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Effects of stoichiometry on electronic states of Au and Pt supported on $TiO_2(110)$

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We have investigated electronic structures and charge transfers of Au and Pt supported on the $TiO_2(110)$ surface, using first-principles calculation. In order to investigate the effect of stoichiometry, we examined Au or Pt adsorption on three kinds of $TiO_2(110)$ surface with different stoichiometry; the stoichiometric surface, the surface formed by removing bridging-oxygen atoms (Ti-rich surface), and the surface formed by removing bridging-oxygen and sixfold titanium atoms (O-rich surface). We considered the on-top site above the bridging-oxygen atom (site A) or above the fivefold titanium atom (site B) for the stoichiometric surface, the bridging-oxygen vacant site (site C) for the Ti-rich surface, and the sixfold titanium vacant site (site D) for the O-rich surface as the adsorption site. The adhesive energies between the metal layer and the $TiO_2(110)$ surface for the nonstoichiometric surfaces are much lager than that of the stoichiometric surface. Moreover, the Pt atom is adsorbed more stable than the Au atom for the all surface stoichiometry. The interaction between the metal and the $TiO_2(110)$ surface depends on the surface stoichiometry and the kind of metal. The reason is that the charge transfers and the electronic structures of adsorbed metal depend on those.

1. Introduction

The nano-particles of the noble metal supported on the metal oxide such as the titanium dioxide are interesting as the catalyst for the low temperature oxidation of CO [1, 2] or the water gas shift reaction [3]. That catalytic activity depends on the kind of metals and metal oxides [3, 4]. This reason is that the electronic structures and the charge transfers of the noble metals supported on the metal oxide depend on the kind of noble metals or metal oxides [5–7]. Ichikawa *et al.* [5, 6] investigated the mean inner potentials of nano-particles of the gold and platinum supported on TiO_2 using the electron holography method. They found that the dependence of the mean inner potential on the size of particles is different between the gold and platinum. Thiên-Nga and Paxton [7] investigated the electronic structures and the charge transfers of 5*d* transition-metal rows adsorbed on the stoichiometric (110) surface of TiO_2, 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 fivefold titanium atom, and only stoichiometric surface of $TiO_2(110)$.

In this paper, we investigated the adsorption of Au or Pt on the stoichiometric $TiO_2(110)$ surface and on the defective nonstoichiometric surfaces, theoretically using the *ab initio* pseudopotential method. We deal with the surface formed by removing bridging-oxygen (O^B) atoms (Ti-rich surface) and the surface formed by removing sixfold titanium (Ti^6) and O^B atoms (O-rich surface), as well as the perfect stoichiometric surface. We have examined the effects of the kind of adsorption atom and the surface stoichiometry on the adsorption energy and electronic structure. The O-rich system is of great importance, because usual noble metal catalysts supported on the TiO_2 are formed by calcinations under air at high temperature. It is found that Pt adatoms are adsorbed more strongly than Au adatoms are done for each surface. Moreover, It is found that Au or Pt adatoms are adsorbed on the Ti-rich and O-rich surfaces more strongly than on the stoichiometric surface. Significant orbital hybridization between noble metal

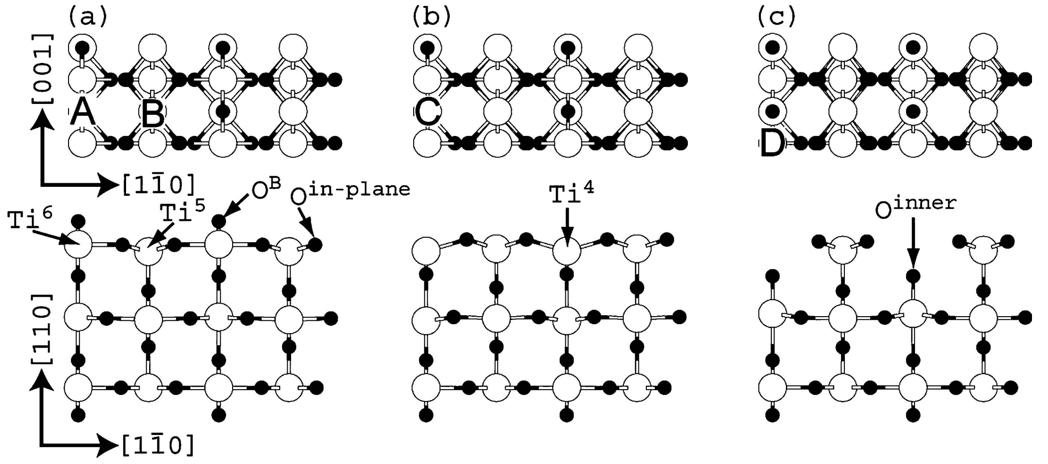

Figure 1 Schematic geometries [top view (upper panel) and site view (bottom panel)] of $TiO_2(110)$ surfaces. Two adsorption sites, A and B, and one adsorption site, C, and one adsorption site, D, are considered in the present study for the stoichiometric surface (a), for the Ti-rich surface (b), and for the O-rich surface (c), respectively. The large open circles represent the Ti atoms and the small filled circles represent the O atoms.

and Ti or O atoms are found for the nonstoichiometric surfaces.

The method of calculations is explained in Section 2. Calculated results of Au or Pt adsorption on the TiO_2 surfaces with various stoichiometric conditions are shown in Section 3. Section 4 is devoted to discussions and conclusions.

2. Method of calculation

In order to investigate Au or the Pt adsorption on the rutile TiO_2 (110) surface, we performed the calculations on periodic slabs containing three O-Ti_2O_2-O units separated by 19.8 Å of vacuum region. We have treated the 1 × 1 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. [8]. All the calculations were carried out using the program package STATE (Simulation Tool for Atom TEchnology), which has been successfully applied for various system including $TiO_2(110)$ [9], Au(111) surfaces [10, 11], and Au/$TiO_2(110)$ systems [8].

In order to investigate the effect of stoichiometry, we considered three kinds of surface with the different defects and stoichiometry; the 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 stoichiometric surface (site A), which is the most stable site for Au/$TiO_2(110)$ at low coverage (one atom per 2 × 2 surface unit cell) [12, 13]. The next is the on-top site above the fivefold titanium (Ti^5) atom for stoichiometric surface (site B), which is the most stable site for Au/$TiO_2(110)$ at medium coverage (one atom per 1 × 1 surface unit cell) [8, 12, 14]. The next is the O^B vacant site for the Ti-rich surface (site C), which is the most stable site for the Au adsorption on the Ti-rich surface [8, 12]. The remain is the Ti^6 vacant site for the O-rich surface (site D), which is the most stable site for the Au adsorption on the O-rich surface [8].

3. Results

We indicate the adsorption energies for each site in Table I. The adsorption energy, E_{ad}, is defined by $E_{ad} = E_{TiO_2} + E_{metal} - E_{metal/TiO_2}$, where E_{TiO_2},E_{metal}, and E_{metal/TiO_2} represent the total energies of the clean relaxed $TiO_2(110)$ slab, the free metal monolayer, and the metal/$TiO_2(110)$ system, respectively. This is because we have to clarify the interfacial interaction between the metal layer and $TiO_2(110)$ surface. If the total energy of the free metal atom is chosen as the origin of E_{ad}, 1.28 and 1.85 eV should be each value of E_{ad} in Table I for the gold and the platinum, respectively. For the stoichiometric surface, Au is stably adsorbed on the on-top site above Ti^5, while Pt is stably adsorbed on the on-top site above O^B. The Pt atom is more stable adsorption than the Au atom for all the surface stoichiometry of $TiO_2(110)$. Moreover, the adsorption on the O-rich surface is strongest for both the Au and Pt atoms.

The bond lengths between the adsorbed metal atom and the nearest Ti atom, d_{M-Ti} (M = Au or Pt), and between the adsorbed metal atom and the nearest O atom, d_{M-O}, are listed in Table II. The M—Ti distance on the Ti-rich surface is smaller than those on

TABLE I Adsorption energies for each adsorption site

	A	B	C	D
Gold	0.05	0.14	1.91	3.85
Platinum	1.04	0.65	3.69	6.81

Unit is eV/adatom

TABLE II The distance between the metal adatom (M) and the nearest surface atoms, Ti and O

	d_{Ti-Au}	d_{O-Au}		d_{Ti-Pt}	d_{O-Pt}
	Gold			Platinum	
A	3.81	2.37	A	3.54	1.93
B	2.97	3.65	B	2.51	2.51
C	2.68	3.27	C	2.47	3.20
D	3.64	2.08	D	3.63	2.05

M is Au or Pt. Unit is Å.

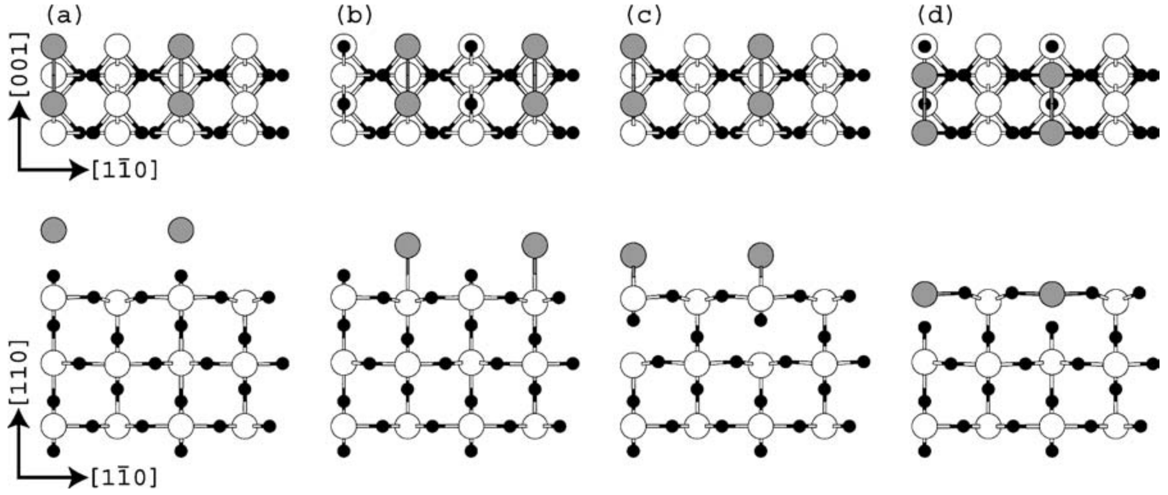

Figure 2 Atomic structures in the case of the Au adsorption. The Au atoms are adsorbed on the site A (a), the site B (b), the site C (c), and the site D (d). The large open, the small filled, and the dark gray circles represent the Ti, O, and Au atoms, respectively.

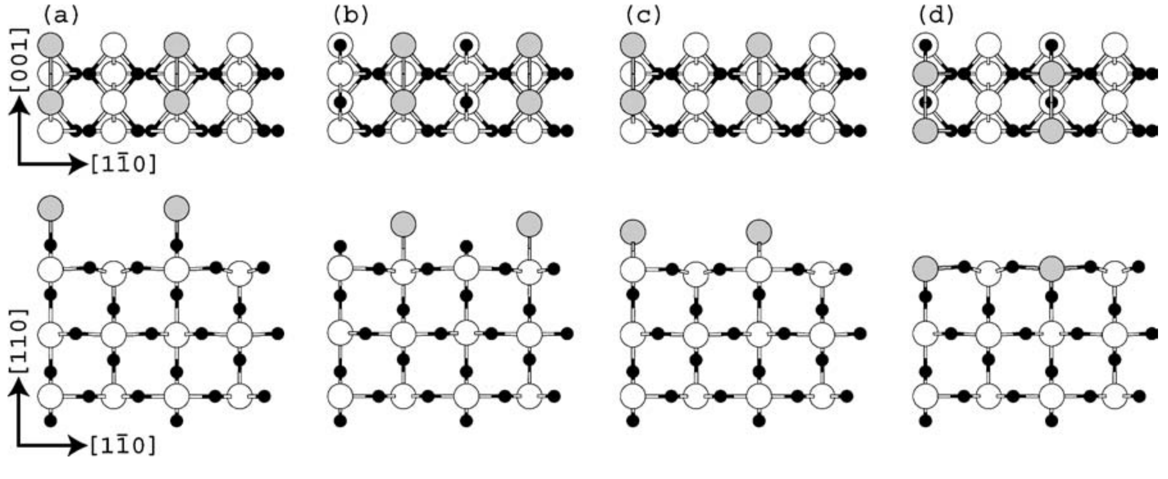

Figure 3 Atomic structures in the case of the Pt adsorption. The Au atoms are adsorbed on the site A (a), the site B (b), the site C (c), and the site D (d). The large open, the small filled, and the bright gray circles represent the Ti, O, and Pt atoms, respectively.

the stoichiometric and the O-rich surfaces, suggesting that the interfacial interaction on the Ti-rich surface is dominated by the interaction between the metal adatom and the Ti^4 atom. The Ti^6 atoms at the stoichiometric surface become the fourfold Ti (Ti^4) atom at the Ti-rich surface by removing the O^B atoms. The Pt—Ti and Pt—O distances are smaller than the Au-Ti and Au-O distances, except for the case at the O-rich surface. Therefore, the Pt atom interacts with $TiO_2(110)$ surface more strongly than the Au atom. For the O-rich surface, the adsorbed metal atoms are located on the position removed the Ti^6 atoms, so that the distances between the Pt atom and the surface atoms is not almost different from those between the Au atom and the surface atoms. The atomic structures of Au/$TiO_2(110)$ for each adsorption site are shows in Fig. 2 and those of Pt/$TiO_2(110)$ for each adsorption site are shown in Fig. 3.

In order to investigate the interaction between the Au or Pt atom and $TiO_2(110)$ in detail, we examined the partial density of states (pDOS) of the adsorbed metal atom and the Ti and O atoms at surface. The cases of the Au adsorption are shown in Fig. 4 and those of the Pt adsorption are shown in Fig. 5. In Figs 4 and 5, the solid, dotted, and dashed lines represent the d, p, and s component of the DOS, respectively. The Fermi level is chosen as zero of energy.

When the Au atom is adsorbed on the stoichiometric surface, the Au $5d$ bands are mainly in the range of -3.5 to -0.5 eV in the top panels of Fig. 4a and b. The density of states (DOS) of Au almost does not change. These features are consistent with the small adsorption energies for the Au adsorption on the stoichiometric surface.

For the Au adsorption on the Ti-rich surface, the Fermi level is lying in the conduction band of the TiO_2 surface, show in pDOS of Ti^5 and Ti^6 in Fig. 4c. This is because the electrons left by removing the O^B atom occupy the surface conduction band consisting of Ti $3d$ orbitals. These electrons partially transfer from the Ti^4 atom to the Au adatom. Moreover, the hybridization between the Au $5d$ orbitals and the Ti $3d$ orbitals cause the appearance of small peak of Au d components above the Fermi level shown in the top panel of Fig. 4c. These features are the origin of the large interaction between the Au atom and the Ti-rich surface.

For the Au adsorption on the O-rich surface, the Au $5d$ bands extend in the energy range of -7 to -0.5 eV and the O $2p$ bands also extend in the same range,

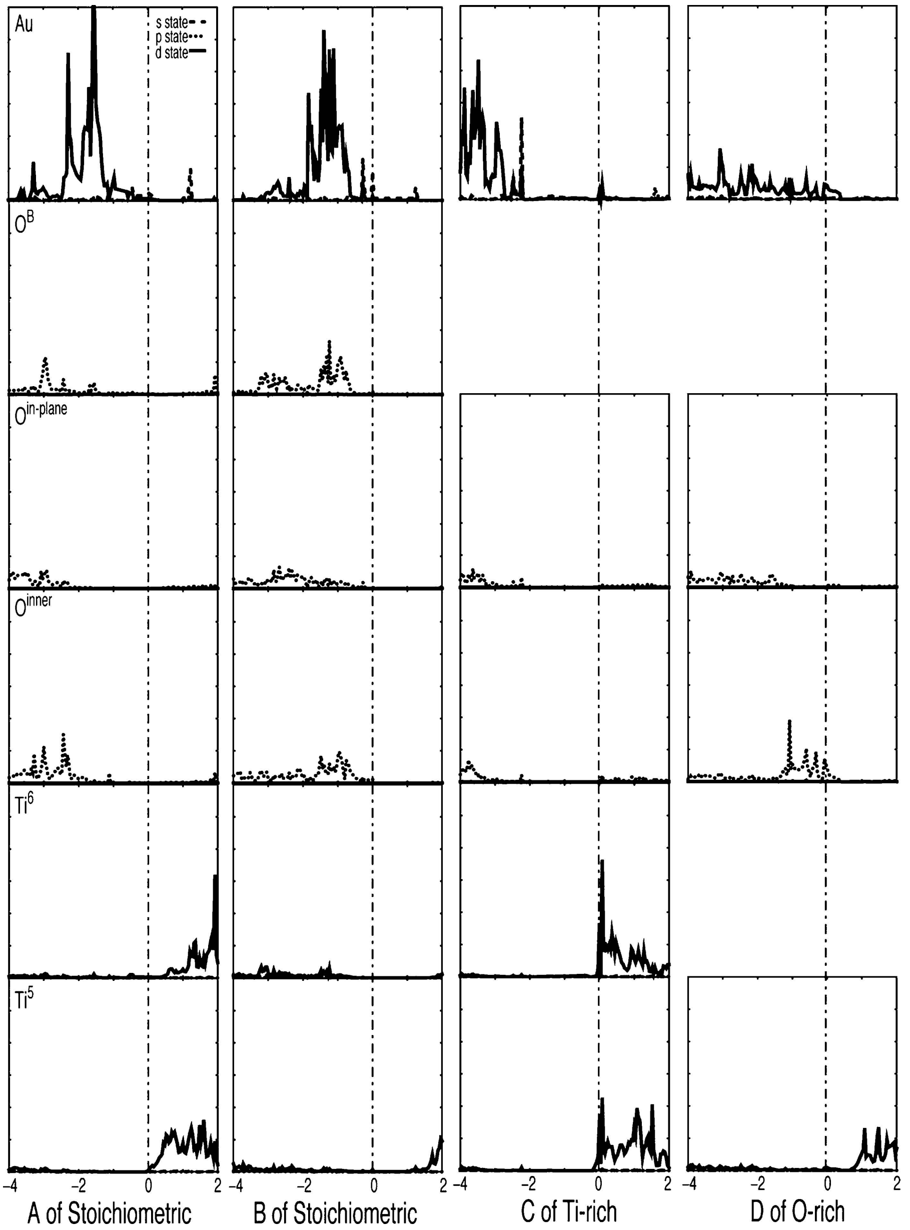

Figure 4 The partial density of states for the Au/TiO_2(110) systems; The solid, dotted, and dashed lines represent the d, p, and s components, respectively. The Fermi level is chosen as zero of energy.

as shown in Fig. 4(d). This is caused by the large hybridization between the Au $5d$ orbitals and the O $2p$ orbitals. This is consistent with large adsorption energy in Table I.

When the Pt atom is adsorbed on the stoichiometric surface, the Pt 5 d bands are in the range of -2 to 0.8 eV for the A site and -3 to 0.2 eV for the B site, as shown in Figs 5a and b, respectively. Electrons transfer from the Pt adatom to the O^B atom on the A site and from the Ti^5 atom to the Pt adatom. Therefore, the d bands in the case of the adsorption on the A site shift to the high energy as compared with the case of the adsorption on the B site. The hybridization for the adsorption on the A site is larger than that for the adsorption on the B site. These features are the origin that the adsorption on the A site is more stable than the adsorption on the B site.

For the Pt adsorption on the Ti-rich surface, the d components of Pt atom exist in not only the range of –4 to 0 eV but also the range of 1 to 1.8 eV, as shown in Fig. 5c. This means that the hybridization between the $5d$ orbital of the Pt adatom and the $3d$ orbital of the Ti^4 atom is large. The electrons transfer from the Ti^4 atom to the Pt adatom and the amount is larger than the case of the Au adsorption. Therefore, the d components of the Ti4 atom below the Fermi level are smaller than the case of the Au adsorption.

For the Pt adsorption on the O-rich surface, the $5d$ components of the Pt adatom expand in the energy range existing of the $2p$ bands of the $O^{\text{in-plane}}$ and O^{inner} atoms, as shown in Fig. 5d. Especially, the orbital hybridization between the Pt adatom $5d$ and the O^{inner} atom $2p$ is larger than the case of the Au adsorption. This means that the hybridization between the $5d$ orbitals of the Pt adatom and the $2p$ orbitals of the $O^{\text{in-plane}}$ and O^{inner} atoms is very large. These features are consistent with the larger adsorption energies on the nonstoichiometric surfaces than on the stoichiometric surface.

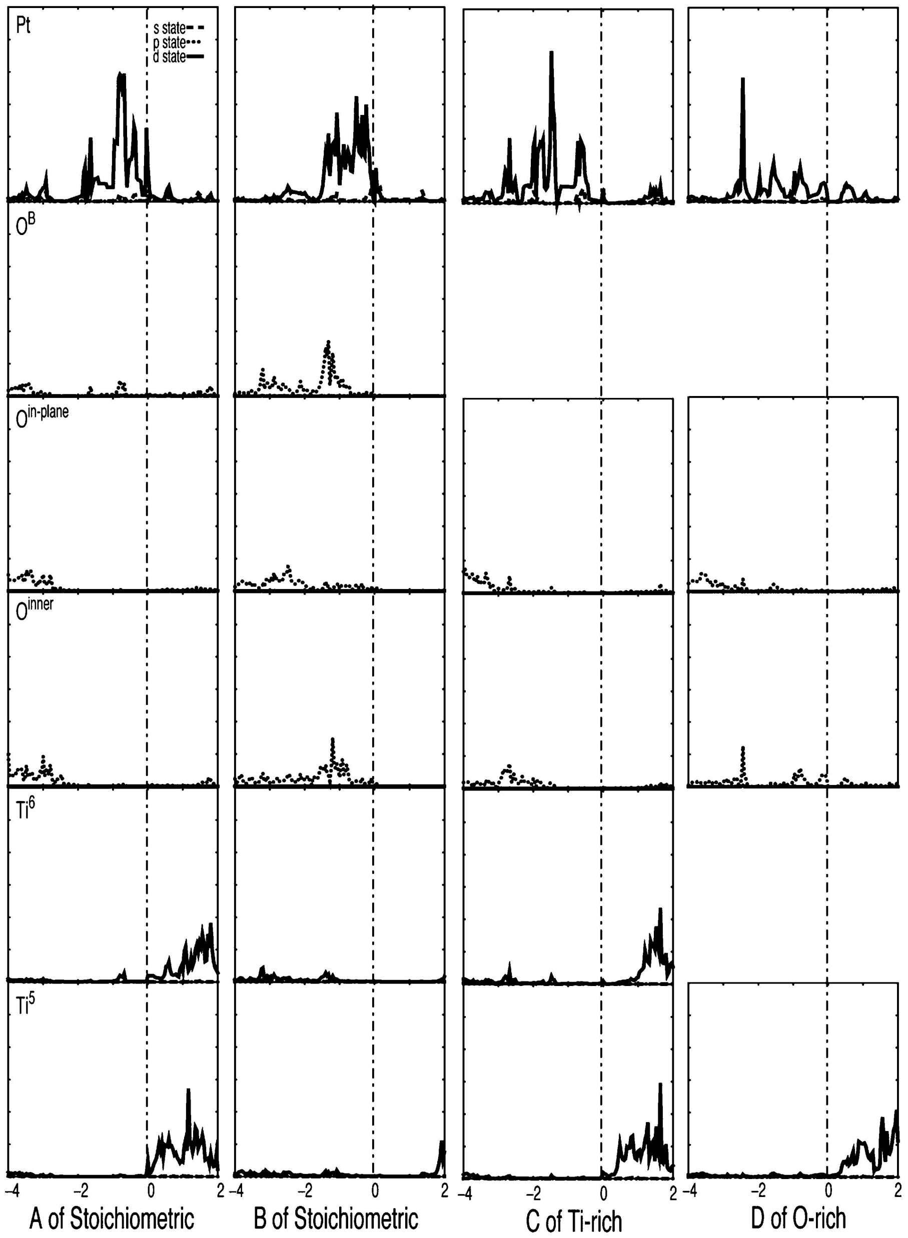

Figure 5 The partial density of states for the Pt/TiO_2(110) systems; The solid, dotted, and dashed lines represent the d, p, and s components, respectively. The Fermi level is chosen as zero of energy.

4. Discussions and conclusions

We have investigated the atomic and electronic structures of the Au/TiO_2(110) and Pt/TiO_2(110) systems using the *ab initio* pseudopotential method based on the DFT. In order to study the effects of the stoichiometry on the interaction between the noble metal atom and the TiO_2(110) surface, we have considered three types of stoichiometry of the TiO_2(110) surface; the perfect stoichiometric surface, the surface formed by removing the bridging-oxygen (O^B) atoms (Ti-rich surface), and the surface formed by removing the O^B and the sixfold titanium (Ti^6) atoms (O-rich surface).

For the stoichiometric surface, the Au atom is adsorbed on the on-top site above the fivefold titanium (Ti^5) atom (site B) more stably than on the on-top site above O^B atom (site A), while the Pt atom is adsorbed on the site A more stably than on the site B. Thiên-Nga and Paxton have investigated the electronic structures of 5d transition metals adsorbed on the on-top site above the Ti^5 atom of the stoichiometric TiO_2(110) surface [7]. The Pt atom, however, interacts with O^B atoms stronger than with Ti^5. The adsorption energy of the Pt atom is larger than that of the Au atom (Table I) and the distance between the Pt adatom and the TiO_2(110) surface is shorter than that of between the Au atom and the TiO_2(110) surface (Table II). The interaction between the Au atom and the stoichiometric surface is weaker than between the Pt atom and the stoichiometric surface.

For the Ti-rich surface, the 5d orbitals of the Au or Pt atom hybridize with the 3d orbitals of the fourfold titanium (Ti^4) atom [Figs 4 and 5], which is the reduced Ti^6 atom at the stoichiometric surface by removing the O^B atoms. Therefore, the interaction between the adsorbed metals and TiO_2(110) for the Ti-rich surface become larger than that for the stoichiometric surface. The adsorption energy of Pt is larger than that of Au. The adsorption energy of Au becomes ten times, but that of

Pt becomes only three times. The difference between the stoichiometric and the Ti-rich surfaces of $d_{\mathrm{Au-Ti}}$ is larger than that of $d_{\mathrm{Pt\text{-}Ti}}$ (Table II). These mean that the interaction between the Au atom and the $TiO_2(110)$ surface become strong by surface reduction in comparison with the case of Pt.

For the O-rich surface, the hybridizations between the $5d$ orbitals of Au or Pt and the $2p$ orbitals of O are very large [Figs 4 and 5]. The distance $d_{\mathrm{M\text{-}Oin\text{-}plane}}$ ($\mathrm{M} = \mathrm{Au}$ or Pt) is the same almost because the adsorbed metal atom is located on the vacant site of the Ti^6 atom. The distance $d_{\mathrm{Pt\text{-}Oinner}}$, however, is smaller than $d_{\mathrm{Au\text{-}Oinner}}$. The O-rich surface 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 occur in real metal/TiO_2 catalysts.

In summary, we have investigated theoretically the dependence of the electronic structure of the noble metal adsorbed on the rutile $TiO_2(110)$ on the kinds of the noble metal and on the interface stoichiometry. The present work is an attempt to clarify the effects of all the three kinds of interface stoichiometry, namely stoichiometric, Ti-rich, and O-rich surfaces, and the effects of the kinds of the adsorbed metal within the same theoretical method and models. Especially, here we have dealt with the O-rich systems, which is important in connection with real nano-catalysts of the noble metals supported on oxide prepared by calcination in air at high temperature. It has been shown that defects or nonstoichiometry have significant effects such as larger adsorption energy and serious changes in the electronic structure of Au or Pt adlayer, as compared with the stoichiometric system. And the Pt adlayer interacts with the $TiO_2(110)$ surface more strongly than the Au adlayer for the all surface conditions of $TiO_2(110)$. Moreover, the Pt atom strongly interacts with the oxygen at surface, while the Au atom strongly interacts the reduced Ti atom at surface. We considered that the difference of the interaction between Au/$TiO_2(110)$ and Pt/$TiO_2(110)$ systems is closely concerned with the difference in catalytic properties and activity.

Of course, it is desirable to deal with Au or Pt multilayers or nanometer-size Au or Pt clusters supported on variously defected TiO_2 surfaces, rather than a Au or Pt monolayer. And it is desirable to examine the dynamical behavior of molecular such as CO in such Au/TiO_2 or Pt/TiO_2 systems, as recently performed for the Au/MgO and Au/TiO_2 systems [15, 16]. We intend to deal with these subjects in the near future.

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