Study of Interaction between Au and TiO$_2$(110) at Low Coverage

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We have investigated the interaction between Au and a rutile TiO$_2$(110) surface at low coverage, using density functional theory. We have examined Au adsorption on three types of TiO$_2$(110) surface with different stoichiometry and structures; the stoichiometric surface, the surface formed by removing bridging-oxygen (defected surface), and the reconstructed 1×2 surface with Ti$_2$O$_3$ rows (added-row surface). For the stoichiometric surface, the most stable site for the Au adsorption is the on-top site above the bridging-oxygen atom. Electrons transfer from the Au adatom to the bridging-oxygen atom after adsorption. For the defected surface, the most stable adsorption site is the bridging-oxygen vacant site. For the added-row surface, the most stable adsorption site is the neighborhood of the Ti$_2$O$_3$ rows. For both the reduced surface, defected and added-row surfaces, electron densities between the Au and the reduced Ti atom increase after adsorption, and it seems that the Au atom covalently interacts with the reduced Ti atoms at the surface. Moreover, we compared the simulated scanning tunneling microscopy (STM) images with the experimental STM images for the added-row surface. The calculated STM images of Au adatom adsorbed near Ti$_2$O$_3$ rows agree with experimental images qualitatively. [doi:10.2320/matertrans.47.2663]

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1. Introduction

Gold does not reveal catalytic activity for hydrogenation or oxidation generally.1) Haruta et al., however, have found that nano-size particles of gold deposited on the oxide supports such as TiO$_2$ have strong catalytic activity.2) For example, oxidation of CO occurs at room temperature when an average diameter of Au particles supported on TiO$_2$ is smaller than about 5 nm.3,4) The catalytic activity of the Au particles on TiO$_2$ strongly depends on the size and structure of the Au particles.5–8) Therefore, it is necessary to control the size and shape of Au particles on the oxide supports in order to make catalysts with higher activity. For this purpose, it is important to investigate the interaction between a Au atom and a TiO$_2$ supports at the initial stage of the nucleation of a Au particle.

There are a lot of studies about the interfacial interaction between Au and TiO$_2$9–13) All the studies have reported that the interaction of Au with the stoichiometric TiO$_2$ surface is very weak and that with the oxygen vacancy at TiO$_2$ surface is strong. Lopez and Nørskov investigated the size dependence of the interaction between Au and TiO$_2$(110) using ab initio pseudopotential calculations based on the density functional theory (DFT).14) They have found that the interaction between Au and TiO$_2$(110) become more weak as increasing the coverage of Au. However, the detailed study about initial stage of the growth of a Au particles is small. Wahlström et al. have investigated the interaction of Au nano-particles with the bridging-oxygen vacancies on the (110) 1×1 surface through an interplay between scanning tunneling microscopy (STM) observations and the DFT calculations.15) They reported that the nucleation and growth of Au clusters on the TiO$_2$(110) surface is strongly related to the presence of surface oxygen vacancies; a single Au atom-vacancy complex is stable and a single oxygen vacancy can bind three Au atoms on average. Recently, Okazawa et al. investigated the growth mode of Au nano-particles on TiO$_2$ using reflection high-energy electron diffraction, a field-emission type scanning electron microscopy and medium energy ion scattering.16)

For the reduced TiO$_2$(110) surface, a 1×2 reconstruction occurs after annealing in vacuum.17,18) It was found that the reconstructed surface has the added Ti$_2$O$_3$ rows by STM observation,17) by non-contact atomic force microscopy observation,19) and by first-principles calculations.20,21) The studies of the interaction of Au with the 1×2 TiO$_2$ supports are only few. The formation and growth of Au nano-particles were studied by STM on the TiO$_2$(110) reconstructed 1×2 surface22) and the local barrier height was measured on the TiO$_2$(110) 1×2 surface with and without Au deposition using STM.23) However, there is no theoretical studies about the interaction of Au clusters with the 1×2 TiO$_2$ surface. Therefore, we examined the Au adsorption on the three types of the rutile TiO$_2$(110) surface; the stoichiometric surface, the surface formed by removing one bridging-oxygen atom per 2×2 unit cell (defected surface), and the reconstructed 1×2 surface with Ti$_2$O$_3$ rows (added-row surface).

2. Method of Calculations

All the calculations are carried out using the program package STATE (Simulation Tool for Atom TEChnology), which has been successfully applied for various systems including TiO$_2$(110),24) Au(111) surfaces,25,26) and Au/TiO$_2$(110) system with coverage of 1/3 ML.13) We adopted the generalized gradient approximation (GGA) in the DFT27,28) with the Perdew-Burke-Ernzerhof formula29) as the exchange-correlation energy functional. We constructed
pseudopotentials of O 2p, Ti 3p and 3d, and Au 5d states by Vanderbilt’s ultra-soft scheme,\textsuperscript{30} while other components of pseudopotentials by the norm-conserving scheme.\textsuperscript{31} Two projectors are used for ultra-soft pseudopotentials. All pseudopotentials are generated from scalar relativistic\textsuperscript{32} all-electron atomic calculations to including relativistic effect. The cutoff energy of the wave function is 25 Ry and that of the augmentation charge is 225 Ry. The equilibrium configurations were determined with a criterion that required the force on each atom to be less than $1 \times 10^{-3}$ hartree/a.u.

A repeated slab model with three layers, where one layer was defined as the O-Ti$_2$O structural plane, and the $2 \times 2$ surface unit cell was used to simulated the TiO$_2$(110) surface. Each slab was separated by a vacuum region of about 19.8 Å. We deal with three kinds of surface structure; the perfect stoichiometric surface, the surface formed by removing one bridging-oxygen atom per $2 \times 2$ unit cell (defected surface), and the reconstructed $1 \times 2$ surface with Ti$_2$O$_3$ rows (added-row surface). These structures are shown in Fig. 1. Au adatoms are introduced on one side of each slab. In this case, the coverage of Au is 1/12 ML. For structural optimization, adatoms and the substrate layers expects the bottom one layer are allowed to relax. As shown in Fig. 1, we examined six possible adsorption sites (A-F) for the stoichiometric surface, thirteen possible adsorption sites (A-M) for defected surface, and ten possible sites (A-J) for the added-row surface.

3. Results

3.1 Stable configurations

Table 1 lists the adsorption energies. The adsorption energy $E_{ad}$ is defined by

$$E_{ad} = E_{Au} + E_{TiO_2} - E_{Au/TiO_2},$$

where $E_{Au}$, $E_{TiO_2}$, and $E_{Au/TiO_2}$ represent the total energies of a free Au atom, the clean relaxed TiO$_2$(110) surface, and the adsorbed Au/TiO$_2$(110) system, respectively. For the stoichiometric surface, a Au atom is adsorbed on the on-top site above the bridging-oxygen atom [site B in Fig. 1(a)]. This result is different from one in the case of medium coverage, 1/3 ML. At medium coverage, Au adsorbed on the hollow site surrounded by two in-plane oxygen and one bridging-oxygen atoms or on the on-top site above five-fold titanium atom, and the adsorption energy is 0.10 eV/adatom.\textsuperscript{10,11,13} The dependence of the adsorption site and energy on the coverage agrees with the result reported by Lopez and Nørskov.\textsuperscript{14} For the defected surface, a Au atom is adsorbed on the vacant site of the bridging-oxygen atom [site C in Fig. 1(b)]. The adsorption energy is larger than that of the stoichiometric surface. These results agree with that reported by Wahlström et al.\textsuperscript{15} The adsorption energy of the site A is comparable with that of the site C. This is because Au atoms starting from the site A moved to the site C, resulting in essentially the same configuration as that starting from the site C. Moreover, Au atoms starting from the site G or site L moved to the site E and ones starting from the site H moved to the site F. The slight difference of the adsorption energy between the site E and the site F is cause by the difference of the distance to the bridging-oxygen vacancy. For the added-row surface, Au is adsorbed near the Ti atom in the Ti$_2$O$_3$ row [site E in Fig. 1(c)]. The adsorption energy for the added-row surface is close to that for the defected surface, because a Au adatom interacts with the reduced Ti atoms for both surfaces. The reason why the adsorption energy for the defected surface is slightly larger than that for the added-row

![Fig. 1 Schematic geometry (top view) of three kinds of rutile TiO$_2$(110) surface; (a) The perfect stoichiometric surface, (b) the surface formed by removing on bridging-oxygen per $2 \times 2$ unit cell, and (c) the reconstructed $1 \times 2$ surface with Ti$_2$O$_3$ rows. The small filled and large open circles indicate oxygen and titanium atoms, respectively. Arrows in (b) indicate oxygen vacancy site.](image)

Table 1 Adsorption energies of Au on the TiO$_2$(110) surfaces with three types of surface condition. Unit is eV/atom.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
<th>K</th>
<th>L</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stoichiometric</td>
<td>0.59</td>
<td>0.65</td>
<td>0.22</td>
<td>0.30</td>
<td>0.64</td>
<td>0.57</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Defected</td>
<td>2.09</td>
<td>0.36</td>
<td>2.08</td>
<td>0.86</td>
<td>1.24</td>
<td>1.22</td>
<td>1.25</td>
<td>1.22</td>
<td>1.23</td>
<td>0.33</td>
<td>0.14</td>
<td>1.25</td>
<td>0.87</td>
</tr>
<tr>
<td>Added-row</td>
<td>1.34</td>
<td>1.09</td>
<td>-0.03</td>
<td>1.81</td>
<td>1.06</td>
<td>1.14</td>
<td>0.82</td>
<td>1.20</td>
<td>0.04</td>
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</table>
The surface is that the added-row surface is more stable than the defected surface due to reconstruction.

The optimized Au/TiO$_2$(110) configurations for each surface condition are shown in Fig. 2. For the stoichiometric surface [Fig. 2(a)], the distance between the Au adatom and the bridging-oxygen atom is 2.01 Å. This distance is shorter than that at medium coverage, 2.37 Å. This is reason why the adsorption energy at low coverage is larger than that at medium coverage. For the defected surface [Fig. 2(b)], the distance between the Au adatom and the reduced Ti atom is 2.66 Å. This distance is the same with that at medium coverage. For the added-low surface [Fig. 2(c)], the distance between the Au adatom and the reduced Ti atom in the Ti$_2$O$_3$ row is 2.44 Å. Although this distance is shorter than that for the defected surface, the adsorption energy for the added-low energy is slightly smaller than that for the defected surface. One of the reasons is that the added-row surface is more stable than the defected surface as the mentioned above. Another reason is because the displacement of the reduced Ti atom interaction the Au atom is large, 1.24 Å.

### 3.2 Electron transfers between Au and TiO$_2$(110) surface

In order to investigate the interaction between Au and TiO$_2$(110) surface in detail, we examine the charge density difference, which is obtained by subtracting the superposition of the respective charge densities of the Au adatom and the TiO$_2$(110) slab from that of the Au/TiO$_2$(110) system, as shown in Fig. 3. For the stoichiometric surface, electrons transfer form the Au adatom to the bridging-oxygen atom. The oxygen 2p bands are filled for the bulk, but the coordination number of the bridging-oxygen reduced from four to two. Therefore, the 2p states of the bridging-oxygen are slightly empty and electron transfer occurs from theAu adatom to the bridging-oxygen atom. At medium coverage (1/3 ML), the electron transfer is negligible. This difference is the reason why the adsorption energy at low coverage is larger than that at medium coverage. For the defected surface, electron densities between the Au adatom and the reduced Ti atoms increase. For the added-row surface, electron densities between the Au adatom and the reduced Ti atom in the Ti$_2$O$_3$ row increase, too. Therefore, it can be said...
that Au is covalently bound to the reduced Ti atoms for the defected and added-row surfaces.

3.3 Comparison with the experimental STM images

It is important that the calculated results are compared with the experimental ones. For the defected surface, Wahlström et al. have already investigated the interaction of Au with the vacancy. Therefore, we have compared the simulated STM images with the experimental ones for the reconstructed surface. The reason why we chose the reconstructed surface is that it is easy to observed and to determined the surface structure by using STM.

Sample preparation and STM observation were preformed in a UHV-STM system (JSTM4500XT, JEOL) with a base pressure of \(2 \times 10^{-8}\) Pa. The substrate was a polished TiO\(_2\) (110) single crystal. A clean surface was obtained by repeated cycles of Ar\(^+\) sputtering (3 keV for 5 min.) and annealing (1073 K for 10 min.). The surface observed by the experiment was reconstructed to the cross-linked structure. This structure is different from the structure dealt with in the present simulation. The cross-linked 1 \(\times\) 2 structure, however, consists of the Ti\(_2\)O\(_3\) rows and the linkage structures, which were modeled by Takakusagi et al. Gold was deposited on it by vacuum evaporation at room temperature. The coverage is 0.006 ML. All STM images were obtained in constant current mode with sample bias voltage of +1.5 V. For further details, see Ref. 23.

In Fig. 4(a), the experimental STM image is shown. Many particles are adsorbed on the linkage structures. A few particles, however, are adsorbed near the Ti\(_2\)O\(_3\) rows. Therefore, we compared the simulated STM images with the experimental ones about the particles near the Ti\(_2\)O\(_3\) rows. In Fig. 4(b), the relation between \(L\) and \(H\) for each Au particle is plotted, where \(L\) is defined as the distance between the center of the Ti\(_2\)O\(_3\) row and the center of the adsorbed particles and \(H\) is defined as the height of the particle from the top of the Ti\(_2\)O\(_3\) row [see the inset of Fig. 4(b)]. Two domains exist in the distribution of the relation between \(L\) and \(H\). The particles in region A are adsorbed near the Ti\(_2\)O\(_3\) row (0.3 nm \(\leq L \leq 0.5\) nm and \(H \approx 0.05\) nm), while the particles in the region B are adsorbed slightly far from the Ti\(_2\)O\(_3\) row (\(L \geq 0.5\) nm and \(H \approx 0.07\) nm). The images of Figs. 4(c) and (d) correspond to the images of a particle belonging to the region A and B, respectively.

In order to simulate the STM images, we calculated the following equation:

\[
\rho(r) = \sum_{\varepsilon_F \leq \varepsilon_{\text{th}} \leq \varepsilon_F + V_B} |\psi_{\text{th}}(r)|^2, \tag{2}
\]

where \(\varepsilon_F\) and \(V_B\) represent the Fermi level and the value corresponded the sample bias voltage, respectively. And we plotted the \(z\) value, where the \(z\)-axis is the [110] direction, to the following conditions:

\[
\rho(r) = \delta, z \geq 0, \tag{3}
\]

where \(\delta\) is a constant corresponded the current. We simulated the STM images of two structures. One is the most stable structure as shown in Fig. 2(c). For this structure, a Au adatom interacts with one Ti atom in the Ti\(_2\)O\(_3\) row. The simulated STM image is shown in Fig. 4(e). Another is the
meta-stable structure of Au adsorbed near the Ti$_2$O$_3$ row. For this structure, a Au atom interacts with two Ti atoms in Ti$_2$O$_3$ row and the adsorption energy is 1.06 eV/adatom. The simulated STM image is shown in Fig. 4(f). Fig. 4(g) shows the line profiles along the line AA’ in Fig. 4(e) [solid line] and along the line BB’ in Fig. 4(f) [dotted line]. As shown in Fig. 4(g), the image of Fig. 4(f) corresponds to the Au adsorption near the Ti$_2$O$_3$ row (region A), with $L$ of 0.48 nm and $H$ of 0.11 nm, and one of Fig. 4(e) corresponds to the Au adsorption slightly far from the Ti$_2$O$_3$ row (region B), with $L$ of 0.54 nm and $H$ of 0.15 nm. The theoretical values of $L$ and $H$ are not necessarily located in the observed two region strictly, although the tendency of the two sets of values of $L$ and $H$ for the most stable and meta-stable configuration is in good agreement with experiment.

4. Discussions and Conclusion

We have investigated theoretically the interaction between Au and a TiO$_2$(110) surface at low coverage, 1/12 ML. We considered three types of surface conditions; the perfect stoichiometric surface, the surface formed by removing the bridging-oxygen (defected surface), and the reconstructed 1 $\times$ 2 surface with Ti$_2$O$_3$ rows (added-row surface). For the stoichiometric surface, the most stable adsorption site is the on-top site above the bridging-oxygen and the adsorption energy is 0.65 eV/adatom. The most stable site is different from that at medium coverage (1/3 ML) and the adsorption energy at low coverage is larger than that at medium coverage. The oxygen 2$p$ bands are filled for the bulk, but the 2$p$ orbitals of the bridging-oxygen become slightly empty due to the reduction of the coordination number. Therefore, the electron transfers can occur from the Au adatom to the bridging-oxygen atom. For the defected surface, the most stable adsorption site is the bridging-oxygen vacancy site and the adsorption energy is 2.09 eV/adatom. Electron density between the Au adatom and the reduced Ti atom at the surface increases. These results agree with the results reported by Wahlström et al.15) Recently, Minato et al. investigated the electronic interaction between Au clusters and TiO$_2$(110) surface by photoelectron spectroscopy and STM.35) They found that Au clusters nucleate at the surface defects of TiO$_2$(110) surface and that the electrons transfer occurs from TiO$_2$(110) to Au clusters at low coverage. Our present results also agree with them results. For the added-row surface, the most stable adsorption site is near the Ti atom in the Ti$_2$O$_3$ row and the adsorption energy is 1.81 eV/adatom. Electron density between the Au adatom and the reduced Ti atom in the Ti$_2$O$_3$ row increases. Therefore, it can be said that Au covalently interacts with the reduced Ti atom for both the reduced surfaces, the defected and added-row surfaces.

In addition, we compared the simulated STM images with the experimental STM ones for the reconstructed TiO$_2$(110) surface with Ti$_2$O$_3$ rows. The TiO$_2$ surface used in our simulation is the 1 $\times$ 2 surface with Ti$_2$O$_3$ rows and that used in experiment is the cross-linked 1 $\times$ 2 structure, consisting of the Ti2O3 row and the linkage structure. The reason why we chose the reconstructed surface as a support is that comparison between the STM observation and the simulation for the non-reconstructed defected surface have already done by Wahlström15) and that it is easy to control and to determine the surface structure. The simulated STM images of Au adsorption on the most stable site and the meta-stable site are similar to experimental ones, and can reproduce the experimentally observed two distinct adsorption states. The energy difference between the most stable site (site E) and the meta-stable one (site F) is larger, 0.75 eV/adatom. Usually, the most stable configuration may be the major configuration. The reason why the meta-stable configuration is observed by the experiment is that the Ti atom interacting with the Au atom displaces from the position of the clean 1 $\times$ 2 surface for the most stable configuration. When the Au atom approaches to the Ti$_2$O$_3$ row, the Ti atom in the Ti$_2$O$_3$ row move toward to the Au atom in order to form the most stable configuration or the Au atom interacts with two Ti atoms in the Ti$_2$O$_3$ row. It can be said that these two processes are caused by the same probability at room temperature. It is necessary to simulate a process of adsorption dynamics in order to make clear this thing. Moreover, we could not detect the Au atom adsorbed on the other meta-stable sites; A, B, G, and I in Fig. 1(c). The Au atoms adsorbed on the sites A and B may be counted as those in region B of Fig. 4(b) or may be confused with a part of the linked structures. In addition, there is the possibility that the Au atoms adsorbed on the sites A, B, G, and I diffuse to the cross-linked site easily. These detailed feature need to be studied by the dynamical simulation.

The present results support the idea that the nucleation of Au clusters is related to some non-stoichiometry or defects at TiO$_2$ substrates.12,13,15) Maeda et al. have investigated size and density of Au particles deposited on TiO$_2$(110)-1 $\times$ 1 and cross-linked 1 $\times$ 2 surfaces using STM.36) They found that Au particles grow large and dominantly cover steps even at room temperature on the 1 $\times$ 1 surface and that the Au particles are of a small size and highly dispersed on terraces on the 1 $\times$ 2 surface. In order to make the catalysts supported on the oxide with the high activity, the particles should be controlled the size and shape and be highly dispersed on the oxide supports. There is a possibility that the catalysts, which the Au particles with the nano-size are highly dispersed, are prepared on the cross-linked 1 $\times$ 2 surface. Therefore, our study about the interaction between the Au atom and the reconstructed 1 $\times$ 2 surface at low coverage is important for the investigation of the initial stage of the growth on the cross-linked 1 $\times$ 2 surface.

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