociation on Au/TiO₂ catalysts. Based on the analysis by Hückel theory, a model of O²⁻–H⁺–H⁻–Au is predicted as the local structure to enhance H₂ dissociation, which is subsequently examined for Au/TiO₂ systems by DFT calculations. And the above questions are discussed.

METHOD OF DFT CALCULATIONS

Periodic DFT calculations using the Vienna Ab Initio Simulation Package (VASP)²⁸ are performed to calculate the H adsorption, H₂ adsorption, and dissociation on gold, TiO₂(110) surfaces, and Au/TiO₂ systems. The exchange–correlation energy and potential are described by generalized gradient approximation (GGA) in the form of Perdew–Burke–Ernzerhof (PBE).²⁹ Plane waves are used to expand wave functions with a cutoff of 400 eV for projector augmented wave (PAW) potentials.^{30,31} The criterion for the convergence in the structural determination is the residual force is less than 0.03 eV Å⁻¹.

For Au(111), Au(100), and Au(321) surfaces, we use a five-layer slab with a vacuum thickness of 15 Å, where adsorbed species are placed on one side. The top three layers are relaxed, while the two bottom-most layers are fixed as their bulk structure. For the periodicity parallel to the surface, a 3 × 3 supercell is used for Au(111) and Au(100) surfaces with Monkhorst–Pack 4 × 4 × 1 k-point mesh. A 2 × 2 supercell is used for a Au(321) surface with 3 × 3 × 1 k-point mesh. To simulate a gold cluster, a gold rod²⁵ is used with 1 × 3 × 1 k-point mesh. For a TiO₂(110) surface, we use two kinds of slabs of three and four trilayers with a vacuum region of 15 Å, and for the periodicity parallel to the surface, a 2 × 4 supercell is used with 2 × 2 × 1 k-point mesh. For the Au/TiO₂(110) system, a gold rod is supported on the TiO₂(110)-surface slab to model the perimeter regions.^{25,32} In the case using the three-trilayer TiO₂ slab, a 2 × 4 supercell is adopted with 2 × 2 × 1 k-point mesh, while in the case using the four-trilayer TiO₂ slab, a 2 × 3 supercell slab is adopted with 2 × 3 × 1 k-point mesh. All the atoms are allowed to fully relax during the calculations on the gold rod, TiO₂(110) surface, and Au/TiO₂(110) system.

For the TiO₂(110)-surface slab, it is well-known that the surface formation energy and work function as well as many other properties display odd–even oscillation with respect to the number of atomic trilayers.^{33–35} According to calculations of He et al.,³⁶ the surface energy of TiO₂(110) does not converge when the slab is thinner than 13 trilayers. In this work, we have to deal with a large 2 × 4 or 2 × 3 surface cell parallel to the surface to weaken the lateral interactions among

adsorbed molecules. Thus practically we cannot deal with thick TiO₂(110) slabs. To estimate the adsorption on TiO₂(110) with infinite-slab, Harris and Quong proposed a “25% rule” that the converged energy values lie 25% of the way between the three- and four-layer values.³⁷ Therefore we calculate the TiO₂ models with three and four trilayers and the estimated value with infinite-slab by the “25% rule” are adopted.

The structures of transition states in a H₂-dissociation process are searched by the force reversed method.³⁸ The H adsorption energy is defined as $E_{\text{ads}} = E(\text{surface} + \text{H}) - E(\text{surface}) - E(\text{H})$, where $E(\text{surface} + \text{H})$, $E(\text{surface})$, and $E(\text{H})$ are the energies of a surface with H adsorption, a clean surface, and an isolated H atom, respectively. The calculated bond energy of H₂ is 4.53 eV, which agrees well with the experimental value of 4.52 eV.³⁹ Spin polarization is considered during all the calculations.

RESULTS AND DISCUSSION

Analysis Based on Hückel Theory. First, H₂ dissociation on gold is analyzed by Hückel theory. According to Slater’s rules,⁴⁰ the energy levels of Au 5d, Au 6s, O 2p, and H 1s orbitals are –52.4, –10.6, –70.4, and –13.6 eV, respectively. Since the atomic orbitals with closer energy levels will mix more effectively in molecular orbitals, Au 6s orbitals instead of Au 5d orbitals will play a key role in H₂ dissociation, which is different from the O₂ dissociation.²⁵ A simple model of Au–H–H–Au (Figure 1a) is first constructed, and the corresponding electron distribution is shown in Figure 1b. If we assume the relations as $\alpha_{\text{Au}} = \alpha$, $\beta_{\text{H-H}} = \beta$, $\beta_{\text{H-Au}} = m\beta$, and $\alpha_{\text{H}} = \alpha + h\beta$, the total energy for Au–H–H–Au is expressed as

$$E = 2E_1 + 2E_2 - 2\alpha_{\text{Au}} - 2\alpha_{\text{H}} \\ = (\sqrt{(h-1)^2 + 4m^2} + \sqrt{(h+1)^2 + 4m^2})\beta \quad (1)$$

Similarly to Au–O–O–Au,²⁵ the relationship between the H₂-dissociation barrier and the Au–H interaction ($m\beta$) can be obtained. Although the electron distributions, dominant orbitals, and bonding type of Au–H–H–Au are quite different from those of Au–O–O–Au, we are astonished to find the same conclusions for H₂ dissociation and O₂ dissociation. Namely, the reaction barrier for H₂/O₂ dissociation decreases as the Au–H/O interaction ($m\beta$) increases. Furthermore, it is easy to prove that this conclusion is generalized for diatomic dissociation regardless of the atomic species or electron numbers of molecules and catalysts. As long as the interaction between the catalytic center (CC) and H/O is strengthened, the reaction barrier for H₂/O₂ dissociation will be decreased. In general, the increase of the interaction is associated with the increase of the atomic adsorption; therefore, the H atomic adsorption energy is calculated to judge the interaction.

In our previous work, we proposed a unique linear O–Au–O structure,^{25,26} which can significantly strengthen the Au–O interaction, thereby effectively enhancing O₂ dissociation. However, for the Au–H interaction, a H–Au–H structure similar to a linear O–Au–O structure fails due to the different bonding type between the Au–H bond dominated by the σ bond with strong directionality and the Au–O bond dominated by the π bond. The linear structure that normally increases the orbital overlapping for the π bond is not favorable for the σ bond formation. In addition, the σ bond is considered to be more localized than the π bond and, thus, is seldom influenced by the surroundings. Therefore the selection of appropriate species for CC is the most efficient way to increase the CC–H interaction.

In Au/TiO₂ systems, surface O and Ti atoms on a TiO₂ surface and surface gold atoms on a gold cluster are possible options for the CC species. According to our DFT calculations, the adsorption energy of a H atom on 2-fold bridge oxygen (O_b), 3-fold surface oxygen, and 5-fold surface titanium of a TiO₂(110)-surface slab are –2.81, –2.21, and –0.07 eV, respectively. In contrast, the adsorption energy of a H atom on the top of the surface Au is –1.88, –1.87, and –2.05 eV for Au(111), Au(100), and Au(321), respectively. Clearly, the interaction between O (especially for O_b) and H is the strongest among all the CC–H interactions, followed by the Au–H and Ti–H interactions. Thus, according to the prediction by Hückel theory that the reaction barrier is dependent on the interaction between CC and H, the reaction activity for H₂ dissociation should follow the orders: O–H–H–O > O–H–H–Au > Au–H–H–Au, O–H–H–Ti. This result implies the possibility that a TiO₂ surface with a large amount of surface O species is the most active site for H₂ dissociation.

This theoretical prediction, however, contradicts with the experimental findings¹⁶ that TiO₂ surfaces are chemically inert for H₂ dissociation. The contradiction may be caused by different valence states of hydrogen in the atomic and molecular adsorption cases. The adsorbed H as OH on a TiO₂ surface has a chemical valence of +1, whereas the chemical valence of H in a H₂ molecule is 0. Since the 2p orbitals of O^{2–} are fully occupied, the interaction between O^{2–} and H is rather weak. The electron on H transfers to the Ti⁴⁺ cation in the H-atom adsorption on O_b, and so the strong binding is attained between H⁺ and O^{2–} instead of H and O^{2–}. Therefore, the model of O–H–H–O should be very active for H⁺–H⁺ dissociation, while the simple transition from O–H–H–O into O–H⁺–H⁺–O is not so easy. As a result, TiO₂ is chemically inert for H₂ dissociation.

Naturally, a question arises: how to use strong O^{2–}–H⁺ interaction to promote H₂ dissociation. Taking inspiration from the Hückel theory analysis, we propose a model of O^{2–}–H⁺–H⁺–Au to enhance H₂ dissociation on a Au/TiO₂ system as shown in Figure 1c. In this model, the chemical valence of H that connected with O is +1 and thus the interaction between O^{2–} and H⁺ is strong. To sustain the neutrality of H₂, the chemical valence of the other H has to be –1. The polarization process of H–H to H⁺–H[–] is endothermic, and the energy required increases with the charge on H (δ). Naturally, H⁺–H[–] with small δ is favorable for H₂ dissociation. Since the total chemical valence of (O^{2–}–H⁺) is –1, the positive charge on H⁺ (+ δ) should be reduced linearly with the reduction in the negative charge on O^{2–}. Figure 2 shows the calculated Bader charge of oxygen in several metal oxides. It is found that the

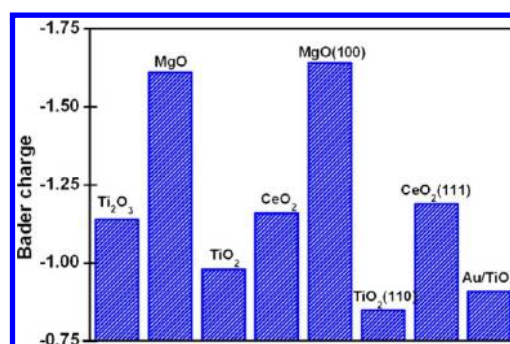


Figure 2. Calculated Bader charge of oxygen in the bulk of Ti₂O₃, MgO, TiO₂, and CeO₂, on the surfaces of MgO(100), TiO₂(110), and CeO₂(111), and at the perimeter interface of Au/TiO₂.

oxygen in TiO₂ has less Bader charge due to the higher electronegativity of Ti⁴⁺.²⁵ The corresponding δ in the TiO₂ system should be the smallest among several metal oxides, and thus the lowest reaction barrier is expected for the Au/TiO₂ system.

Examination by DFT Calculations. 1. H₂ Dissociation on Gold Surfaces. We first investigated H₂ dissociation on gold surfaces, including two flat Au(100) and Au(111) surfaces, a stepped Au(321) surface, and a gold cluster (rod). We examined several reaction pathways on each surface. Figure 3a–c show three transition-state structures of H₂ dissociation on a Au(100) surface, and the structure with the lowest reaction barrier is shown in Figure 3b. Figure 3e–g also show three transition-state structures on a Au(111) surface, and the structure with the lowest reaction barrier is shown in Figure 3f. Likewise, there are also several dissociation reaction pathways on the stepped Au(321) and gold rod surfaces, while only the transition-state structures with the lowest barrier are shown in Figure 3d and 3h. The calculated bond length of H–H at the transition state on the Au(321) surface is 1.342 Å and the reaction barrier is 0.64 eV, which are in good agreement with those of 1.33 Å and 0.56 eV in Fajin's calculations.⁴¹ The slight difference may originate from different calculation parameters.

We found a common feature for the transition-state structures with the lowest barrier heights on the Au(111), Au(100), Au(321), and Au cluster (rod) surfaces: the two H atoms are located near the bridge site and near the top site, respectively, which is denoted by a top–bridge structure. The possible reason for the top–bridge structure to reveal the lowest dissociation barrier is that the bridge site could greatly strengthen the Au–H interaction. This can be seen in Figure 4a, indicating that the bridge site is the most or the second most stable site for H adsorption on Au surfaces. In the Au(111) surface, the adsorption energy of H at the bridge site is higher only by 0.05 eV than the most stable hole site. The stronger Au–H interaction at the bridge site of gold surfaces leads to a lower H₂ dissociation barrier, compared to the transition-state structure in the other pathway with both H atoms located near the top sites (top–top structure, Figure 3e).

Since the bridge site could greatly strengthen the Au–H interaction, the transition-state structure with two H atoms near the bridge sites (bridge–bridge structure, Figure 3a, 3c, and 3g) may be expected to be more favorable for H₂ dissociation than the top–bridge structure with only one H atom locating near the bridge site (Figure 3b and 3f). However, it is not the case: the pathway with the bridge–bridge structure has a larger barrier by 0.03–0.13 eV than the pathway with the top–bridge

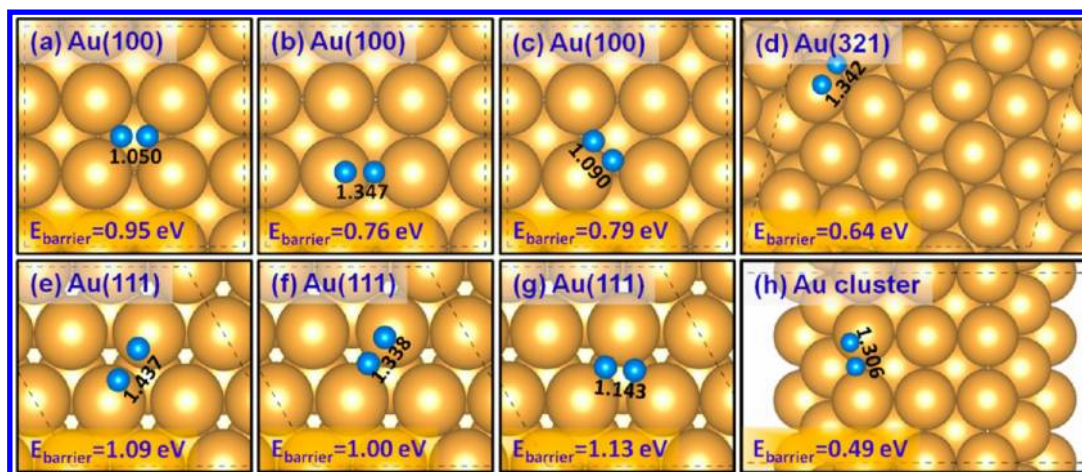


Figure 3. Transition-state structures of H_2 dissociation on Au(100), Au(321), Au(111), and Au-cluster (rod) surfaces. In each panel, the blue balls are H atoms and the golden balls are Au atoms. The H–H bond lengths at the transition states are shown in units of Å.

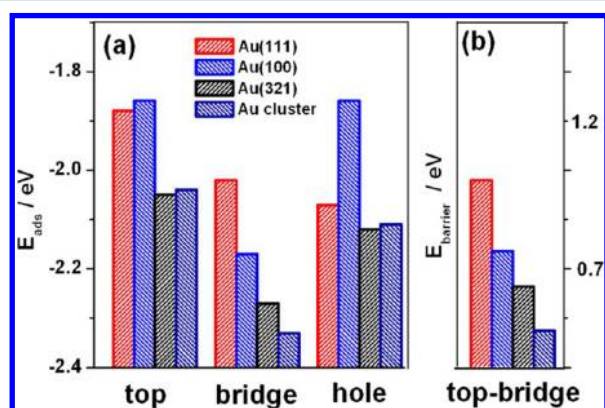


Figure 4. Adsorption energy of H (a) and the reaction barrier for H_2 dissociation (b) at each adsorption site on Au(111), Au(100), Au(321), and Au-cluster surfaces.

structure in each surface. This can be ascribed to the short H–H bond length, resultantly weakening the H–Au interaction in the bridge–bridge structure. This point can be seen in the bond length between the bridge H and Au atoms ($B_{\text{Au–H}}$) for the bridge–bridge and top–bridge structures. The shortest $B_{\text{Au–H}}$ for the bridge–bridge structure at the transition state is longer than that for the top–bridge structure by 0.026–0.186 Å. Figure 4b shows the reaction barrier for H_2 dissociation at the top–bridge site. Compared with Figure 4a, it is clear that the reaction barrier at the top–bridge site is almost linearly correlated with the adsorption energy of H at the bridge site. This agrees well with the prediction from Hückel theory that the stronger CC–H interaction results in a lower reaction barrier for the H_2 dissociation.

Our calculations show that the H_2 dissociation barriers are 0.76 and 0.64 eV on flat Au(100) and stepped Au(321) surfaces, which are in reasonable agreement with the experimental results with an activation energy of 0.74–0.78 eV on gold surfaces.^{42–44} The lower H_2 dissociation barrier on the stepped surface originates from the stronger Au–H interaction at the corner site of the gold surface.²³ Thus the gold cluster (rod) presents the lowest reaction barrier of 0.49 eV among all the Au surfaces considered. The corner gold atoms as active sites are in good agreement with the theoretical and experimental observation indicating H adsorption at low-coordinated edge or corner atoms of gold nanoparticles.^{7,21,23}

2. H_2 Dissociation on $\text{TiO}_2(110)$ Surface and Au/ TiO_2 . We then examined the transition state for H_2 dissociation on various sites on a $\text{TiO}_2(110)$ surface. No transition states with the O–H–H–O configuration were found, while the O–H–H–Ti configuration was found as the transition state on a $\text{TiO}_2(110)$ surface as shown in Figure 5. H atoms are bonded to O and Ti, and the O–H and Ti–H bond lengths are 1.362 and 1.949 Å for the three-trilayer slab and 1.171 and 1.889 Å for the four-trilayer slab. The estimated H_2 dissociation barrier

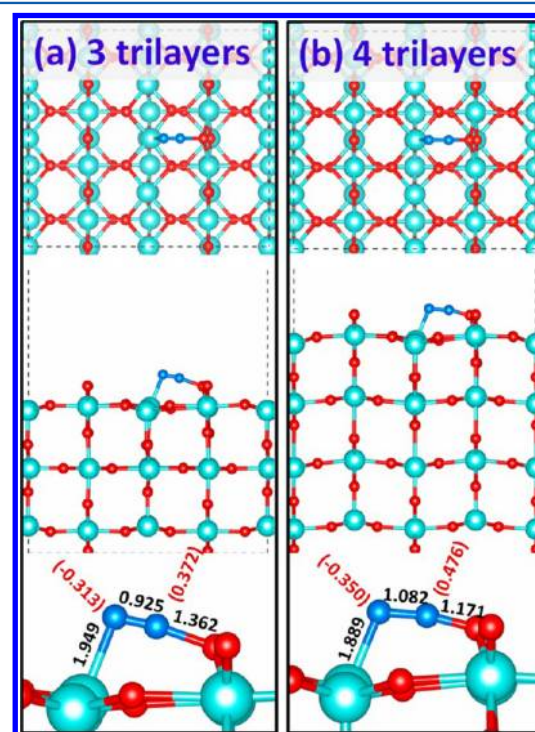


Figure 5. Transition-state structures of H_2 dissociation on a $\text{TiO}_2(110)$ surface modeled by three-trilayer (a) and four-trilayer (b) slabs. Top view (top), side view (middle), and enlarged configuration (bottom) are shown. In each panel, the cyan, red, and blue balls are Ti, O, and H atoms, respectively. The black numbers show the bond lengths in units of Å. The red numbers in the parentheses show the Bader charge of H. The negative Bader charge means the gain of electrons.

is 0.81 eV, higher than that on Au rods. For the transition-state structure, the Bader charge analysis shows that H connected with O has 0.372 and 0.476 positive charges for the three-trilayer and four-trilayer slabs, respectively, while the H connected with Ti has 0.313 and 0.350 negative charges for the three-trilayer and four-trilayer slabs, respectively. Therefore, the transition-state structure is $\text{O}^{2-}-\text{H}^+-\text{H}^--\text{Ti}$, in accordance with the prediction from Hückel theory that the chemical valence of the H connected with O^{2-} should be +1.

To investigate H_2 dissociation at the perimeter of Au/TiO_2 , Au/TiO_2 models consisting of three-trilayer and four-trilayer TiO_2 slabs with a gold rod are used as shown in Figures 6 and

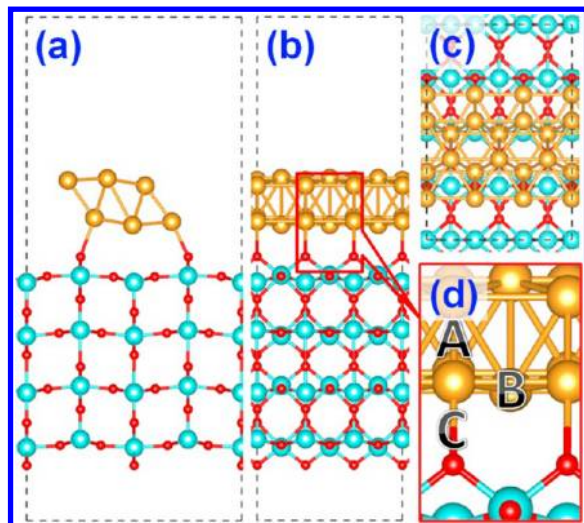


Figure 6. Two side views and one top view of the Au/TiO_2 model, consisting of a four-trilayer TiO_2 slab and a gold rod (a, b, and c). In (d), sites A, B, and C are proposed as active sites for H_2 dissociation at the perimeter of the Au/TiO_2 interface.

7. Figure 6 explains the H_2 -dissociative adsorption sites A, B, and C at the perimeter of Au/TiO_2 . For sites A and B, the transition-state structures as $\text{Au}-\text{H}-\text{H}-\text{Au}$ are observed, while the transition-state structure as $\text{O}-\text{H}-\text{H}-\text{Au}$ is observed for site C. Figure 7a–c show these transition-state structures for the three-trilayer model, and Figure 7e–g show those for the four-trilayer model. The estimated reaction barrier of H_2 dissociation is 0.89, 0.63, and 0.54 eV at site A, B, and C respectively. The reaction barrier for H_2 dissociation at site C is lower than those at sites A and B, which shows that site C at the perimeter of Au/TiO_2 is the active site for H_2 dissociation. This result agrees well with other theoretical calculations.²⁴

In the transition-state structures at site C in Figure 7c and 7g, a H atom connected with O has 0.289 and 0.338 positive charges for the three-trilayer and four-trilayer models, respectively, while the other H atom connected with Au has 0.146 and 0.161 negative charges for the three-trilayer and four-trilayer models, respectively. This clearly shows that the active site for H_2 dissociation forms $\text{O}^{2-}-\text{H}^+-\text{H}^--\text{Au}$, as predicted from Hückel theory. In addition, Hückel theory also predicts that O^{2-} with less electrons will display higher activity for H_2 dissociation. As shown in Figure 2, the bridge oxygen on the bare TiO_2 surface has less Bader charge than those at the perimeter of Au/TiO_2 . Therefore, the free bridge O^{2-} in the TiO_2 surface, not directly in contact with Au, should be more active for H_2 dissociation than the perimeter O^{2-} in contact with Au at Au/TiO_2 . To prove this, we built a model to dissociate H_2 using free O^{2-} , and the transition-state structures are shown in Figure 7d and 7h. The charge on H connected with free O^{2-} is 0.279 and 0.323 for the three-trilayer and four-trilayer models, respectively, which is less than that connected with perimeter O^{2-} in Figure 7c and 7g (0.289 and 0.338). The reaction barrier is reduced to 0.27 eV, compared to the values of 0.54 eV at site C. This proved the conclusion from Hückel theory that O^{2-} with less electrons leads to a lower H_2 -dissociation barrier via a smaller magnitude of δ in $\text{O}^{2-}-\text{H}^+-\text{H}^--\text{Au}$. The calculated reaction barrier with 0.27 eV is

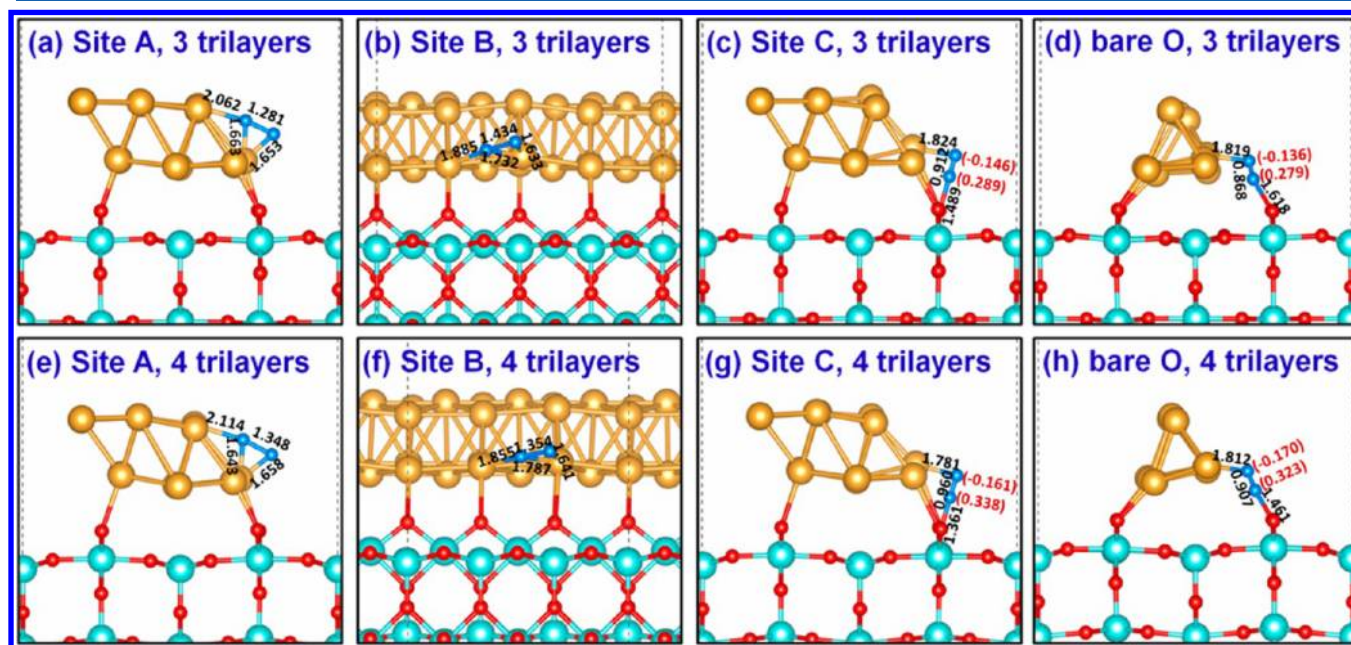


Figure 7. Transition-state structures for H_2 dissociation at the perimeter of Au/TiO_2 . The black numbers show the bond lengths in units of Å. The red numbers in the parentheses show the Bader charge of H.

consistent with the theoretical result of 0.29 eV,²⁴ but lower than the experimental results of 0.38 eV.²² The difference between the theoretical and experimental results was assigned to the contribution of entropy.²⁴ The reaction barrier for H₂ dissociation with 0.27 eV is the lowest barrier among all the systems, indicating that the perimeter of Au/TiO₂ is the active site for H₂ dissociation.

Finally, we investigate the phenomenon of the inactivity of reduced TiO_x/Au systems¹⁶ based on the O²⁻-H⁺-H⁻-Au model. As mentioned above, the dissociation energy barrier for the O²⁻-H⁺-H⁻-Au structure depends on the charge on O²⁻: the higher the number of electrons on O²⁻, the higher the energy barrier for H₂ dissociation. The charge on O²⁻ in a metal oxide depends on the electronegativity of metal cations,⁴⁵ corresponding to the ability to attract electrons. A simple method to estimate the electronegativity of the M^{Z+} cation is developed by Tanaka⁴⁶ as follows:

$$X^{Z+} = (1 + 2Z)X^0 \quad (2)$$

where Z is the chemical valence of the cations, and X^{Z+} and X^0 are the electronegativity values of the cations and corresponding neutral atom ($Z = 0$). Thus the electronegativity of the Ti cations in TiO_x ($0 < x \leq 2$) is expressed as

$$X_{Ti}^{2x+} = (1 + 4x)X_{Ti}^0 \quad (3)$$

From this formula, the electronegativity of Ti cations reaches the maximum when x is equal to 2, corresponding to stoichiometric TiO₂. The electronegativity of Ti cations in a reduced TiO_x ($0 < x < 2$) surface is less than that of Ti⁴⁺ in stoichiometric TiO₂ ($x = 2$). Therefore, the electrons on O²⁻ in reduced TiO_x are more than those in stoichiometric TiO₂. This can be proved by DFT calculations as shown in Figure 2. The Bader charge of oxygen in Ti₂O₃ and TiO₂ is -1.14 and -0.98, respectively. Therefore, the charge on H⁺ (δ) in an O²⁻-H⁺-H⁻-Au structure for reduced TiO_x should be higher than that for stoichiometric TiO₂, and the reaction barrier for H₂ dissociation on Au/TiO_x ($0 < x < 2$) is higher than that on Au/TiO₂. In this manner, the reduced TiO_x/Au system dealt with in ref 16 should be less active for H₂ dissociation in contrast to the stoichiometric TiO₂/Au system. This finding that appropriate oxides with less electrons on O²⁻ reveal higher catalytic activity for H₂ dissociation in supported gold catalysts opens a new avenue for catalyst design in hydrogenation reactions.

CONCLUSIONS

Hückel theory is used to analyze H₂ dissociation on Au/TiO₂. It is found that the increase of the interaction of H and catalytic center (CC) could promote H₂ dissociation. DFT calculations of H-atom adsorption show that the O²⁻-H⁺ displays the strongest H-CC interaction in a Au/TiO₂ system, and thus O²⁻-H⁺-H⁻-Au is proposed as the transition-state structure in an active reaction pathway for H₂ dissociation on Au/TiO₂. To prove this, H₂ dissociation was examined on various surface sites on Au, TiO₂, and Au/TiO₂ surfaces by DFT calculations. For pure gold systems, the gold cluster displays the highest activity for H₂ dissociation, associated with the stronger Au-H interaction for corner or edge gold atoms. For TiO₂ and Au/TiO₂ systems, we observed that local O²⁻-H⁺-H⁻-Ti and O²⁻-H⁺-H⁻-Au structures become the transition states of active reaction pathways, respectively. We observed that the O²⁻-H⁺-H⁻-Au structure at the perimeter of Au/TiO₂

displays the lowest reaction barrier with 0.27 eV. The origin of experimental inactivity of reduced TiO_x/Au systems can be explained by more electrons on oxygen than stoichiometric TiO₂, leading to the higher positive charge on H⁺ (δ) in the O²⁻-H⁺-H⁻-Au structure, resulting in a higher H₂-dissociation barrier.

AUTHOR INFORMATION

Corresponding Author

*E-mail: keju.sun@aist.go.jp. Tel: +81-72-751-9732.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors greatly thank Prof. M. Haruta and Dr. T. Fujitani for fruitful discussions on the reaction mechanism of gold catalysts. This study was supported by Grant-in-Aid for Specially Promoted Research Grant No. 19001005 from the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT). A part of this study was supported by the Management Expenses Grants for National Universities Corporations from MEXT and by Japan Science and Technology Agency (JST), Core Research for Evolutional Science and Technology (CREST).

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