Electronic Structures of Ag and Au Adsorbed on TiO₂(110) Surfaces by First-Principles Calculations

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We have investigated electronic structures and charge transfers of Ag and Au supported on the TiO₂(110) surface, using first-principles calculation. In order to investigate the effect of stoichiometry on the electronic structures, we examined Au and Ag adsorption on three kinds of TiO₂(110) surface with different stoichiometry; the perfect stoichiometric surface, Ti-rich surface, and O-rich surface. We considered the on-top site above the bridging-oxygen atom (site A) and above the five-fold titanium atom (site B) for the perfect stoichiometric surface, the bridging-oxygen vacant site (site C) for the Ti-rich surface, and the six-fold titanium vacant site (site D) for the O-rich surface as the adsorption site. The adhesive energies between the metal layer and the TiO₂(110) surface for the non-stoichiometric surfaces are much larger than that for the stoichiometric surface. And the Ag atom strongly interacts with the surface oxygen atoms at surface, while the Au atom strongly interacts with the surface titanium atoms at surface. The interaction between the metal and the TiO₂(110) surface depends on the surface stoichiometry and the kind of metal species. [doi:10.2320/matertrans.47.2669]

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1. Introduction

The particles of noble metal supported on the metal oxide such as titanium dioxide are interesting as the catalyst for the low temperature oxidation of CO^{1,2)} or the water-gas shift reaction.³⁾ Those catalytic activities depend on the kind of metals and metal oxides.^{3,4)} This is because the electronic structures of the noble metal supported on the metal oxide or the charge transfers between the noble metal and the metal oxide depend on the kind of noble metals and metal oxides.⁶⁻⁸⁾ Thiên-Nga and Paxton⁸⁾ investigated the electronic structures and the charge transfers of 5d transition-metal rows adsorbed on the stoichiometric TiO₂(110) surface, using the full potential linear muffin-tin orbital method based on the density functional theory (DFT). They, however, considered only one adsorption site, the on-top site above the five-fold titanium (Ti⁵) atom of the stoichiometric surface. Ichikawa *et al.*^{6,7)} investigated the mean-inner potentials of nano-particles of gold, platinum, and silver supported on TiO₂ using the electron holography method. They found that the mean inner potential of the Au particle increases when the particle size is below 5 nm. Furthermore, it increases suddenly below about 2 nm. However, the mean inner potential of the Ag particle dose not increase though the particle size decreases to less than 2 nm. It may be said that the reason why the dependence of the mean inner potential on the particle size is different between Au and Ag is the difference of the interfacial interaction between the metal and TiO₂. About the interactions between metals and TiO₂ surfaces, we theoretically investigated the adsorption of Au and Pt on TiO₂(110) surfaces.^{9,10)} We reported that the charge

transfers and the electronic structures of the metal/TiO₂ systems depend on the surface stoichiometry and the kind of the adsorbed metal.

In this paper, we investigate the adsorption of Au or Ag on the stoichiometric and the defective non-stoichiometric surfaces of TiO₂(110), theoretically using the *ab initio* pseudopotential method. We deal with the perfect stoichiometric surface, the surface formed by removing bridging-oxygen (O^B) atoms (Ti-rich surface) and the surface formed by removing O^B and six-fold titanium (Ti⁶) atoms (O-rich surface). We have examined the effects of the kind of adsorption metal and the surface stoichiometry on the adsorption energy and electronic structure. It is found that Ag adatoms favorably interact with oxygen at the TiO₂(110) surface and that Au adatoms favorably interact with titanium at the TiO₂(110) surface. Moreover, it is found that Au or Ag adatoms are adsorbed on the non-stoichiometric, Ti-rich and O-rich, surfaces more strongly than on the stoichiometric surface, through significant orbital hybridizations.

2. Method of Calculation

In order to investigate the electronic structures of Ag or Au adsorbed on the rutile TiO₂(110) surface, we performed the calculation on periodic slabs containing three O-Ti₂O₂-O units separated by 1.98 nm of vacuum region. We have treated the 1 × 1 unit cell as the calculating surface unit cell. The adsorbed atom is one per the 1 × 1 unit cell. The surface Brillouin zone is sampled by a 2 × 4 uniform mesh of k-points. For further details, see Ref. 10). All the calculations were carried out using the program package STATE (Simulation Tool for Atom TEchnology), which has been successfully applied to various systems including TiO₂(110),¹¹⁾ Au(111),^{12,13)} and Au/TiO₂(110) and Pt/TiO₂(110) systems.^{9,10)}

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Fig. 1 Schematic geometries (top view in upper panels and side view in bottom panels) of $\text{TiO}_2(110)$ surfaces; (a) stoichiometric, (b) Ti-rich, and (c) O-rich surfaces. The large gray and the small filled circles represent the Ti and O atoms, respectively. The marks, A to D, indicate the adsorption sites dealt in this work.

Table 1 Adhesion energies for each adsorption site. Unit is eV/adatom.

	A	B	C	D
Silver	0.19	0.08	1.01	4.27
Gold	0.05	0.14	1.91	3.85

In order to investigate the effect of the surface stoichiometry, we considered three kinds of surfaces with different defects and stoichiometry; the perfect stoichiometric surface, the Ti-rich surface, and the O-rich surface. We considered the following adsorption sites (see Fig. 1); one is the on-top site above the O^{B} atom for the stoichiometric surface (site A), which is the most stable site for $\text{Au}/\text{TiO}_2(110)$ at low coverage.¹⁴ The next is the on-top site above the five-fold titanium (Ti^5) atom for the stoichiometric surface (site B), which is the most stable site for $\text{Au}/\text{TiO}_2(110)$ at medium coverage.^{10,14,15} The next is the O^{B} vacant site for Ti-rich surface (site C), which is the most stable site for the Au adsorption on the Ti-rich surface.^{10,14} The remain is the Ti^6 vacant site for O-rich surface (site D), which is the most stable site for the Au adsorption on the O-rich surface.¹⁰

3. Results

We list the adhesion energies for each site in Table 1. The adsorption energy, E_{ad} , is defined by $E_{\text{ad}} = E_{\text{TiO}_2} + E_{\text{metal}} - E_{\text{metal/TiO}_2}$, where E_{TiO_2} , E_{metal} , and $E_{\text{TiO}_2/\text{metal}}$ represent the total energies of the clean relaxed $\text{TiO}_2(110)$ surface slab, the free metal monolayer, and the relaxed metal/ $\text{TiO}_2(110)$ system, respectively. This is because we have to clarify the interfacial interaction between the metal layer and $\text{TiO}_2(110)$ surface. For the stoichiometric surface, Ag is stably adsorbed on the on-top site above O^{B} (site A), while Au is stably adsorbed on the on-top site above Ti^5 (site B). The adhesive energy of Ag adsorbed on the site A is very similar to that of Au adsorbed on the site B. For the Ti-rich surface, Au is more stably adsorbed than Ag. However, for the O-rich surface, Ag is more stably adsorbed than Au. From these results, it can be said that gold is easy to interact with reduced titanium and silver is easy to interact with oxygen on $\text{TiO}_2(110)$ surfaces. The adsorption on the O-rich surface is strongest for both the Ag and Au atoms.

The bond lengths between the adsorbed metal atom and the nearest Ti atom, $d_{\text{M-Ti}}$ ($\text{M} = \text{Ag}$ or Au), and between the

Table 2 The distances between the metal adatom (M) and the nearest surface atoms, Ti and O. M is Ag or Au. Unit is nm.

	$d_{\text{Ti-Ag}}$	$d_{\text{O-Ag}}$		$d_{\text{Ti-Au}}$	$d_{\text{O-Au}}$
	Silver			Gold	
A	0.376	0.226	A	0.381	0.237
B	0.323	0.354	B	0.297	0.334
C	0.281	0.332	C	0.268	0.327
D	0.364	0.210	D	0.364	0.208

Fig. 2 Stable configurations in the case of the Ag adsorption. The Ag adsorbed on the site A (a), the site B (b), the site C (c), and the site D (d). The large open circles represent the Ag atoms.

Fig. 3 Stable configurations in the case of the Au adsorption. The Au adsorbed on the site A (a), the site B (b), the site C (c), and the site D (d). The large dark gray circles represent the Au atoms.

adsorbed metal atom and the nearest O atom, $d_{\text{M-O}}$, are listed in Table 2. The stable atomic configurations of $\text{Ag}/\text{TiO}_2(110)$ for each adsorption site are shown in Fig. 2 and those of $\text{Au}/\text{TiO}_2(110)$ for each adsorption site are shown in Fig. 3. The M-Ti distance on the Ti-rich surface (site C) is smaller than those on the stoichiometric and O-rich surfaces (sites A, B, and D), suggesting that the interfacial interaction on the Ti-rich surface is dominated by the interaction between the metal adatom and the four-fold Ti (Ti^4) atom at the surface. Note that the Ti^6 atoms at the stoichiometric surface become the Ti^4 atoms at the Ti-rich surface by removing the O^{B} atoms. Similarly, the M-O distance on the O-rich surface (site D) is smaller than those on the stoichiometric and Ti-rich surfaces (sites A, B, and C), suggesting that the interfacial interaction on the O-rich surface dominated by the metal-O interaction. The O-Ag distance is smaller than the O-Au distances for the site-A adsorption on the stoichiometric surface. For the O-rich surface, the metal adatoms are located on the position removed the Ti^6 atoms, so that the distances between the Ag atom and the surface atoms is not almost different from those

Fig. 4 Local density of states for the Ag/TiO₂(110) system. The Ag atoms are adsorbed on the site A (a), the site B (b), the site C (c), and the site D (d). The solid and dotted lines represent the densities of states for the Ag adlayer and the top layer of TiO₂(110) slab, respectively. The Fermi level is chosen as zero of energy.

Fig. 5 Local density of states for the Au/TiO₂(110) system. The Au atoms are adsorbed on the site A (a), the site B (b), the site C (c), and the site D (d). The solid and dotted lines represent the densities of states for the Au adlayer and the top layer of TiO₂(110) slab, respectively. The Fermi level is chosen as zero of energy.

between the Au atom and the surface atoms. However, the O^{inner}-Ag distance (0.220 nm) is smaller than the O^{inner}-Au distance (0.228 nm), where the O^{inner} atom is the oxygen atom under the Ti⁶ atom at the stoichiometric surface (see Fig. 1). In this way, Ag atoms seem to favorably interact with the O atoms, consistently with the results in Table 1. On the other hand, the Ti-Au distances are smaller than the Ti-Ag distances on the site B of the stoichiometric surface and the Ti-rich surface. Therefore, the Au adatoms seem to favorably interact with the Ti atom on the TiO₂(110) surface, consistently with the results in Table 1.

In order to investigate the interaction between the Ag or Au atom and TiO₂(110) in detail, we examined the local density of states (LDOS) of the adsorbed metal atom and the first layer of TiO₂(110) slab. Results of the Ag adsorption are shown in Fig. 4 and those of the Au adsorption are shown in Fig. 5. In Figs. 4 and 5, the solid and dashed lines represent DOS's of the adsorbed metal and the first layer of TiO₂(110) slab, respectively. The Fermi level is chosen as zero of energy.

For the stoichiometric surface, the DOS's of the Ag and Au layers almost do not change from those of the free metallic layers, although the relative energy positions against the TiO₂ surface DOS are changed depending on the adsorption site. These features are consistent with the small adhesive energies for the Ag and Au adsorptions on the stoichiometric surface. For the Ti-rich surface, the Fermi level lies in the conduction band of the TiO₂(110) surface, shown in LDOS in Figs. 4(c) and 5(c). This is because the electrons left by removing the O^B atoms occupy the surface conduction band consisting Ti 3*d* orbitals. The hybridization between the Ti 3*d* orbitals and Au 5*d* or Ag 4*d* orbitals causes the appearance above the Fermi level shown in Figs. 4(c) and 5(c). For the O-rich surface, the Ag 4*d* bands or the Au 5*d* bands expand in the same energy range of the O 2*p* bands, as shown in Figs. 4(d) and 5(d). This is caused by the strongly hybridization between the O 2*p* orbitals and the Ag 4*d* or the Au 5*d* orbitals. This is consistent with larger adsorption

energies in Table 1.

To investigate the electron transfer between the TiO₂(110) surface and the metal adatom, we have calculated the charge density difference ρ_d , which is obtained by subtracting the superposition of the respective charge densities of the metal adlayer and the TiO₂(110) slab from that of the metal/TiO₂(110) system. ρ_d 's of the Ag/TiO₂(110) systems are shown in Fig. 6 and those of the Au/TiO₂(110) systems are shown in Fig. 7. For the adsorption of the site A, the electron transfers from O^B to Ag slightly occur, while those between O^B and Au do not occur. For the adsorption of the site B, the electron density between Au and Ti⁵ increases, while that between Ag and Ti⁵ does not change. These differences are consistent with the above results in Tables 1 and 2, indicating the favorably Au-Ti and Ag-O interactions.

For the Ti-rich surface, electron densities between the Ti⁴ atoms and Ag or Au atoms increase. As shown in Figs. 6(c) and 7(c), the increase of the electron density between Ag and Ti⁴ is smaller than that between Au and Ti⁴. This is also consistent with the result that the adhesive energy of Au is larger than that of Ag for the Ti-rich surface. For the O-rich surface, electron transfers from Ag or Au to O^P and O^{inner} occur. As shown in Figs. 6(d) and 7(d), the electron transfers from Ag to O is larger than those from Au to O. This is also consistent with the result that the adhesive energy of Ag is larger than that of Au for the O-rich surface.

4. Discussions and Conclusions

For the stoichiometric surface, the Ag atom is stably adsorbed on the on-top site above the O^B atom (site A), while the Au atom is stably adsorbed on the on-top site above the Ti⁵ atom (site B). The O^B-Ag distance is smaller than the O^B-Au distance for the adsorption on the site A and the Ti⁵-Au distance is smaller than the Ti⁵-Ag distance for the adsorption on the site B. These differences are associated with the differences in the electronic charge distribution and transfer.

Fig. 6 Calculated charge density difference distributions for the Ag/TiO₂(110) systems. (a) The Ag atoms are adsorbed on the site A, (b) on the site B, (c) on the site C, and (d) on the site D. Red and blue regions indicate the regions increasing and decreasing the electron density, respectively.

Fig. 7 Calculated charge density difference distributions for the Au/TiO₂(110) systems. (a) The Au atoms are adsorbed on the site A, (b) on the site B, (c) on the site C, and (d) on the site D. Red and blue regions indicate the regions increasing and decreasing the electron density, respectively.

For the Ti-rich surface, the $4d$ orbitals of the Ag atom or the $5d$ orbitals of the Au atom hybridize with the $3d$ orbitals of the Ti⁴ atom, which is the reduced Ti⁶ atom at the stoichiometric surface by removing the O^B atoms. These hybridizations cause the appearance of states above the Fermi level, as shown in Figs. 4(c) and 5(c). The electron densities between the Ti⁴ atoms and the Ag or Au atoms increase. Therefore, the interaction between the adsorbed metal and the TiO₂(110) surface for the Ti-rich surface is larger than that for the stoichiometric surface. The adsorption energy of Au is larger than that of Ag, which is associated with the shorter Au-Ti distance and the larger charge accumulation.

For the O-rich surface, the $4d$ orbitals of the Ag atom or the $5d$ orbitals of the Au atom strongly hybridize with the $2p$ orbitals of the O atoms. These hybridizations cause the expansion of the d bands of the adsorbed metal atoms, and there occur significant electron transfers from the O atoms to the adsorbed metal atoms. Therefore, the interaction between the adsorbed metal and the TiO₂(110) surface for the O-rich surface is larger than those for the stoichiometric surface and for the Ti-rich surface. The M-O^P (M = Ag or Au) distances are almost the same with each other, because the adsorbed metal atom is located on the vacant site of the Ti⁶ atom. The Ag-O^{inner} distance, however, is shorter than the Au-O^{inner} distance. Thus the adsorption energy of Ag is larger than that of Au. Here it should be noted that the O-rich surface itself may not stably exist. However, the catalyst of the nanoparticles supported on the oxide is usually prepared by the calcination in air at high temperature. Under this condition, there is a possibility that O-rich metal/oxide interface configurations with metal atom directly bound to oxygen atoms similar to the present system should occur in real metal/TiO₂ catalysts.

In summary, we have investigated the atomic and electronic structures of the Ag/TiO₂(110) and Au/TiO₂(110) systems, using the *ab initio* pseudopotential method based on the DFT. In order to study the effects of the interface stoichiometry and the adsorbed metal species, we have dealt with the three kinds of surface stoichiometry; the stoichiometric, Ti-rich, and O-rich surfaces for each metallic species within the same theoretical method framework. Especially, the O-rich system is important in connection with real catalysts of the nanoparticles supported on the oxide prepared by calcination in air at high temperature. It has been shown that both the surface stoichiometry and the kind of adsorbed metals have significant effects on adsorption energies, the interface bond lengths, and the electronic structures such as charge distribution or transfers and orbital hybridizations. We found that the tendency that silver favorably interacts with the oxygen at the TiO₂ surface and gold favorably interacts with the reduced titanium at the TiO₂ surface. We considered that the difference of the interaction between Ag/TiO₂ and Au/TiO₂ is closely concerned with the difference in catalytic properties and activity.

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