CO adsorption on small Au_n $(n = 1 - 7)$ clusters supported on a reduced rutile $TiO_2(110)$ surface: a first-principles study*

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CO adsorption on small Au_n $(n = 1 - 7)$ clusters which are supported by a partially reduced rutile $TiO_2(110)$ surface has been investigated by the first-principles method. The low coordinated sites of Au clusters are favorable for CO adsorption. CO–Au_n–TiO_2 system displays surface magnetism. There is a strong interaction between the adsorbed CO molecule and the supported Au clusters.

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1. Introduction

Gold nanoparticals dispersed on transition metal oxides surface have been widely recognised as a kind of new catalyst for CO and NO oxidation.[1,2] For example, many works have shown that Au clusters supported on rutile $TiO_2(110)$ surface are good catalysts for CO oxidation even at low temperature.[3−9] The catalytic property is found to depend not only on the size and structure of a cluster, but also on the morphology of the oxide support.[10−16] Furthermore, it has been shown to be a quantum size effect for the CO adsorption on supported Au clusters.[11] Much theoretical work has treated CO adsorption on gas-phase clusters directly.[17−20] The study of catalytic activity of supported Au clusters is still challengeable for theoretical calculation in view of the large atom numbers of the substrate.[21]

In the past decade, a large amount of studies were carried out to determine the adsorption properties of gold particles on both the stoichiometric and defected $TiO_2(110)$ surfaces,[22−33] which demonstrated that the bridging oxygen vacancy sites play an important role in the catalytic capability of Au nanoparticles. Recently, Chrétien and Metiu systematically studied the adsorption of small Au_n $(n = 1−7)$ clusters on stoichiometric, partially reduced, and partially hydroxylated rutile $TiO_2(110)$ surfaces.[34−37] They concluded that the gold clusters prefer to bind directly to the oxygen vacancy site. A previous study from Pilly and Hwang[38] showed that the oxygen vacancy dramatically alters the adsorption and surface diffusion of Au particles because of the delocalised electrons from the bridging O vacancies, which results in a low-energy diffusion channel for Au clusters compared to the stoichiometric surface. Very recently, Pabisiak and Kiejna reported first-principles calculations of Au nanorows and clusters on a defected rutile surface.[39] They also found that Au clusters tend to bind strongly to the vacancy defected bridging oxygen row at the $TiO_2(110)$ surface. It should be noted that a AuCO complex adsorbed on an oxygen vacancy on rutile $TiO_2(110)$ surface has been studied theoretically and experimentally in great detail by Anke S. Wörz *et al.*[40]

In this paper, we perform first-principles calculations to examine the adsorption mechanisms of CO on Au_n $(n = 1−7)$ supported by a partially reduced rutile $TiO_2(110)$ surface clusters. The adsorption property and the electronic structure are discussed. Our study will give valuable insight into the catalytic activity of supported small Au clusters.

2. Computational details

The spin-polarised calculations are carried out using the Vienna *ab initio* simulation package VASP[41−43] within the framework of density functional theory (DFT). The projector augmented wave

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potential[44] and the generalised gradient approximation with Perdew–Wang (PW91) functional[45] are used to describe the core electrons and the exchange–correlation energy respectively. The cut-off energy for the plane-wave basis set is set to 400 eV. Single Γ point is used to sample the Brillouin zone of large supercell.

The bulk properties of rutile TiO_2 are determined with theoretical parameters (a = 4.64 Å, c = 2.98 Å (1 Å=0.1 nm)), which are in agreement with the previous calculation.[39] A 4×2 supercell is used to model the partially reduced surface by removing a bridging oxygen atom from the surface. The oxide surface contains 12 atomic layers (four triple atomic layers). The supercell is separated from its periodic images by a large vacuum space of about 17 Å, which can insure that the separation between slabs is larger than 8 Å when adsorbing both Au cluster and CO. The atoms in the bottom triple layer are fixed and the others are fully relaxed untill the Hellman–Feynman force less than 0.05 eV/Å. The binding energy E_b of the system is defined as $E_b = E_t - E_a$, where E_t is the total energy of the system and E_a is the sum of each atomic energy. In this case, the binding energy is usually negative.

We first repeat the calculation for Au_n ($n = 1-7$) clusters and obtain consistent results with the previous DFT studies[46–49] except for Au_7. A nonplanar structure of Au_7 (see the Au7a shown in Fig. 1) is found to be the most stable one. The binding energy is lower than that of the planar hexagonal structure by 0.02 eV. The obtained lowest-energy Au_n clusters are used to search for the ground state of Au clusters adsorbed on the reduced TiO_2(110) surface. Figure 1 presents the most stable and the metastable structures with the energy difference within 0.6 eV. Our results for the adsorption energy, the binding site, and the geometry basically agree with the previous works.[36,38,39] The oxygen vacancy site on TiO_2(110) surface is mainly responsible for arresting Au cluster.

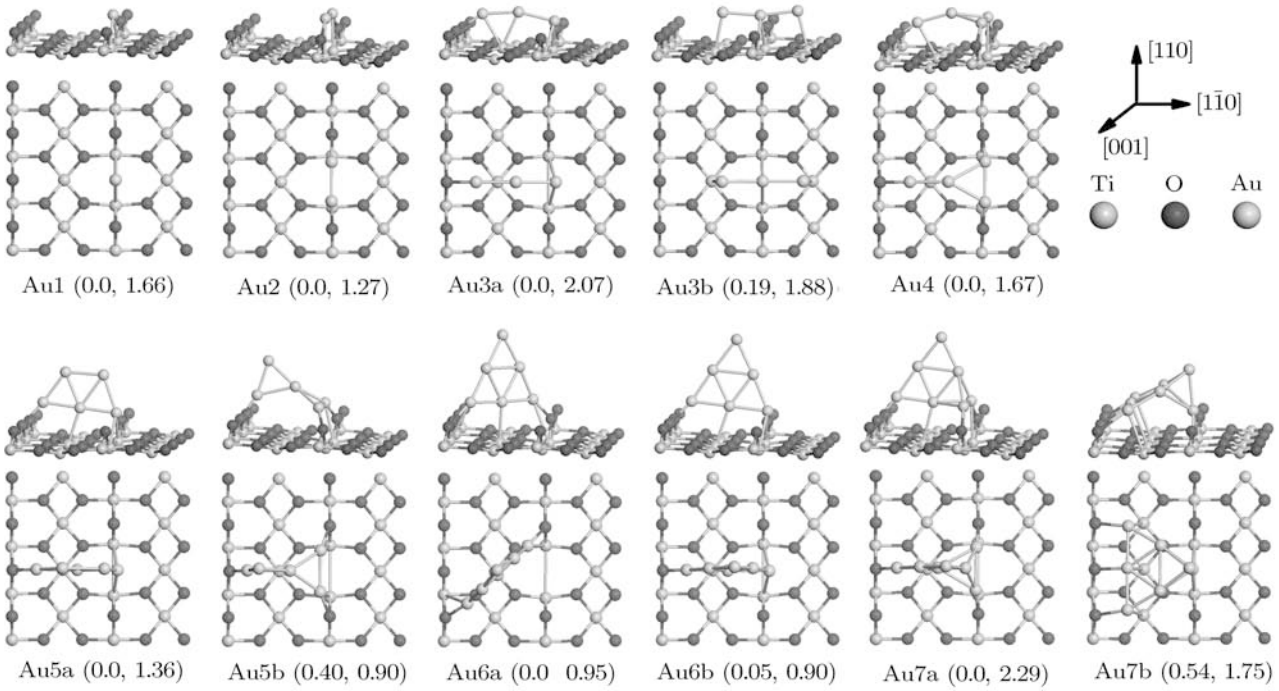


Fig. 1. Lowest-energy structures of Au_n ($n = 1-7$) clusters adsorbed on partially reduced TiO_2(110) surface. The metastable structures with the energy difference within 0.6 eV relative to the ground state are also listed. The upper and lower parts for each case correspond to the side and the top views respectively. The two numbers in the parenthesis are the binding energy of Au_n–TiO_2 system and the adsorption energy of Au_n clusters on the reduced TiO_2 surface respectively. The unit is eV. The binding energy of the lowest-energy structure is set to zero.

The obtained stable Au_n–TiO_2 structures are then used to study the CO adsorption on titania-supported small Au clusters. We have searched almost all possible binding sites of CO on titania-supported Au_n ($n = 1-7$) clusters. The adsorption energy of CO on titania-supported Au_n clusters is given by

$$E_{\rm a}({\rm CO}) = E({\rm Au}_n - {\rm TiO}_2) + E({\rm CO}) - E({\rm CO} - {\rm Au}_n - {\rm TiO}_2), \quad (1)$$

where E(Au$_n$–TiO$_2$), E(CO) and E(CO–Au$_n$–TiO$_2$) are the total energies of Au$_n$–TiO$_2$ system, free CO molecule and CO–Au$_n$–TiO$_2$ system respectively. The charge density differences for CO–Au$_n$–TiO$_2$ system are calculated by using

$$\Delta\rho = \rho({\rm CO} - {\rm Au}_n - {\rm TiO}_2) - \rho({\rm CO}) - \rho({\rm Au}_n - {\rm TiO}_2), \quad (2)$$

where ρ(CO–Au$_n$–TiO$_2$) and ρ(CO) are the charge densities of TiO$_2$–Au$_n$–CO system and CO molecule respectively, while ρ(Au$_n$–TiO$_2$) is the charge density of TiO$_2$–Au$_n$ with the atomic configuration in CO–Au$_n$–TiO$_2$ system.

3. Results and discussion

3.1. Adsorption site and adsorption energy

The lowest energy structure and those metastable structures with energy difference within 0.4 eV are presented in Fig. 2. The corresponding structural and electronic properties of the CO–Au$_n$–TiO$_2$ system are listed in Table 1.

Table 1. The calculated electronic properties of CO–Au$_n$–TiO$_2$ system: the calculated binding energy $E_{\rm b}$ (in eV), the CO adsorption energy $E_{\rm a}$ (in eV), the bond length r (in Å), and the magnetic momemt M (in $\mu_{\rm B}$). The $E_{\rm b}$ of the lowest-energy structure is set to zero.

	$E_{\rm b}$	$E_{\rm a}$	$r_{\rm C-O}$	$r_{\rm Au-C}$	M
Au1	0.00	0.41	1.15	2.09	0.8
Au2	0.00	1.26	1.15	1.94	1.8
Au3-a	0.00	1.18	1.15	1.94	0.8
Au3-b	0.16	1.23	1.15	1.96	0.8
Au4-a	0.00	1.22	1.15	1.96	0.2
Au4-b	0.19	1.03	1.15	1.94	1.8
Au5	0.00	1.37	1.15	1.93	0.8
Au6-a	0.00	1.10	1.15	1.97	0.2
Au6-b	0.39	0.71	1.15	2.01	1.8
Au7-a	0.00	0.97	1.15	1.94	1.8
Au7-b	0.11	0.86	1.15	2.00	0.8
Au7-c	0.14	0.83	1.15	2.00	2.9
Au7-d	0.15	0.82	1.15	1.95	2.9

There is only one binding site for CO adsorbing on the supported Au monomers and dimers. The adsorption energies of them are 0.41 and 1.26 eV respectively, smaller than those of CO binding on free Au particles (0.80 and 1.53 eV respectively).[19] The obvious increase of adsorption energy from monomer to dimer is accompanied by the remarkable decrease of Au–C bond length (from 2.09 to 1.94 Å). It is interesting to note that the adsorption of CO on the supported dimer breaks the Au–O bond. While the Au–Au bond length keeps the gas-phase value.

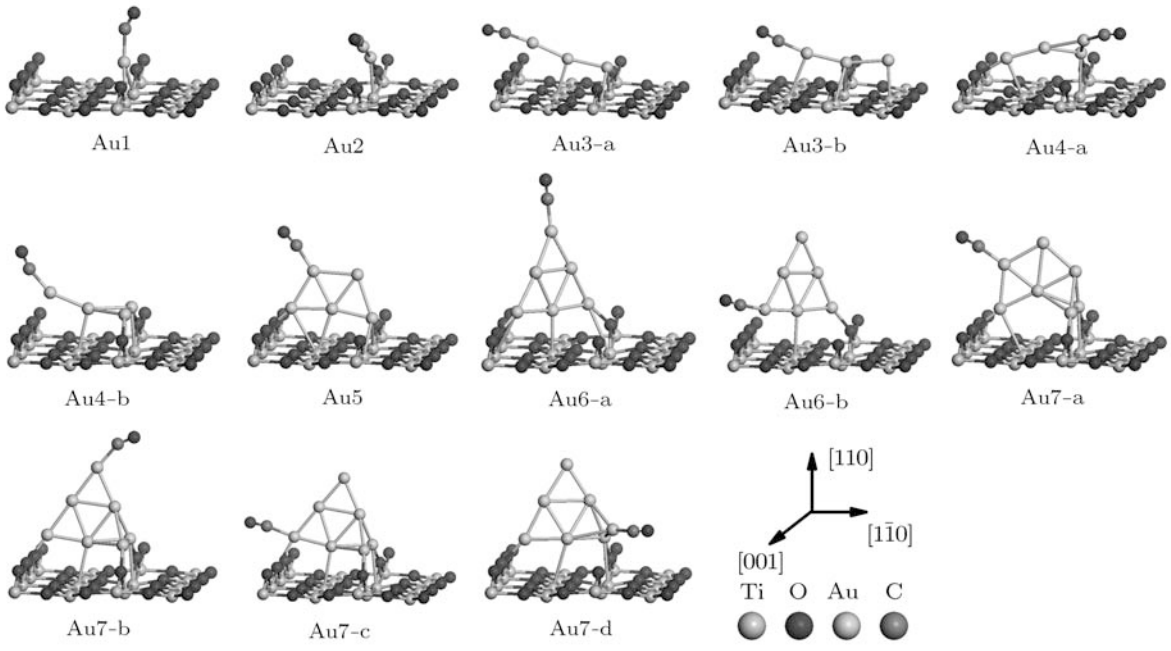


Fig. 2. Lowest-energy structures of CO adsorbed on Au$_n$ ($n = 1 - 7$) clusters supported by a partially reduced TiO$_2$(110) surface. The metastable structures with the energy difference within 0.4 eV relative to the ground state are also listed.

Based on the two different stable Au_3–TiO_2 structures, we have two lowest energy sites for CO adsorption, which are shown as Au3-a and Au3-b in Fig. 2. CO tends to be adsorbed on the outer Au atom in both cases, and the adsorption energies are 1.18 and 1.23 eV respectively. The Au–C bond lengths of the two structures are almost the same. Similar to the case of Au_3, we also obtain two possible CO adsorption sites on the supported 'Y'-shaped Au_4, which are at the head and the tail of Au_4 respectively. The corresponding adsorption energies are 1.22 and 1.03 eV respectively. For the gas-phase 'Y'-shaped Au_4, CO also prefers to be adsorbed at the head of Au atom,[19] which is consistent with our prediction.

There are more possible binding sites for the Au_5 case. However, we only found one most stable adsorption structure for the 'M'-shaped Au_5. The top Au atom is preferable for CO adsorption. The adsorption energy (1.37 eV) is the largest one when CO is adsorbed on the supported Au_n clusters in our calculations. The Au–C bond length is 1.93 Å, close to that (1.95 Å) of CO adsorbed on gas-phase Au_5 cluster.[19]

For pyramid Au_6 case, the most preferable adsorption site is the top atom, which is more active than the bottom atom. The adsorption energy of Au6-a is larger than that of Au6-b by about 0.40 eV. Obviously, the Au–C bond length in Au6-a is 1.97 Å, shorter than 2.01 Å of Au6-b. CO binds more strongly to the supported Au_6 than to the gas-phase Au_6. The adsorption energy of Au6-a is 1.10 eV, larger than that (0.89 eV) of CO adsorbed on free pyramid Au_6.[19]

For the pyramid Au_7 case, we found one stable and three nearly degenerate metastable structures as shown in Fig. 2. The adsorption energy differences can be reflected from the variation of Au–C bond length. A shorter bond corresponds to a tighter adhesion. The CO adsorption on the waist atom in Au7-a is quite different from the others, which causes a strong distortion to the supported Au_7 cluster. This is the only reconstruction case of supported Au clusters in our study. The Au–C bond length of 1.94 Å is shorter than that of other adsorption site. The Au_7 cluster is the one that keeps the gas-phase geometry best among the three metastable structures.

3.2. Electronic structure

The magnetic moments are summarised in Table 1. Our results of magnetic moment show directly that the CO–Au_n–TiO_2 system is magnetic. We carefully analysed the source of the magnetism and found that it originates from the surface atoms of the reduced TiO_2(110). The charge transfer occurs not only between CO and Au cluster, but also between Au cluster and TiO_2 surface. As a result, the unpaired electrons in the odd number Au clusters paired and the odd–even oscillation of magnetism shown in the gas-phase Au clusters disappears when they are adsorbed on the reduced TiO_2(110) surface. This is consistent with previous DFT results.[36,38] Furthermore, we compared the results of spin-polarised and spin-restricted calculations, and found that the magnetism has little effect on the adsorption energy and the structure of CO on support-cluster systems.

As an illustration, we choose CO–Au_5–TiO_2 that has the largest CO adsorption energy to analyse the charge distribution and the density of state (DOS). Compared to Au_5–TiO_2, we can observe a noticeable charge density redistribution between CO and Au as shown in Fig. 3.

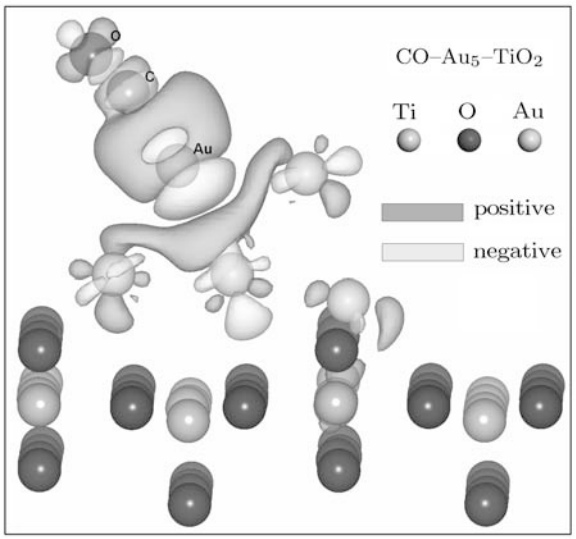


Fig. 3. The isosurface of charge density difference in CO–Au_5–TiO_2 system.

There are both increased and decreased electronic density around Au atom. The results imply the orbital hybridizations between CO and Au cluster as well as the electrons transfer within the orbitals. This can be confirmed by the DOS analysis. Figures 4 and 5 show the total DOS and partial DOS respectively. It is surprising that the total DOS of Au_5 becomes rather localised compared with that of gas-phase state, which results from not only the interaction between Au_5 and TiO_2(110) surface, but also that between Au_5 and CO. Actually, the antibonding π^* orbitals of free CO

molecule are very active in CO adsorption. We can notice that the antibonding π^* states (the peaks above the Fermi level, in dashed lines shown in Fig. 4) almost disappear when CO adsorbed on the supported Au cluster.

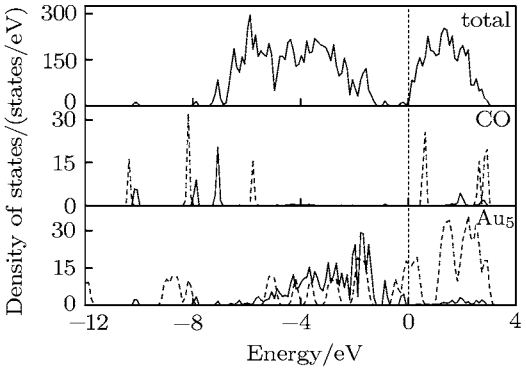


Fig. 4. The total density of states of the CO–Au_5–TiO_2 system, the adsorbed CO, and Au_5. For comparison, the total density of states of gas-phase CO and Au_5 are included and plotted as in dashed curves. Fermi level is shifted to zero.

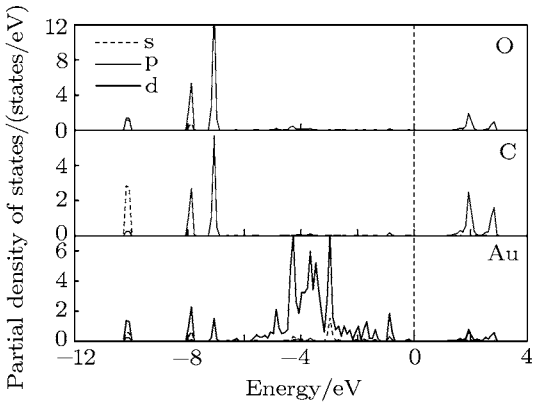


Fig. 5. The partial density of states of O, C, and the absorbed-site Au atom in CO–Au_5–TiO_2 system. Fermi level is shifted to zero.

New strong covalent d(Au)-π^*(CO) bonds are formed as a result of the interaction between Au-d orbitals and the p-orbitals of CO. The details of the interaction between Au and the CO molecule can be found in the partial DOS shown in Fig. 5. The most important characteristic is the hybridization between Au-d, C-s and C(and O)-p orbitals across the energy scope of 7 eV to 10 eV below the Fermi level. The triple bond of CO still exists and is enhanced strongly by mixing the Au-d states.

4. Conclusion

We have investigated the adsorption of CO molecule on Au_n ($n = 1 - 7$) clusters supported on the partially reduced TiO_2(110) surface by using first-principles calculation. CO adsorption has little effect on the morphology of Au_n–TiO_2 system with the exception of Au_7. The on-top low coordinated Au atoms are the most favourable sites for CO adsorption, which indicates they are the chemical active sites and beneficial for Au catalysis. The support indeed affects the adsorption properties of Au clusters. CO adsorption on the supported Au cluster shows differences in structural and energy properties as compared with the adsorption on free cluster. Strong covalent d(Au)-π^*(CO) bonds are formed and the TiO_2(110) surface becomes magnetic. The magnetism is found to affect little the CO adsorption behaviour. Our results provide a concise insight into the effect of supported small Au cluster on catalysing CO reaction.

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