

Ab Initio Study of the Effect of Oxygen Defect on the Strong-Metal–Support Interaction between Pt and TiO₂(Rutile)(110) Surface

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The interaction between Pt and ideal and oxygen-defective TiO₂(rutile)(110) surfaces are studied by ab initio SCF methods. The result reveals that the interaction between the Pt and TiO₂ is very strong; the bond energy reaches 16.5 eV for the ideal surface and 23.0 eV for the oxygen-defective TiO₂(rutile)(110) surface. It seems that Pt is preferentially adsorbed upon the oxygen vacant site on the TiO₂(rutile)(110) surface. Based on the density of states and charge distribution, a more detailed discussion about the SMSI effect between Pt and TiO₂(rutile)(110) is presented. © 1995 Academic Press, Inc.

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1. INTRODUCTION

It is well known that a small amount of Pt loading can increase the photocatalytic activity of TiO₂(rutile) greatly (1). This effect is attributed to the strong metal–support interaction (SMSI), which, in the past, has stimulated much effort to develop new kinds of catalytic materials. Generally, it is believed that SMSI results from the bond formation between the metal and substrate but until now the exact nature of this bonding is still unknown.

Experimentally, Bahl *et al.* (2) verified that charge transfer from TiO₂ to Pt and oxygen vacancies can promote this process. Although the quantity of charge transferred from the TiO₂ to the Pt is not large (0.6 e/Pt), it greatly changes the surface chemical properties of the TiO₂(rutile) surface, for example, H₂ and CO adsorption are totally depressed on these samples.

Schierbaum *et al.* (3) and Aspnes *et al.* (4) studied a model system of Pt/TiO₂, and found that the Schottky barrier is formed at the interface between Pt and TiO₂. They also observed that this Schottky barrier collapses upon hydrogenation to ohmic or nearly ohmic contacts. Yamamoto *et al.* (5) attributed this transformation to the

decrease in the Fermi level of the Pt due to hydrogen adsorption. Hope *et al.* (6) studied the depth profile for Pt/TiO₂ contacts which had been heated by holding the sample at 800°C for 15 min at a pressure of 5×10^{-5} Torr and found that the interface region becomes wider. They concluded, therefore, that the interdiffusion is probably responsible for the loss of barrier properties between the Pt and TiO₂. However, according to the experiments performed in this laboratory, interdiffusion only occurs after the platinum is oxidized (7). In fact, if the sample is heated at 600°C for 30 min at a pressure lower than a 5×10^{-9} Torr (under these conditions, no oxidized Pt can be formed), the contact becomes ohmic; we ascribe this change to the effect of the surface oxygen defects, however, because the Schottky contact can be recovered immediately by leaking a small amount of oxygen (pressure lower than 5×10^{-6} Torr) into the system (8). This means that in the real catalysis, the Pt/TiO₂ junctions would be ohmic rather than Schottky in character, because powdered TiO₂ is usually formed under conditions where a high density of interface states would be produced. More recently, Jian-Mei Pan *et al.* (9) studied the interaction between chromia and the TiO₂(rutile)(110) surface and found that the adsorption of chromia can create different reduced Ti species on the surface of the TiO₂(rutile)(110). Based on their systematic work, they propose the existence of a relation between the metal reactivity with oxygen and the dispersion of metal on oxides. Their instructive conclusion is very important in the preparation of a catalyst.

Theoretical efforts to explain the origin of this strong metal–support interaction include two aspects: (i) to calculate the electronic structure of pure TiO₂, and (ii) to calculate the electronic structure of the Pt-loading TiO₂. Until now, most research is focused on understanding the electronic structure of the TiO₂. Tsukada *et al.* (10) calculated the surface electronic structure and defect

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states of the TiO_2 (rutile) by the DV-Xa method and found that the bridge oxygen on the TiO_2 (rutile)(110) surface can be removed easily and both the surface and bulk oxygen vacancies can create bandgap states, which are located at 0.7 eV below the Fermi level. Their results fit the UPS spectra very well. However, using scattering methods based on band theory, Munnix and Schmeits (11) calculated the DOS for oxygen defects on the TiO_2 (rutile)(110) surface and found that the removal of bridge oxygen from the surface of the TiO_2 does not create a bandgap state. Their conclusion is consistent with results of the STM equipment (12). Therefore they proposed that the bandgap state results from sublayer oxygen vacancies. Kasowski and Tait (13) calculated the DOS for thick slabs of the TiO_2 (rutile) using the linear combination of Muffin-tin orbitals (LCMTO) energy band method. They found that, for the ideal surface structure of rutile TiO_2 (110), there are not bandgap states if the puckered O atoms relax inward by $\Delta z = 0.2 \text{ \AA}$. Therefore, they made a reasonable assumption that the occupied surface states in the bulk bandgap arise from thermodynamically unstable configurations. More recently, different groups made contributions to the theoretical elucidation of the electronic structure of the TiO_2 (rutile) (14, 15).

In catalysis, we are more interested in the interaction between Pt and the TiO_2 surface because it is a typical SMSI catalyst. Earlier work was performed by Horsley (16), using the SCF-Xa method. In his calculation, two different models are used. The first (I) consists of a single Pt atom interacting with the Ti in an octahedral (TiO_6)⁸⁻ but the nearest neighbors of the Pt are the triangle of oxygen atoms (see Fig. 1c). The second (II) consists of a Pt bonded to a TiO_5 ⁻ unit, in which the nearest neighbor of the Pt atom is the Ti ion (see Fig. 1b). Horsley concluded that the metal-support interaction in the Pt- TiO_2 SMSI catalyst should be represented by model II rather than model I. In addition, the covalent bonding alone is not sufficient to account for the strength of the metal-support interaction and an ionic component makes some contribution to the bond formation between the Pt and the TiO_2 . However, this model seems to be oversimplified if we try to consider the effect of the oxygen defects on the interface properties of the Pt/ TiO_2 . In this work, we report the calculation results first for ideal and oxygen-defective TiO_2 (rutile)(110) surface electronic structure and then for the interaction of the Pt with these surfaces, based on an ab initio SCF method.

2. COMPUTATIONAL METHODS

The calculations were performed with the Gaussian 90 program, developed by Pople *et al.* (17) on a Convex computer. In our calculations we adopt Wadts' scheme for the Ti and the Pt and Kraus's (see Refs. 18-21) for

the O, namely, to replace the chemically inert core electrons with an effective potential and hence to reduce the calculation to a computationally more feasible and chemically more important valence-electron problem. Starting with the basis set they proposed, we adequately enlarge $\text{Ti}d$ and $\text{O}p$ primitive sets (but we removed the polarization function from the original basis set for O) and optimized these basis sets until we reached the best description of the electronic structure of the small TiO_6^{8-} cluster in the ground state (singlet), for which many theoretical data are found in the literature. As is well known, the Hartree-Fock method usually underestimates the binding energy by 20-50% by ignoring the electron correlation effect. However, in our case, the correlation only makes a few percent contribution to the Pt- TiO_2 bonding energy. The correction to the HF bonding energy is included following Wilson's recent work (22).

The geometric parameters are obtained from experimental results for the rutile TiO_2 structure (see Fig. 1a). The geometry of the TiO_2 cluster is fixed in the calculation and only the distance between the Pt and the surface of the TiO_2 cluster is optimized. The cluster charge is determined as the summation of the formal charge: +4 for the Ti and -2 for the O. In the pure ionic picture, the $\text{O}2p$ orbitals are fully filled and form a valence band of the TiO_2 . The empty $\text{Ti}3d$ orbitals form the conduction band. We take this as the starting point for the calculation. The binding energy in this work is defined as $E(A-B) = E_{A-B} - E_A - E_B$. The effect of the rest of the lattice on the cluster wavefunction is usually considered as the point-charge approximation. However, for the noncomplete ionic compound, such as TiO_2 , the rationality to do so is in doubt and a more detailed discussion will be given in a forthcoming paper.

3. RESULTS AND DISCUSSION

3.1. Electronic Structures of $\text{Ti}_4\text{O}_{16}^{6-}$ and $\text{Ti}_4\text{O}_{15}^{6-}$

We take the cluster $\text{Ti}_4\text{O}_{16}^{6-}$ as the ideal (110) rutile surface model (see Fig. 1d). As can be seen from the DOS (Fig. 2a), there is significant $\text{Ti}3d$ - $\text{O}2p$ hybridization in TiO_2 , although the valence band is predominantly $\text{O}2p$ and the conduction band is predominantly $\text{Ti}3d$ in character. This means that the bond between Ti and O is not purely ionic but has some covalent character. From the gross orbital population (Table 1), we can see that the $\text{Ti}3d$ orbital is partially occupied, namely, the formal charge on the Ti is lower than +4. One may argue that the cluster is isolated by the boundary and too much negative charge is included in the cluster. In order to answer this question, we have repeated calculations, using differently charged clusters, such as neutral clusters and clusters that are negatively charged but saturated by proton or positive point charge surroundings. We will discuss this problem

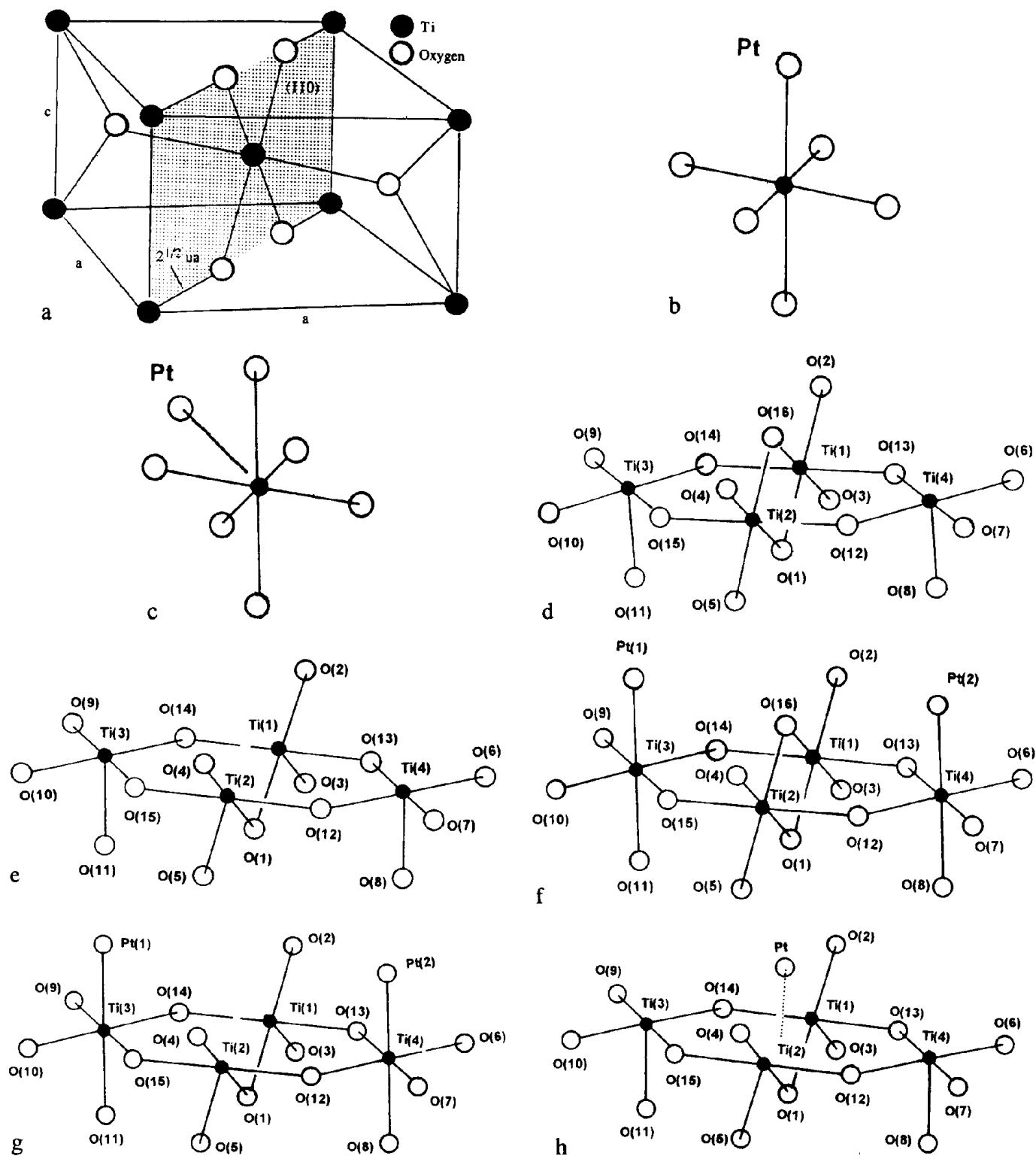


FIG. 1. The geometries of the clusters in calculation. (a) rutile TiO₂; (b) Pt/TiO₅⁶⁻; (c) Pt/TiO₆⁸⁻; (d) point symmetry C_{2v} Ti₄O₁₆¹⁶⁻; (e) point symmetry C_{2v} Ti₄O₁₅¹⁵⁻; (f) point symmetry C_{2v} 2Pt/TiO₁₆¹⁶⁻; (g) point symmetry C_{2v} 2Pt/Ti₄O₁₅¹⁵⁻; (h) point symmetry C_{2v} Pt/Ti₄O₁₅¹⁵⁻.

TABLE 1
The Gross Orbital Population of $Ti_4O_{16}^{16-}$ and $Ti_4O_{15}^{16-}$

				$Ti_4O_{16}^{16-}$						
	Ti(1,2) ^a	Ti(3,4)		O(16)	O(1)	O(2,4)	O(3,5)	O(6,7,9,10)	O(8,11)	O(12-15)
3s	2.00112	2.00202	2s	1.57254	1.52974	1.70446	1.69272	1.80268	1.64023	1.50616
4s	0.29991	0.29327	2P _x	1.72142	1.66080	1.79770	1.84656	1.94625	1.90830	1.56810
3P _x	2.00027	2.00024	2P _y	1.35495	1.37210	1.89735	1.87368	1.88540	1.96864	1.74633
3P _y	2.00058	1.99986	2P _z	1.76336	1.58645	1.93760	1.88801	1.93737	1.72072	1.67156
3P _z	2.00012	1.99955								
3d ₀	1.10278	0.63101								
3d + 1	0.36368	0.70012								
3d - 1	0.82397	0.27366								
3d + 2	0.89929	1.20106								
3d - 2	0.37960	0.74361								
Total charge (a.u.)										
Ti(1)	Ti(2)	Ti(3)	Ti(4)	O(16)	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
0.1287	0.1287	0.1556	0.1556	-0.412	-0.149	-1.337	-1.301	-1.337	-1.301	-1.572
O(7)	O(8)	O(9)	O(10)	O(11)	O(12)	O(13)	O(14)	O(15)		
-1.572	-1.238	-1.572	-1.572	-1.238	-0.492	-0.492	-0.492	-0.492		
				$Ti_4O_{15}^{16-}$						
	Ti(1,2) ^a	Ti(3,4)		O(1)	O(2,4)	O(3,5)	O(6,7,9,10)	O(8,11)	O(12-15)	
3s	2.00125	2.00278	2s	1.52449	1.77792	1.61202	1.80512	1.64402	1.5590	
4s	0.2972	0.28434	2P _x	1.48951	1.97068	1.92488	1.94752	1.89599	1.60236	
3P _x	2.00022	2.00013	2P _y	1.61391	1.90070	1.84829	1.92602	1.95730	1.74057	
3P _y	1.99990	1.99982	2P _z	1.68843	1.83793	1.88930	1.94261	1.74988	1.61068	
3P _z	1.99984	1.99955								
3d ₀	0.45026	0.61993								
3d + 1	0.69711	1.16321								
3d - 1	0.77687	0.24397								
3d + 2	0.80065	0.78121								
3d - 2	0.69432	0.75263								
Total charge (a.u.)										
Ti(1)	Ti(2)	Ti(3)	Ti(4)	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	O(7)
0.2824	0.2824	0.1524	0.1524	-0.316	-1.487	-1.275	-1.487	-1.274	-1.621	-1.621
O(8)	O(9)	O(10)	O(11)	O(12)	O(13)	O(14)	O(15)			
-1.247	-1.621	-1.621	-1.247	-0.513	-0.513	-0.513	-0.513			

^a The number in parentheses represents the atoms at the different positions (see Fig. 1), e.g., Ti(1,2) corresponds to the ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) lattice position and Ti(3,4) corresponds to (0, 0, 0).

in more detail in a separate paper. What we can say here is that the covalent effect plays a major role in lowering the formal charge on the Ti because the different calculations, performed by other researchers, give similar results. Therefore, we could not treat the oxygen in the TiO_2 as inert O^{2-} . This conclusion has special meaning in relation to surface reactivity: the TiO_2 surface is more active than that of the pure ionic compound. Experimentally, it is verified that the oxygen ions on the outermost layer can be removed easily by bombardment with Ar ions or electrons. In our calculation, we take the cluster $Ti_4O_{15}^{16-}$ with removal of one bridge oxygen (see Fig. 1e) to represent this situation. The DOS (Fig. 2b) shows that the shapes

of valence and conduction bands are changed but we do not observe the bandgap state as in the literature (10). In fact, this model only represents the slightly destroyed $TiO_2(110)$ surface. If we remove more bridge oxygens, we do observe the bandgap state. This case corresponds to the heavily destroyed $TiO_2(110)$ surface. Ar⁺ and electron bombardments may already be strong enough to create such a heavily destroyed surface structure. Compared to the DOS of $Ti_4O_{16}^{16-}$, the compositions of the valence and conduction band are similar. This implies that for the slightly reduced surface, the bond nature of Ti-O is still qualitatively the same as that for the ideal surface. The gross orbital population (Table 1) shows that the electron

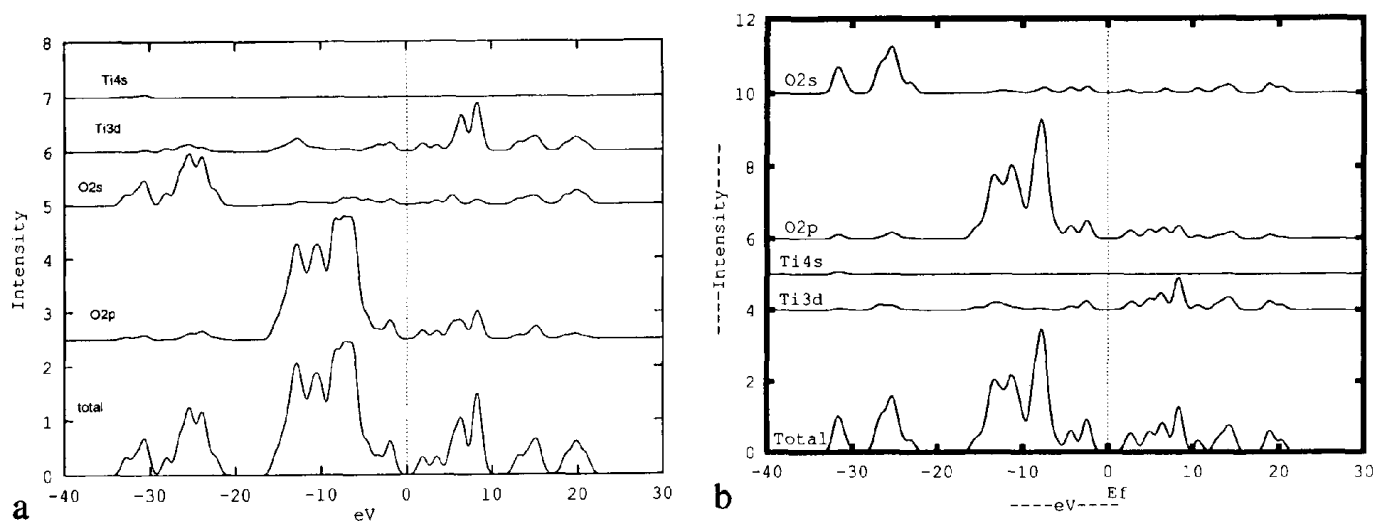


FIG. 2. (a) Density of states for Ti₄O₁₆⁶⁻ cluster; (b) density of states for Ti₄O₁₃⁵⁻ cluster.

density in the *dz* orbital of the Ti that is nearest to the oxygen vacancy is decreased. Therefore, the Ti at this site has a stronger “acceptor” character; that is, its acidity increased. As a result, it is easier for the basic molecule (“donor”) to be adsorbed on this site. This result is different from that of a semiempirical calculation but is consistent with the experimental observation: namely, removal of surface oxygen creates a strong acid site; in other words, it exposes more fully the Ti, which has a high positive charge on the surface. In the following, we demonstrate that Pt adsorption on this position is strong and electrons flow from Pt5*dz* to Ti3*dz*. Consequently, the electron density in Ti3*dz* increased.

3.2. Pt Adsorption on the Ideal TiO₂(rutile)(110) Surface

Experimentally, the existence of the strong interaction between the Pt and the TiO₂ is already verified. However, at the theoretical level, little knowledge about the nature of this bond has been obtained. This is partially due to the extremely long computational times required to deal with such a system. The pioneering work of Horsley (16), using the semiempirical method (Xa-SW-SCF), shows that Pt is preferentially adsorbed on the five fold-coordinated Ti position. However, a Pt/TiO₅⁶⁻ cluster seems too simplified to describe the Pt adsorption on the oxygen-defective surface. In fact, the fivefold-coordinated Ti position also exists on the ideal TiO₂(rutile)(110) surface. According to the XPS result obtained in this laboratory (23), for the ideal surface of the TiO₂(rutile)(110), the Pt is still preferentially adsorbed on the fivefold-coordinated Ti position. Based on these experimental and theoretical results, we take 2Pt/Ti₄O₁₆⁶⁻ (see Fig. 1f) as the calculation model for Pt adsorption on the ideal TiO₂(rutile)(110) sur-

face. The DOS of 2Pt/Ti₄O₁₆⁶⁻ (Fig. 3) shows that the Pt5*d*,6*p*,6*s* orbitals are mixed into the valence band of Ti₄O₁₆⁶⁻. According to the discussion in Section 3.1, the valence band of Ti₄O₁₆⁶⁻ is composed of O2*p* but mixed with Ti3*d*. This means that the charge flows from O2*p* to Pt6*p* and Pt6*s* and from Pt5*d* to Ti3*d* and O2*p* orbitals. From the gross orbital population (Table 2), we can see that the charge density of the Ti(3)3*dz* orbital increases by 0.2 a.u. but on the neighbor Ti(1)3*dz*, it decreases by 0.4 a.u. (compared with that of Ti₄O₁₆⁶⁻); this fact verifies that the charge transfers from the Pt5*dz* orbital to the Ti3*dz* orbital because this process is symmetrically allowed. By the same reasoning, the electron density on Ti(3)3*d*₊₂ and 3*d*₋₂ orbitals decreases from 1.9 to 1.3 a.u.. The decrease in the charge density on Ti(1) may result from the spin

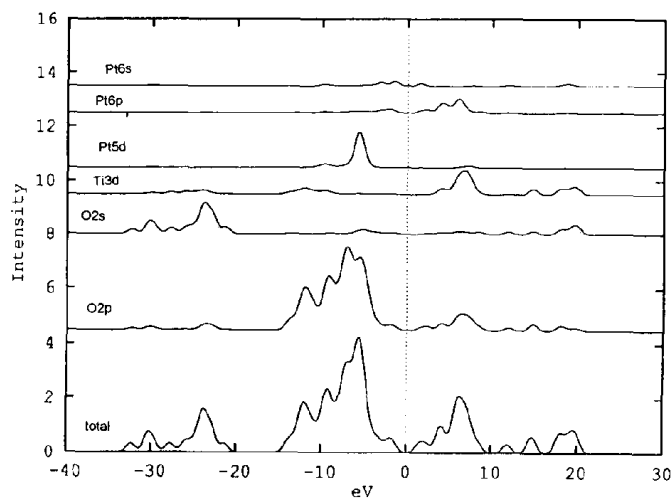


FIG. 3. Density of states for 2Pt/Ti₄O₁₆⁶⁻ cluster.

TABLE 2
The Gross Orbital Population of $2\text{Pt}/\text{Ti}_4\text{O}_{15}^{6-}$

	Ti(1,2) ^a	Ti(3,4)		O(16)	O(1)	O(2,4)	O(3,5)	O(6,7,9,10)	O(8,11)	O(12-15)		
3s	2.00022	1.99987	2s	1.53373	1.57503	1.67095	1.68071	1.66875	1.64646	1.45194		
4s	0.30610	0.30873	2P _x	1.55893	1.60523	1.88898	1.82614	1.89622	1.86360	1.45220		
3P _x	2.00048	2.00047	2P _y	1.21065	1.27301	1.88126	1.88052	1.86477	1.89003	1.75087		
3P _y	2.00042	2.00035	2P _z	1.82537	1.74826	1.68858	1.75173	1.90184	1.78474	1.61813		
3P _z	2.00008	1.99944										
3d ₀	0.74179	0.84999										
3d + 1	0.55994	0.59286										
3d - 1	0.88324	0.49141										
3d + 2	0.86475	0.40704										
3d - 2	0.44098	0.86484										
Pt(1,2)	6s	6P _x	6P _y	6P _z	5d ₀	5d + 1	5d - 1	5d + 2	5d - 2			
	1.67885	0.24030	-0.03818	0.65303	1.80468	1.73869	1.79944	1.98345	1.99906			
Free Pt (1S) ⁰	0.0	0.0	0.0	0.0	2.0	2.0	2.0	2.0	2.0	2.0		
Total charge (a.u.)												
Ti(1)	Ti(2)	Ti(3)	Ti(4)	O(16)	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	O(7)	O(8)
0.202	0.202	0.485	0.485	-0.129	-0.202	-1.130	-1.139	-1.130	-1.140	-1.331	-1.331	-1.185
O(9)	O(10)	O(11)	O(12)	O(13)	O(14)	O(15)	Pt(1)	Pt(2)				
-1.331	-1.331	-1.185	-0.273	-0.273	-0.273	-0.273	-1.859	-1.859				

^a The number in parentheses represents the atoms at the different positions (see Fig. 1), e.g., Ti(1,2) corresponds to the ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) lattice position and Ti(3,4) corresponds to (0, 0, 0).

repulsion of the Ti(3). From the charge distribution on the Pt, we can see that it is true that the charge flows from the Pt5d orbital to the Ti3d and O2p orbitals and from the O2p orbitals to the Pt6s,6p orbitals. The net charge on the Pt depends on the relative extent of two interactions. In our case, the charge transfer from O2p to Pt6s,6p takes a predominant role in this process. Therefore, the Pt is negatively charged. The optimized bond

length (defined as the distance between the Pt and the nearest Ti) is 2.24 Å. This value is approximately equal to the sum of the Pt covalent radius and the average of the Ti⁴⁺ ionic radius and the Ti covalent radius (2.38 Å). This fact tells us that the bond between the Pt and the TiO₂ is a covalent and ionic mixture. The bond energy is calculated to be 16.5 eV. This bond strength could not be described well by considering only the interactions

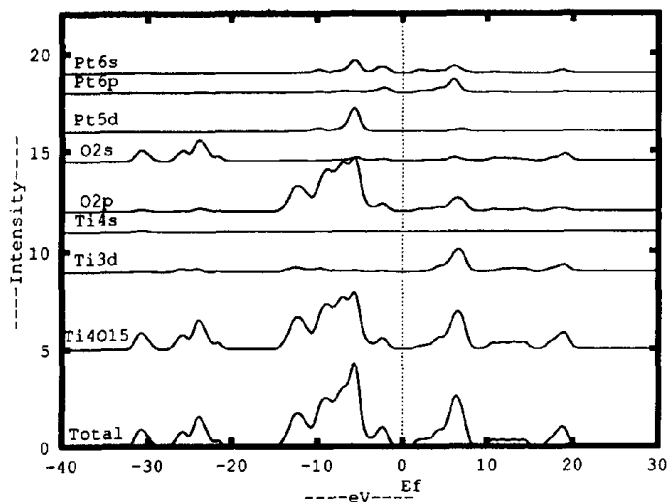


FIG. 4. Density of states for $2\text{Pt}/\text{Ti}_4\text{O}_{15}^{6-}$ cluster.

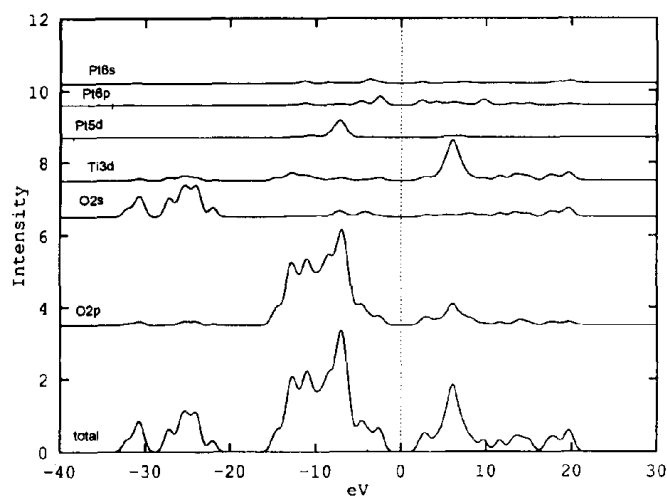


FIG. 5. Density of states for $\text{Pt}/\text{Ti}_4\text{O}_{15}^{6-}$ cluster.

TABLE 3
The Gross Orbital Population of 2Pt/Ti₄O₁₆⁶⁻ and Pt/Ti₄O₁₆⁶⁻

	Ti(1,2) ^a	Ti(3,4)		O(1)	O(2,4)	O(3,5)	O(6,7,9,10)	O(8,11)	O(12-15)		
3s	2.00012	1.99972	2s	1.59126	1.76528	1.60935	1.65757	1.64047	1.49391		
4s	0.30087	0.30716	2P _x	1.48964	1.85493	1.84707	1.91001	1.86270	1.46584		
3P _x	2.00045	2.00039	2P _y	1.61126	1.93322	1.85193	1.87109	1.93767	1.73954		
3P _y	1.99997	2.00044	2P _z	1.71387	1.68389	1.84182	1.90609	1.80136	1.50245		
3P _z	1.99993	1.99943									
3d0	0.67903	0.83895									
3d + 1	0.50646	0.57169									
3d - 1	0.80982	0.48458									
3d + 2	0.90271	0.38797									
3d - 2	0.40116	0.91518									
Pt(1,2):	6s	6P _x	6P _y	6P _z	5d0	5d + 1	5d - 1	5d + 2	5d - 2		
	1.59149	0.25606	0.12335	0.75757	1.77829	1.68422	1.80024	1.97767	1.99937		
Free Pt(1S ⁰):	0.0	0.0	0.0	0.0	2.0	2.0	2.0	2.0	2.0		
Total charge (a.u.)											
Ti(1)	Ti(2)	Ti(3)	Ti(4)	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	O(7)	O(8)
0.399	0.399	0.495	0.495	-0.406	-1.237	-1.150	-1.237	-1.150	-1.345	-1.345	-1.242
O(9)	O(10)	O(11)	O(12)	O(13)	O(14)	O(15)	Pt(1)	Pt(2)			
-1.345	-1.345	-1.242	-0.202	-0.202	-0.202	-2.202	-1.968	-1.968			
	Ti(1,2) ^a	Ti(3,4)		O(1)	O(2,4)	O(3,5)	O(6,7,9,10)	O(8,11)	O(12-15)		
3s	1.99987	2.00036	2s	1.50952	1.69201	1.64997	1.79236	1.61312	1.49248		
4s	0.31088	0.29396	2P _x	1.53381	1.86667	1.86523	1.93802	1.89091	1.34140		
3P _x	1.99978	2.00035	2P _y	1.56861	1.87321	1.91309	1.90033	1.95519	1.80291		
3P _y	2.00029	1.99968	2P _z	1.70161	1.80750	1.85542	1.89534	1.74979	1.66961		
3P _z	1.99935	1.99979									
3d0	0.59522	0.72899									
3d + 1	0.48349	0.56768									
3d - 1	0.879117	0.38381									
3d + 2	0.84537	0.81578									
3d - 2	0.37993	0.82384									
Pt(ad.):	6s	6P _x	6P _y	6P _z	5d0	5d + 1	5d - 1	5d + 2	5d - 2		
	1.31766	0.98999	0.37973	0.59129	1.80785	1.85768	1.86791	1.95198	1.91320		
Free Pt: (1S ⁰)	0.0	0.0	0.0	0.0	2.0	2.0	2.0	2.0	2.0		
Total charge (a.u.)											
Ti(1)	Ti(2)	Ti(3)	Ti(4)	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	O(7)	O(8)
0.507	0.507	0.386	0.386	-0.313	-1.239	-1.284	-1.239	-1.284	-1.526	-1.526	-1.209
O(9)	O(10)	O(11)	O(12)	O(13)	O(14)	O(15)	Pt				
-1.526	-1.526	-1.209	-0.306	-0.306	-0.306	-0.306	-2.677				

^a The number in parentheses represents the atoms at different positions (see Fig. 1). e.g., Ti(1,2) corresponds to the ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) lattice position and Ti(3,4) corresponds to (0, 0, 0).

between the Pt6p,6s and O2p orbitals and those between Pt5d and Ti3d orbitals because the overlap between these orbitals is not so large (see Fig. 3); therefore, the interaction between the Pt5d and O2p orbitals must be taken into account. From the DOS of 2Pt/Ti₄O₁₆⁶⁻ (see Fig. 3), we can see that the overlapping between the Pt5d and O2p orbitals is very large. This kind of interaction certainly makes a contribution to bond formation because,

according to the discussion in Section 3.1, the O2p shell is not fully filled in Ti₄O₁₆⁶⁻; therefore the electrons flow from the Pt5d to the O2p orbitals. The gross orbital population analysis in Table 2 gives support to this conclusion, that is, the electron density in the Pt5d orbital decreases, compared to that in the free Pt. (It is established that the most stable spectroscopic state of the Pt atom is the 3D³ state (5d⁹6s¹). In our discussion, we will take 1S⁰(5d¹⁰)

as the reference state (24).) Our conclusion here is different from that in the literature (16). From the gross orbital population analysis given in Table 2, there is a strong repulsion between Pt_{py} and the bridge oxygen. This means that the adsorption of Pt on the surface will make the bridge oxygen vacancy stabilized.

3.3 Pt Adsorption on the Slightly Oxygen Defective $Ti_4O_2(\text{Rutile})(110)$ Surfaces

In practice, the interaction between the Pt and the TiO_2 is very complicated because little detailed information has been obtained about the geometry of the oxygen defects on the surface. Here we consider only two simple situations: the first is to take the model $2Pt/Ti_4O_{16}^{16-}$ but with removal of the bridge oxygen (see Fig. 1g) and the second is to take $Ti_4O_{15}^{16-}$ but with the Pt positioned upon the bridge oxygen vacancy (see Fig. 1h). The DOS of $2Pt/Ti_4O_{15}^{16-}$ (Fig. 4) shows that, compared to $2Pt/Ti_4O_{16}^{16-}$ (Fig. 3), the $Pt6s$ has high density located in the $O2p$ band. This means that the $Pt6s$ orbital should get more electrons from the $O2p$ orbital. However, from the gross orbital population (Tables 2 and 3), we found that the electron density decreases in the $Pt6s$ orbital (from 1.67885 a.u. for $2Pt/Ti_4O_{16}^{16-}$ to 1.59149 a.u. for $2Pt/Ti_4O_{15}^{16-}$) but increases in the $Pt6p$ orbital (from 0.85515 a.u. for $2Pt/Ti_4O_{16}^{16-}$ to 1.13698 a.u. for $2Pt/Ti_4O_{15}^{16-}$). The reason may be that the strong repulsion from the same sign charge makes more electrons occupy the $Pt6p$ rather than the $Pt6s$ orbitals. According to the discussion in Section 3.2, the strong repulsion between the $Pt6py$ orbital and the bridge oxygen $2p$ orbital does not now exist; so, this effect also increases the electron densities in the $Pt6p$ orbital. As can be seen from Table 3, electron densities in the $Pt5d$ orbitals decrease from 9.3 a.u. ($2Pt/Ti_4O_{16}^{16-}$) to 9.2 a.u.; this means that a little more electron density flows from the $Pt5d$ orbital to the $Ti3d$ and $O2p$ orbitals. Due to the opposite effects of charge repulsion between Pt and O and the orbital overlapping in the bond formation between $2Pt$ and $Ti_4O_{15}^{16-}$, the net result is that there is no effect on the bond strength. The binding energy and the optimized bond length are the same as that in the $2Pt/Ti_4O_{16}^{16-}$ case.

Now, we consider the second model, in which the Pt is directly positioned upon the bridge oxygen vacancy (see Fig. 1h). The DOS of $Pt/Ti_4O_{15}^{16-}$ (see Fig. 5) shows that, compared to that in $2Pt/Ti_4O_{15}^{16-}$ (Fig. 1g), the $Pt5d$ band is shifted by ca. 1.5 eV to lower energy. As a consequence, electron density in the $Pt5d$ orbital increases from 9.2 ($2Pt/Ti_4O_{15}^{16-}$) to 9.5 a.u. (for free $Pt(1S^0)$, the electron population of $Pt5d$ orbital is 10 a.u.). This means that the ability of the $Pt5d$ orbitals to bond with $O2p$ and $Ti3d$ orbitals decreases and they behave more like nonbonding orbitals. According to the discussion in Section 3.1, re-

moval of the bridge oxygen increases the positive charge on the Ti(1) position (see Table 1). Therefore, the $Pt5d$ band shift results from the decrease in the charge repulsion. From the DOS of $Pt/Ti_4O_{15}^{16-}$ (Fig. 5), we also notice that the $Pt6p$ density in the valence band increases. Correspondingly, the electron density in the $Pt6p$ orbital increases from 1.1 a.u. ($2Pt/Ti_4O_{15}^{16-}$) to 2.0 a.u. (see Table 3). This means that the contribution from overlap between the $Pt6p$ and $O2p$ orbitals to the metal-support bond increases. However, this increase in overlap between the $Pt6p$ and $O2p$ orbital, does not compensate for the decrease in the contribution from overlap between the $Pt5d$ and the $O2p$ and $Ti3d$ orbitals; thus, the optimized bond length (2.37 Å) is longer but the bond energy (23.0 eV) is still larger than that in $2Pt/Ti_4O_{15}^{16-}$ or $2Pt/Ti_4O_{16}^{16-}$. The reason is that, in $Pt/Ti_4O_{15}^{16-}$, the "bond number" is different from that in $2Pt/Ti_4O_{15}^{16-}$. According to our calculated result, it is obvious that the Pt preferentially occupy the oxygen vacant site on the $TiO_2(\text{rutile})(110)$ surface.

4. CONCLUSION

According to the calculation, the interaction between the Pt and the TiO_2 is very strong and overlap between the $Pt5d$ and $O2p$ orbitals also makes a certain contribution to the Pt- TiO_2 bond formation. The bond energy for the Pt is larger at the oxygen defect site than at the normal site on the $TiO_2(\text{rutile})$ surface.

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