

# Identifying an O<sub>2</sub> Supply Pathway in CO Oxidation on Au/TiO<sub>2</sub>(110): A Density Functional Theory Study on the Intrinsic Role of Water

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**Abstract:** Au catalysis has been one of the hottest topics in chemistry in the last 10 years or so. How O<sub>2</sub> is supplied and what role water plays in CO oxidation are the two challenging issues in the field at the moment. In this study, using density functional theory we show that these two issues are in fact related to each other. The following observations are revealed: (i) water that can dissociate readily into OH groups can facilitate O<sub>2</sub> adsorption on TiO<sub>2</sub>; (ii) the effect of OH group on the O<sub>2</sub> adsorption is surprisingly long-ranged; and (iii) O<sub>2</sub> can also diffuse along the channel of Ti (5c) atoms on TiO<sub>2</sub>(110), and this may well be the rate-limiting step for the CO oxidation. We provide direct evidence that O<sub>2</sub> is supplied by O<sub>2</sub> adsorption on TiO<sub>2</sub> in the presence of OH and can diffuse to the interface of Au/TiO<sub>2</sub> to participate in CO oxidation. Furthermore, the physical origin of the water effects on Au catalysis has been identified by electronic structure analyses: There is a charge transfer from TiO<sub>2</sub> in the presence of OH to O<sub>2</sub>, and the O<sub>2</sub> adsorption energy depends linearly on the O<sub>2</sub> charge. These results are of importance to understand water effects in general in heterogeneous catalysis.

## 1. Introduction

Since the pioneering work of Haruta, Au clusters supported by oxides (Au/oxides) have perhaps become the most interesting systems in heterogeneous catalysis because of their unique catalytic properties at low temperatures for many reactions. In particular, they are excellent catalysts for removing CO, i.e., CO oxidation, which is important to industries.<sup>1–11</sup> Therefore, to obtain insight into CO oxidation on Au/oxides is of great importance. In addition, water molecules inevitably exist in any real catalytic system, and have been found that to have a significant effect on the chemistry of many systems. Thus, to gain the physical origin of water effect on CO oxidation on Au/oxides is not only essential to obtain a comprehensive understanding of the reaction, but also fundamental in heterogeneous catalysis in general.

Scientifically, Au/oxides are very interesting: neither inert gold nor oxides, individually, are good catalysts for CO

oxidation, but a combination of the two, Au/oxides, will produce an excellent catalyst.<sup>12–21</sup> There have been extensive studies on Au/TiO<sub>2</sub> both experimentally and theoretically due to their important application in industries, and scientific interests and also their simplicities as models for theoretical investigations. The CO oxidation mechanism has been long concerned, and the general consensuses in this field are the following:<sup>1–11,22–30</sup> (i) CO can adsorb on dispersed gold clusters; (ii) Molecular oxygen can directly participate in reactions; and (iii) The reaction occurs at the interface between Au and TiO<sub>2</sub>. However,

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there is evidence that  $O_2$  cannot adsorb on the perfect  $TiO_2$  surface and the possibility of  $O_2$  adsorption on the gold cluster should not be high either because of the very low adsorption energy.<sup>25,31</sup> Therefore, the  $O_2$  adsorption and supply is still unclear.

Recently, there have been several studies, which showed some evidence that  $O_2$  can adsorb at the interface of  $Au/TiO_2(110)$ . From DFT calculations on a two-layer gold strip on the  $TiO_2(110)$  surface, Liu et al.<sup>31,32</sup> found that  $O_2$  can adsorb at the  $Au/TiO_2(110)$  interface with an adsorption energy of 0.8 eV. Adsorbed  $O_2$  reacts with CO adsorbed on the gold with a very low reaction barrier, 0.1 eV. Molina, Rasmussen, and Hammer<sup>33,34</sup> also studied  $O_2$  adsorption and CO oxidation at the interface, employing a gold rod on  $TiO_2(110)$ . They found that  $O_2$  cannot adsorb on a perfect  $TiO_2(110)$  surface without gold cluster. But  $O_2$  adsorption is reasonably strong on the  $Au/TiO_2$  interface. They also found that the reaction barrier for CO oxidation is very low (0.15 eV). More recently, using a gold cluster of 10 atoms supported on  $TiO_2(110)$ , Remediakis, Lopez, and Nørskov<sup>35,36</sup> also reported that  $O_2$  can adsorb at the  $Au/TiO_2$  interface and the CO oxidation reaction can proceed with a low barrier (about 0.4 eV).

However, the total area of the  $Au/TiO_2(110)$  interface in a typical system is very limited, and thus the probability of direct  $O_2$  adsorption at the  $Au/TiO_2(110)$  interface is expected to be low, considering the fact that adsorption events are random. Although the barrier of CO oxidation at the  $Au/TiO_2$  interface is very low, the reaction rate will also be low if  $O_2$  adsorption is poor. In UHV, some experiments show that very high  $O_2$  exposures or exposures to atomic O can avoid the low sticking probability for  $O_2$ .<sup>30,37–42</sup> But CO oxidation usually happens without high  $O_2$  exposures or atomic O. Recently, Libuda, and Freund<sup>43,44</sup> emphasized the important role of a capture zone. This is an area in the support at which reactants can adsorb. It was suggested that  $O_2$  adsorbs at the capture zone and it is then supplied to the reaction center. Thus, turnover frequencies (TOF) may depend on  $O_2$  adsorption at the capture zone and  $O_2$  supply to the reaction center. Experimentally, it was found that gold clusters supported on reducible oxides are more active than irreducible oxides.<sup>1–3,45</sup> Behm and co-worker<sup>45,46</sup> suggested that the main difference among the supports may lie in their ability to supply  $O_2$  during the CO oxidation:  $O_2$  can adsorb on the reducible oxide supports from where  $O_2$  is supplied to the

reaction center, while the irreducible oxide supports do not have the ability to supply  $O_2$ . These important experimental results indicate that  $O_2$  adsorption and supply play an important role in CO oxidation.

Using scanning tunneling microscopy (STM), Besenbacher and co-workers showed that  $O_2$  can adsorb and diffuse on  $TiO_2(110)$ .<sup>47,48</sup> They suggested that oxygen vacancies can facilitate  $O_2$  adsorption on  $TiO_2$  and hence to enhance the rate of oxidation reaction.<sup>49</sup> On the other hand, some studies have shown that oxygen vacancies can be healed under oxidation conditions.<sup>50,51</sup> Furthermore, Rasmussen, Molina and Hammer reported that  $O_2$  can strongly bind at vacancies, and once adsorbed diffusion away from the vacancy is hindered by large barriers.<sup>52</sup> If vacancies are healed,  $O_2$  would not adsorb on the  $TiO_2$  surface.<sup>50</sup> Therefore, one of the greatest puzzles in the field is: Where does  $O_2$  come from for the reaction at the  $Au/TiO_2(110)$  interface? Considering that the CO oxidation possesses a very low barrier, the  $O_2$  supply may well be the bottleneck for the whole process.

Regarding water effects on CO oxidation, moisture certainly exists in any real system. There have been extensive experimental studies, which showed that water plays an important role in CO oxidation.<sup>53,54</sup> For example, Haruta and co-workers<sup>55,56</sup> systematically studied the effect of moisture on CO oxidation on different oxide supports; they suggested that the water effect on the different oxide supports depended on the nature of support. Although water is very important for CO oxidation, theoretical studies on the water effect are rare.

There is a great desire to clarify the basic role of water in  $Au/TiO_2$  systems at the atomic scale. In this paper, we present the first density functional theory (DFT) study on the water effect on both adsorption and diffusion of  $O_2$  on  $TiO_2(110)$ , which we believe is the key step in CO oxidation in these systems. We aim to address the following questions: (i) Where is the  $O_2$  reservoir for CO oxidation on  $Au/TiO_2(110)$ ? (ii) Does water facilitate  $O_2$  adsorption on the surface? (iii) If the answer is yes, how can we understand the water effect? (iv) Can  $O_2$  diffuse to the active interfacial region?

This work is organized as follows. Calculation details will be present in the next section. At the beginning of section 3, we first check the possibility of  $O_2$  adsorption on the perfect  $TiO_2(110)$  surface and the surface with vacancies. Then, we discuss  $O_2$  adsorption on  $TiO_2(110)$  in the presence of OH. Both long range effect and coverage effect of OH will be fully explored. The physical origin of  $O_2$  adsorption on  $TiO_2(110)$  in the presence of OH will also be analyzed. In the last part of

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section 3, the general rule for the water effect on the different oxide (reducible and irreducible) supports will be discussed. Finally, conclusions are summarized in section 4.

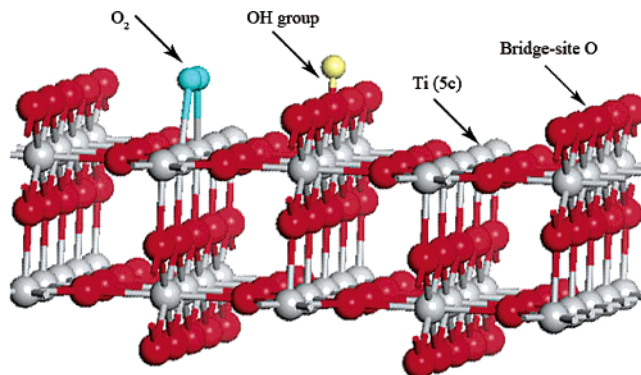
## 2. Calculations

All of the calculations were performed using the DFT with a localized basis set, as implemented in the SIESTA code.<sup>57</sup> The electron exchange-correlation is described by the GGA-PBE functional.<sup>58</sup> Spin polarization is included whenever necessary. Troullier–Martins norm-conserving scalar relativistic pseudopotentials<sup>59</sup> were used. The semi-core states (3s, 3p) for Ti were treated explicitly. A double- $\zeta$  plus polarization (DZP) basis set was employed. The energy cutoff for the real space grid used to represent the density was 160 Ry. The localization radii of the basis functions were determined from an energy-shift of 0.01 eV. Monkhorst Pack meshes of  $(2 \times 2 \times 1)$  and  $(4 \times 1 \times 1)$  k-point sampling in the surface Brillouin zone were used for  $p(2 \times 4)$  and  $p(1 \times 8)$  unit cell, respectively. Transition states (TSs) of the catalytic reactions were searched by constraining the distance between the reactants and relaxing all the others degrees of freedom, the so-called constrained minimization techniques. The TS was verified when (i) all forces on atoms vanish; and (ii) the total energy is a maximum along the reaction coordinate but a minimum with respect to the rest of the degrees of freedom.<sup>60,61</sup>

The TiO<sub>2</sub>(110) surface is modeled by a large unit cell,  $p(2 \times 4)$ , except they are specified. The oxide slab contains 6 layers (32 units of TiO<sub>2</sub> per slab), and there is a more than 15 Å vacuum between the slabs. The bottom two layers are fixed, and all other atoms are fully relaxed as in our previous studies.<sup>32,62</sup> The convergence with respect to the number of layers was checked by calculating the diffusion barrier using 9 layers (48 units of TiO<sub>2</sub> per slab). There are many studies dealing with the water interaction with TiO<sub>2</sub> surfaces.<sup>63–66</sup> Besenbacher and co-workers found that water can readily dissociate at oxygen vacancies on TiO<sub>2</sub> to form two OH groups, and that the hydroxyl group prefers to sit at the bridge-site oxygen vacancy.<sup>64</sup> On the basis of this result, we replace one of the bridge-site O atoms with an OH group to simulate the effect of water dissociation at the O vacancy. This is equivalent to placing a H atom on a perfect TiO<sub>2</sub>(110) (hereafter referred as OH groups on TiO<sub>2</sub>(110)). In our previous work, the accuracy of the calculation method and model was fully checked, especially for the calculation of reaction barrier in heterogeneous catalysis.<sup>24,31,67–68</sup>

## 3. Results and Discussion

**3.1. O<sub>2</sub> Adsorption on the Perfect TiO<sub>2</sub>(110).** As discussed in the Introduction, O<sub>2</sub> adsorption and supply are very important steps for CO oxidation. Thus, it is necessary to know where O<sub>2</sub> can adsorb on TiO<sub>2</sub>(110) and how O<sub>2</sub> is supplied. To investigate the capture zone for O<sub>2</sub> adsorption and supply, we first checked whether O<sub>2</sub> can bind on the perfect TiO<sub>2</sub>(110). We tried many different initial geometries for O<sub>2</sub> adsorption on the TiO<sub>2</sub> surface. After geometry optimization, we found that O<sub>2</sub> desorbs from the TiO<sub>2</sub> surface for all the geometries we tried, indicating that



**Figure 1.** Side view of O<sub>2</sub> adsorption on TiO<sub>2</sub>(110),  $p(2 \times 4)$ , in the presence of one OH group. The bridge-site O atom, Ti (5c) atom, OH group and the adsorbed O<sub>2</sub> are labeled, respectively. The most stable configuration of O<sub>2</sub> adsorption on the TiO<sub>2</sub> in the presence of OH group is also shown.

O<sub>2</sub> cannot chemisorb on the perfect TiO<sub>2</sub>(110), consistent with other experiments and theoretical calculations.<sup>29,33</sup> This means that the perfect TiO<sub>2</sub>(110) surface cannot be the O<sub>2</sub> capture zone and supply O<sub>2</sub> for CO oxidation.

**3.2. O<sub>2</sub> Adsorption on TiO<sub>2</sub>(110) with O Vacancies.** On a real TiO<sub>2</sub>(110) surface, there should always be some bridge-site oxygen vacancies, and it was suggested that such oxygen vacancies can help O<sub>2</sub> adsorption.<sup>47,48</sup> To investigate whether adsorbed O<sub>2</sub> can be supplied to the interface for CO oxidation, we first calculated O<sub>2</sub> adsorption on an O vacancy. The results show that O<sub>2</sub> can strongly bind on the O vacancy on TiO<sub>2</sub>(110). The calculated adsorption energy (2.33 eV) is in good agreement with other result (2.3 eV).<sup>52</sup> However, such adsorbed O<sub>2</sub> cannot diffuse away from the vacancy.<sup>52</sup> In other words, although the defected TiO<sub>2</sub>(110) surface may catch some O<sub>2</sub>, such a surface still cannot supply adsorbed O<sub>2</sub> to the interface for CO oxidation. We also calculated O<sub>2</sub> adsorption in the vicinity of the O vacancy, and the adsorption energy (1.72 eV) is obviously lower than that of O<sub>2</sub> adsorption on the vacancy (2.33 eV). Hence O<sub>2</sub> is more liable to adsorb on the O vacancy. It is interesting to find that if an O<sub>2</sub> binds on the vacancy, further O<sub>2</sub> adsorption on the TiO<sub>2</sub>(110) is not possible. Therefore, the O<sub>2</sub> supply for CO oxidation would not be possible in the system.

**3.3. O<sub>2</sub> Adsorption on TiO<sub>2</sub>(110) in the Presence of OH.** In any catalytic systems, some water molecules always exist. It is widely accepted that water can readily dissociate on TiO<sub>2</sub> at oxygen vacancies to form OH groups.<sup>64</sup> This means that in order to understand the water effect, one must study OH groups on Au/TiO<sub>2</sub>. In the following subsections, we will show our calculated results of O<sub>2</sub> adsorption and diffusion on TiO<sub>2</sub>(110) in the presence of OH.

**3.3.1. O<sub>2</sub> Adsorption on TiO<sub>2</sub>(110) in the Presence of Low Coverage of OH.** Experiments show that a trace of water can greatly improve the catalytic property of Au/TiO<sub>2</sub>(110).<sup>55</sup> Under such conditions, the concentration of OH groups should not be high. Thus, we first concentrated on the adsorption of O<sub>2</sub> on TiO<sub>2</sub>(110) at low OH coverage (1/8 ML, which is in fact 1/8 ML of H on the perfect TiO<sub>2</sub>(110) as mentioned above). Many possible geometries of O<sub>2</sub> adsorption were calculated. The most stable configuration is that O<sub>2</sub> sits over two Ti (5c) atoms near the OH group, as shown in Figure 1. The adsorption energy of this geometry is 0.8 eV and the bond length (1.32 Å) of adsorbed O<sub>2</sub> is significantly longer than in the gas phase (1.24 Å). The TiO<sub>2</sub>(110) surface also experiences a considerably large relax-

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**Table 1.** Calculated Adsorption Energies with Different Distances between O<sub>2</sub> and OH Using P(1×8) Unit Cell

distances (Å)	3.32	4.93	7.48	10.22
adsorption energies (eV)	0.82	0.69	0.65	0.62

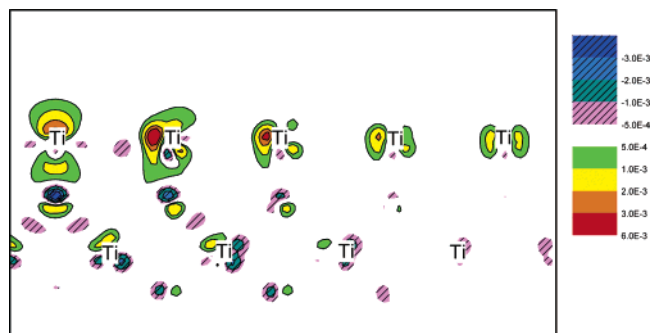
ation: the two surface Ti (5c) atoms bound to O<sub>2</sub> are pushed up by 0.07 Å from the surface due to the formation of new Ti–O bonds. Furthermore, O<sub>2</sub> can also adsorb over a single surface Ti (5c) atom. The surface Ti (5c) extrudes even more (0.28 Å) from the surface. The adsorption energy of this geometry with an OH group nearby is 0.6 eV, which is only slightly lower than the most stable one (Figure 1a, 0.8 eV). These results clearly show that the OH group can facilitate O<sub>2</sub> adsorption on TiO<sub>2</sub>(110), which is important for the O<sub>2</sub> supply.

**3.3.2. Long-Range Effect of OH on O<sub>2</sub> Adsorption.** We have showed in the last section that O<sub>2</sub> can adsorb on TiO<sub>2</sub>(110) if there is a OH group nearby. If the O<sub>2</sub> supply indeed originates from the O<sub>2</sub> adsorption on TiO<sub>2</sub>(110), then the following two questions must be answered: (i) Is the OH effect on O<sub>2</sub> adsorption long-ranged? (ii) How does O<sub>2</sub> diffuse on TiO<sub>2</sub>? The first question is addressed in this section and the second one in section 3.4.

The reason to consider whether the OH effect on O<sub>2</sub> adsorption is long-ranged is the following. If the OH effect is short-ranged (i.e., O<sub>2</sub> can only adsorb near the OH group) and the OH coverage is low, O<sub>2</sub> would readily desorb to the gas-phase once the O<sub>2</sub> diffuses away from the OH group. This would result in a very limited O<sub>2</sub> supply for CO oxidation. On the other hand, the O<sub>2</sub> diffusion to the reaction site (interface regions) on TiO<sub>2</sub>(110) in the presence of OH may be possible if the OH effect is long-ranged.

To further examine the effect of the OH group, we investigated how far the OH group can stabilize the O<sub>2</sub> adsorption on Ti (5c) atoms of TiO<sub>2</sub>(110). We employed a rather long unit cell,  $p(1 \times 8)$ , and O<sub>2</sub> was placed on several sites with different distances from the OH group. Table 1 shows calculated adsorption energies of O<sub>2</sub> on all the sites. It is intriguing that all the surface Ti (5c) atoms become active: O<sub>2</sub> can adsorb on the surface Ti (5c) atoms even with a distance over 10 Å; the adsorption energy of O<sub>2</sub> with an O<sub>2</sub>–OH distance of 10.22 Å is only 0.2 eV lower than that with an O<sub>2</sub>–OH distance of 3.32 Å. It is obvious that the change of distance between the O<sub>2</sub> and the OH does not significantly affect the adsorption energy of O<sub>2</sub>. The major change of O<sub>2</sub> adsorption energy occurs actually from the distance of 3.32 Å to 4.93 Å, being 0.12 eV. After that, the increase of the distance between the O<sub>2</sub> and the OH has little effect on the adsorption energies. This result clearly demonstrates that the OH group on TiO<sub>2</sub>(110) possesses a long-range effect on O<sub>2</sub> adsorption. As we will show in the next section, the adsorbed O<sub>2</sub> on the surface in the presence of OH can diffuse along the Ti (5c) atoms on TiO<sub>2</sub>(110).

**3.3.3. Physical Origin of O<sub>2</sub> Adsorption in the Presence of OH.** O<sub>2</sub> adsorption on the Au/TiO<sub>2</sub>(110) interface has been the topics in several recent studies. Liu et al.<sup>31</sup> found that TiO<sub>2</sub>(110) support enhances electron transfer from gold to the adsorbed O<sub>2</sub>, which results in the ionic bonding between the O<sub>2</sub> and the metal cation (Ti, Au). Molina, Rasmussen, and Hammer<sup>33</sup> suggested that the existence of excess charge at the Au/TiO<sub>2</sub>(110) interface is essential for the O<sub>2</sub> adsorption. The question is: what is the physical origin of the O<sub>2</sub> adsorption on TiO<sub>2</sub>(110) in the presence of OH?



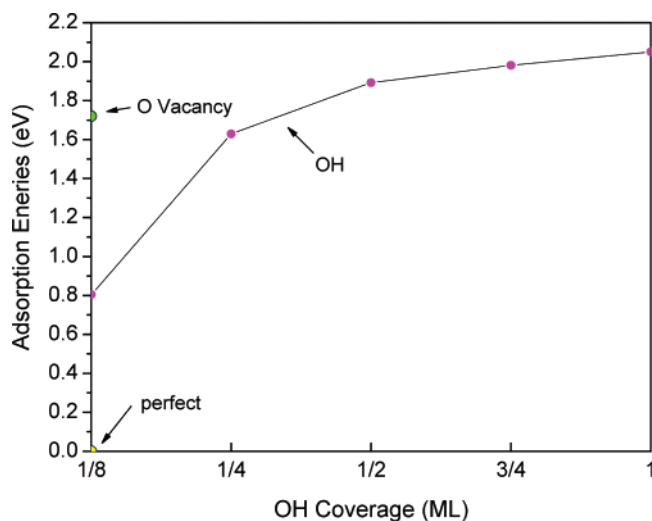
**Figure 2.** Electronic density difference contour plots showing the electronic redistribution on the plane perpendicular to the surface, cutting along Ti (5c) atoms. The electronic density difference is defined in the text. A long unit cell,  $p(1 \times 8)$ , is used in the calculation and only half unit cell is shown in the figure. The first Ti (5c) atom on the left is the nearest to the OH group on the TiO<sub>2</sub>(110).

To understand the origin of OH group effect on O<sub>2</sub> adsorption, we calculated the electronic density difference:  $\rho(H/TiO_2) - \rho(H) - \rho(TiO_2)$ , where  $\rho(H/TiO_2)$ ,  $\rho(H)$  and  $\rho(TiO_2)$  are the total electronic densities of H/TiO<sub>2</sub>, isolated H atom, and a clean TiO<sub>2</sub> surface, respectively. Figure 2 shows a plane of electronic density difference cutting perpendicularly to the surface along Ti (5c) atoms. It can be seen that the excess electrons as a result of reduction by H are not localized but spread over all the surface Ti (5c) atoms. It is obvious that the excess electrons on the Ti (5c) atoms decrease slowly from the left (the nearest to the OH group) to the right. The main changes occurs between the position of the nearest to the OH group and the next nearest. By analyses of density of states (DOS), we found that the excess electrons occupy the bottom of the original conduction band of clean TiO<sub>2</sub> surface. Our calculations also show that upon O<sub>2</sub> adsorption on the Ti (5c) atoms of TiO<sub>2</sub>(110), the excess electrons will be transferred from the Ti (5c) atoms to the O<sub>2</sub>, filling to O<sub>2</sub> 2 $\pi$  orbitals and resulting in an ionic bonding between the O<sub>2</sub> and the Ti (5c) atoms. These results are consistent with recent experiments,<sup>69</sup> which show that the electrons associated with OH groups are delocalized across the TiO<sub>2</sub> surface, and O<sub>2</sub> can reversibly abstract such electrons from the shallow trapping states. These results will be further supported by Mulliken population analyses, which will be discussed later.

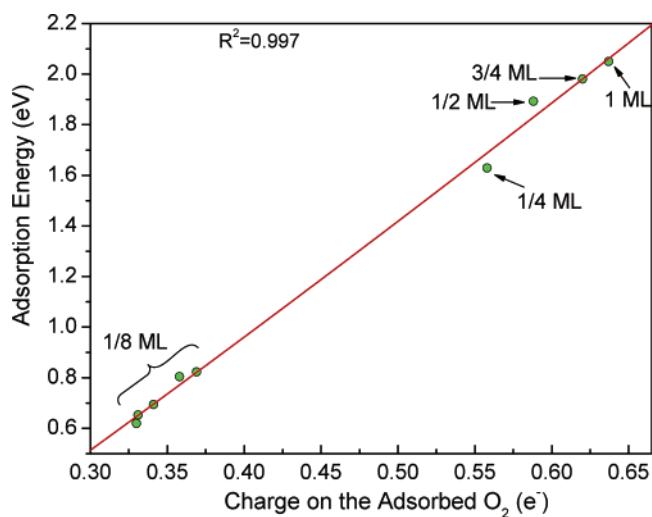
**3.3.4. Coverage Effect of OH.** It is obvious that the coverage of OH group is strongly related to the water concentration in the reaction system. Experimentally, it has been found that the water concentration can dramatically affect the reactivity of Au/TiO<sub>2</sub>(110).<sup>55</sup> It is, therefore, crucial to further investigate whether and how the coverage of OH group influences O<sub>2</sub> adsorption.

To address this issue, we calculated the adsorption energies of O<sub>2</sub> at different coverages (1/8 ~ 1 ML) of OH group. The result is plotted in Figure 3. At low coverages (1/8 ~ 1/4 ML), it is evident from the figure that the O<sub>2</sub> adsorption energy changes considerably with the concentration of OH group: It increases almost by a factor of 2 from the 1/8 ML to 1/4 ML. Interestingly, at the coverage of 1/8 ML the magnetic moment of O<sub>2</sub> is 1.0  $\mu_B$ , and it completely disappears at the coverage of 1/4 ML. Above the coverage of 1/4 ML, the adsorption energy still increases but quite slowly. These results suggest that the

(69) Szczepankiewicz, S. H.; John, A. M.; Hoffmann M. R. *J. Phys. Chem.* **2002**, *106*, 7654.



**Figure 3.** Calculated O<sub>2</sub> adsorption energies with respect to the OH coverages. For comparison, the O<sub>2</sub> adsorption energies on the perfect surface and in the vicinity of the O vacancy are also showed.



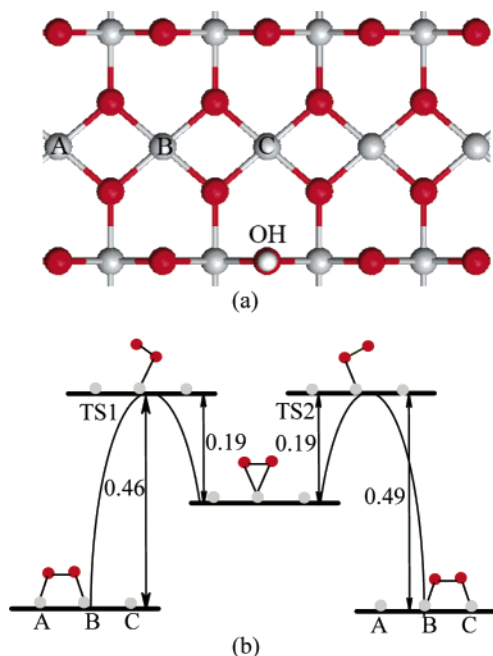
**Figure 4.** Calculated adsorption energies with respect to the charge on O<sub>2</sub>. The charge is calculated by the difference of Mulliken population between the adsorbed O<sub>2</sub> and the gas-phase one. At OH coverage of 1/8 ML, the data for different sites are shown in Table 1.

coverage of OH greatly affects the O<sub>2</sub> adsorption on TiO<sub>2</sub>(110): With the increase of the OH coverage, the O<sub>2</sub> adsorption energy on TiO<sub>2</sub>(110) is considerably enhanced. It is interesting to compare O<sub>2</sub> adsorption on different TiO<sub>2</sub>(110) surfaces at this stage. As mentioned before, O<sub>2</sub> cannot chemisorb on the perfect TiO<sub>2</sub>(110), but it can adsorb on TiO<sub>2</sub>(110) in the vicinity of an oxygen vacancy with the chemisorption energy of 2.33 eV. However, the O<sub>2</sub> is more likely to diffuse to the oxygen vacancy to bind on the defect, while OH groups will block oxygen vacancies but allow O<sub>2</sub> adsorption on TiO<sub>2</sub>(110).

### 3.3.5. Physical Origin of Long Range and Coverage Effect.

To reveal the physical origin of the long range and the coverage effects of OH, Mulliken population analyses have been carried out on the adsorbed O<sub>2</sub>. The charge on the adsorbed O<sub>2</sub> is calculated by the difference of Mulliken population between the adsorbed O<sub>2</sub> and the free one. All results are showed in Figure 4.

It can be seen that all the points at the coverage of 1/8 ML with different OH–O<sub>2</sub> distances center at the left low corner.



**Figure 5.** (a) A top view of the TiO<sub>2</sub>(110) surface in the presence of an OH group. (b) The energy profiles and geometries of O<sub>2</sub> diffusion along the Ti (5c) atoms from the side A–B to B–C side. The red circles represent oxygen atoms and the gray surface Ti (5c) atom and the white H atom.

The charge difference is only 0.07 e<sup>−</sup> over the whole distance range. The largest change of charge on the O<sub>2</sub> (0.04 e<sup>−</sup>) occurs when the O<sub>2</sub> is on the sites of the nearest and next nearest to OH group. The small charge differences on all the sites at 1/8 ML are consistent with the fact that the adsorption energies changes little with the distance between the OH and O<sub>2</sub>. When the OH coverage increases from 1/8 ML to 1/4 ML, the charge on the O<sub>2</sub> is considerably enhanced, which corresponds to a significant increase of adsorption energy. Beyond the coverage of 1/4 ML, the charge on the O<sub>2</sub> changes much slowly. For example, the charge difference between the 3/4 and 1 ML is only 0.02 e<sup>−</sup>. Perhaps most importantly, Figure 3 reveals a striking correlation between the charge on the adsorbed O<sub>2</sub> and the adsorption energy, irrespective of the distance of OH–O<sub>2</sub> and the OH coverage. It shows that the magnitude of electronic transfer from the surface Ti (5c) atoms to the O<sub>2</sub> determines the O<sub>2</sub> adsorption energy.

**3.4. O<sub>2</sub> Diffusion and Supply in the Presence of OH.** It is clear from the above results that the presence of OH on TiO<sub>2</sub>(110) can significantly increase O<sub>2</sub> adsorption. Now we address the OH effect on the O<sub>2</sub> adsorption in the context to CO oxidation. As mentioned above, CO oxidation reaction occurs at the interface of Au/TiO<sub>2</sub>. It is crucial to have enough O<sub>2</sub> at the interface, which may be supplied by direct O<sub>2</sub> adsorption from the gas phase at the interface. However, the possibility of this event is not high as stated in the Introduction. One may suggest that the adsorbed O<sub>2</sub> in the presence of OH may diffuse to the interface. To investigate this possibility, we thoroughly studied whether O<sub>2</sub> can diffuse on TiO<sub>2</sub>(110). Several possible O<sub>2</sub> diffusion pathways have been tried and the pathway with the lowest energy is illustrated in Figure 5. Figure 5, parts a and b, shows our calculated sites, geometries and energy profiles of O<sub>2</sub> diffusion.

For clarity, we only present how O<sub>2</sub> diffuses from sites A–B to B–C. The structure with the O<sub>2</sub> on sites A–B is considered

as the initial state of the adsorbed  $O_2$  diffusion. If the Ti–O bond at site A breaks, then leading to the transition state (TS1) with a barrier of 0.46 eV. After this step, the adsorbed  $O_2$  sits at site B. Then, if the right side Ti–O bond breaks, the dangling O atom may bond with the Ti (5c) atom at site C. This step possesses a barrier of 0.19 eV.<sup>70</sup> Repeating these two steps gives rise to the adsorbed  $O_2$  diffusion. It is clear that the adsorbed  $O_2$  in the presence of OH can diffuse readily along the Ti (5c) channel, which may be considered as an  $O_2$  supply to the interface, which we believe is very crucial to CO oxidation on Au/TiO<sub>2</sub>.

**3.5. General Discussion of the Intrinsic Effect of Water on Different Au/oxides.** Recently, Bongiorno and Landman<sup>71</sup> studied the water effect on Au/MgO using DFT calculations and they revealed a very interesting finding: Water molecules can facilitate  $O_2$  adsorption on the gold cluster by forming a complex with  $O_2$ . It is known that MgO is an irreducible oxide. Experimentally, it has been found that water can improve the TOF of CO oxidation in the systems of Au clusters supported by both irreducible and reducible oxides.<sup>55,56</sup> However, the Au clusters supported by reducible oxides appears to be far superior to the systems with irreducible oxides.<sup>45,55</sup> TiO<sub>2</sub> is one of these irreducible oxides and hence it is worth comparing MgO and TiO<sub>2</sub>.

As for the MgO support, the  $O_2$  adsorption energy on the Au/MgO interface is not high and the  $O_2$  adsorption mainly depends on the formation of CO– $O_2$  complex at the interface.<sup>72,73</sup> Therefore, the rate-limiting step in the systems with such irreducible oxides may be  $O_2$  adsorption. As for the TiO<sub>2</sub> support, on the other hand,  $O_2$  can strongly bind on the Au/oxide interface. The adsorbed  $O_2$  itself is rather active, and the reaction barrier is rather low. The rate-limiting step may well be the  $O_2$  supply in the whole CO oxidation process. For such a reducible oxide support, it is not necessary for water to promote the  $O_2$  adsorption at the Au/oxide interface and to activate the adsorbed  $O_2$  to react with CO. On the contrary, the ability of supply  $O_2$  from the capture zone of the oxide support to the reaction center may be the most important.

## 4. Conclusions

In summary, this study represents one of the systematical investigations on the important role of water on the Au/TiO<sub>2</sub>-(110) catalyst by DFT calculations. We have provided direct evidence that OH groups play a key role in  $O_2$  adsorption on TiO<sub>2</sub>(110). A deeper understanding of water effect on CO oxidation on Au/oxides has been obtained. The key findings are summarized as follows:

(1) Both the perfect TiO<sub>2</sub>(110) and the surface with O vacancies cannot supply  $O_2$ :  $O_2$  cannot adsorb on the perfect surface;  $O_2$  cannot further adsorb on the surface once  $O_2$  binds on the O vacancies.

(2)  $O_2$  can adsorb on TiO<sub>2</sub>(110) in the presence of OH even at low OH coverages. The adsorption geometry is quite flexible: there are several  $O_2$  adsorption geometries and the optimal one that  $O_2$  binds with two Ti (5c) atoms is only about 0.2 eV more stable than others.

(3) OH groups possess a long-range effect on  $O_2$  adsorption on TiO<sub>2</sub>(110). With the increase of the distance between the  $O_2$  and OH, the  $O_2$  adsorption energy does not considerably change. On the other hand, the  $O_2$  adsorption is significantly affected by the coverage of OH.

(4) The long range and coverage effects of OH on  $O_2$  adsorption have been analyzed and the physical origin of these effects have been identified: (i) OH groups donate some electrons to TiO<sub>2</sub>(110); (ii) the excess electrons are delocalized among Ti (5c) atoms; and (iii) there is a charge transfer from Ti (5c) atoms to  $O_2$  upon  $O_2$  adsorption. The magnitude of the electronic transfer determines the  $O_2$  adsorption energy.

(5) We have also identified, for the first time, the  $O_2$  supply pathway for CO oxidation on Au/TiO<sub>2</sub>(110), perhaps the bottleneck in the reaction: The adsorbed  $O_2$  can readily diffuse along the surface Ti (5c) atoms in the presence of OH, which is a large reservoir of  $O_2$  for CO oxidation on the interface of Au/TiO<sub>2</sub>.

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(70) The convergence of number of layers of TiO<sub>2</sub> was tested: The barrier of 9 layers TiO<sub>2</sub> is 0.14 eV.

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