The Influence of the Oxygen Vacancies on the Pt/TiO₂ Single-atom Catalyst – a DFT Study

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Abstract

The titanium dioxide (TiO_2) surface is suitable as a substrate for single-atom catalysts (SACs). As a common defect on TiO_2 , oxygen vacancies may have a significant impact on the adsorption and activity of the adatoms. This work aims to investigate whether titanium dioxide containing surface oxygen vacancies is more suitable as a base material for SACs. This paper calculates the changes in the adsorption energy of Pt atom and the energy of the d-band center on the perfect surface and the surface containing oxygen vacancies. Concerning the perfect surface, the surface containing oxygen vacancies fixes the Pt atom more firmly, and increases the center energy of the d-band of Pt, thereby improving the performance of Pt atom as SACs. Consequently, the (110) surface of Rutile TiO_2 with oxygen vacancies may be the best substrate for SACs.

1. Introduction

Oxygen reduction reaction (ORR) plays a vital role in various energy conversion and storage systems (such as fuel cells and metal-air batteries), and understanding which electronic factors are involved in the oxygen reduction reaction is a top priority. With the advent of single-atom catalysts (SACs), using a single metal atom to promote chemical reactions has become a more efficient method. The interaction between the substrate (holding materials) and the active metal atoms may have a significant impact on the catalytic activity of the metal. On one hand, to obtain a stable contact, the adsorption energy of the metal atom on the substrate needs to be high. On the other hand, the influence of the substrate on the electronic structure of the metal needs to be taken into account. Hammer and Nørskov^[1-3] proposed the d-band center theory, which claims that the adsorption energy of the molecule is mainly determined by the occupancy rate of the bonding and anti-bonding states formed by the hybridization of the d-state electrons wave function of the adsorbate and the substrate. If the anti-bonding state lies below the Fermi level (E_F), the interaction between the adsorbate and the metal surface will become repulsive, resulting in weak chemical adsorption. This situation can be well characterized by the position of the d-band center of the metal. The downshift of the d-band center will lead to stronger chemisorption. In addition, Stamenkovic et al.^[4] found that ORR activity is correlated with the d-band center of the platinum crystal. As the center of the d-band moves away from the E_F , the observed ORR activity of Pt is higher. Lu et al.^[5] also observed a strong correlation between the d-band center and oxygen adsorption energy on the surface of various single-crystal metals, which is consistent with the d-band center model.

TiO_2 is considered to be an excellent substrate for loading noble metal atoms as catalysts. FB Li et al.^[6] used Pt/ TiO_2 catalyst to improve photodegradation efficiency. The TiO_2 /Pt catalysts in the ORR reaction of proton exchange membrane fuel cells (PEMFCs) have been studied by Mirshekari G R and Rice C A^[7]. In order to improve the utilization of noble metal atoms, scattered Pt/ TiO_2 catalyst and single-atom Pt/ TiO_2 catalyst are growing. For scattered Pt loaded on TiO_2 , Humphrey N presents a multi-scale modeling study of atomically dispersed Pt on the (110) surface of Rutile TiO_2 , probing the dynamic evolution of the catalytic surface at elevated temperatures.^[8] Tianyi Wang et al. calculated the different

transition metals' d-band centers of single atom loaded on the perfect (001) surface and (101) surface of Anatase TiO₂^[9], including Pt single atom, and obtained the relationship between the different adsorption energies and the center of the d-band center, it is believed that the (001) and (101) faces of Anatase TiO₂ are suitable for single-atom catalyst substrates. Therefore, the study of Anatase and Rutile TiO₂ as a single-atom catalyst substrate is important.

Besides, the surface defects of the substrate usually have a great influence on the adsorption energy and the center of the d-band. Oxygen vacancies in metal are of great importance in the structural evolution of active center in single-atom catalysts (SACs)^[10]. Among the various defects in TiO₂, oxygen vacancy is the most common one due to its low formation energy. However, the oxygen vacancies rich surface is more likely to affect the d-band center and further affect the ORR performance^[11–13]. Therefore, it is necessary to explore the influence of oxygen vacancies of the TiO₂ substrates on the d-band center.

In this study, we systematically calculated the adsorption energy of the single Pt adatom on the (001) and (101) surface of Anatase TiO₂ and (100), (011), (110) surface of Rutile TiO₂ in the presence of oxygen vacancy, and the d-band center of the Pt adatoms by Density functional theory(DFT) method. The calculation results show that the (110) surface of Rutile TiO₂ with oxygen vacancies has a better balance between the adsorption energy and the center of the d-band among the five common surfaces calculated, and is more suitable for SACs.

2. Computational Method

We used the DFT method by Vienna Initio Simulation Package (VASP) to calculate the single-point energy and spin polarization geometry calculations and used GGA to process the corrected Perdew-Burke Ernzerhof (RPBE) electronic correlation function. Grimme's zero-damping DFT-D3 method is used to consider van der Waals interaction. The cutoff energy for geometric optimization and self-consistent calculation is set to 520eV, and the K point is selected as 3×3×1.

For the adatom-TiO₂ system, a single Pt atom is adsorbed on the (2×2) supercell of Anatase TiO₂ (001) (101) surface and (2×2) supercell of Rutile TiO₂ (100),(011),(101) surface. A vacuum space of 15Å is applied in the vertical direction to eliminate non-physical interactions between adjacent images. All geometric structures were optimized until the residual force is less than -0.001 eV /Å.

The interaction between Pt atom and TiO₂ surface is described as average adsorption energy (E(ads)). The calculation formula is defined as $E(\text{ads}) = E(\text{Pt}+\text{TiO}_2) - E(\text{TiO}_2) - E(\text{Pt})$, where $E(\text{Pt}+\text{TiO}_2)$ is the total energy after adsorption of Pt atom, $E(\text{TiO}_2)$ is the energy of the TiO₂ surface without Pt atom, $E(\text{Pt})$ is the energy of a single platinum atom. $E(\text{ads})$ is usually calculated to check the adsorption stability, and a negative value indicates exothermic adsorption^[14, 15]. The greater the negative value of $E(\text{ads})$, the more stable the system should be. Therefore, negative $E(\text{ads})$ means that the single metal can be stably fixed on TiO₂. In addition, the calculation formula of cohesive energy $E(\text{coh})$ is defined as $E(\text{coh}) = E(\text{metal}) -$

E(single), where E(metal) and E(single) represent the total energy derived from bulk Pt metals and single Pt metal.

3. Computational Models

The adsorption positions of single atoms or clusters on the perfect surface have existing research. Tianyi Wang et al.^[9] constructed the models for the adsorption of transition metal atoms on Anatase's (001) (101) perfect surface. The computational models of Pt atom on Anatase TiO_2 with different designed sites are presented in Fig. 1, which include $\text{Pt-O}_{2\text{C}}$, $\text{O}_{2\text{C}}\text{-Pt-O}_{2\text{C}}$, $\text{Ti}_{5\text{C}}\text{-O}_{2\text{C}}\text{-Pt-O}_{2\text{C}}$ models in Anatase(001), and $\text{Pt-O}_{2\text{C}}$, Pt-dimer of $\text{O}_{2\text{C}}$, Pt-trimer of $\text{O}_{2\text{C}}\text{-O}_{3\text{C}}\text{-O}_{2\text{C}}$ models in Anatase(101). Anatase(001)-a illustrates the Pt atom is adsorbed on the topmost $\text{O}_{2\text{C}}$. Anatase(001)-b presents the Pt atom is adsorbed on the bridge sites of the two edge $\text{O}_{2\text{C}}$ and Anatase(001)-c shows the Pt atom adsorption on two $\text{O}_{2\text{C}}$ with nearest $\text{Ti}_{5\text{C}}$ atom. Anatase(101)-a illustrates Pt atom is adsorbed on the topmost $\text{O}_{2\text{C}}$ which is coordinated with two $\text{Ti}_{5\text{C}}$. Anatase(101)-b presents the dimer of $\text{O}_{2\text{C}}$ with the nearest $\text{Ti}_{5\text{C}}$ atom as the active site to fix the Pt atom. Anatase(101)-c shows the single Pt atom is loaded on the $\text{O}_{2\text{C}}\text{-O}_{3\text{C}}\text{-O}_{2\text{C}}$ trimer. Similarly, considering the possible adsorption sites of Pt atom on Rutile TiO_2 ^[16–19], the computational models of Pt atom on Rutile TiO_2 with different designed sites are presented in Fig. 2. Rutile(100)-a and Rutile(100)-b illustrates the topmost $\text{Ti}_{3\text{C}}$ and $\text{O}_{3\text{C}}$ is the active site to fix the Pt atom. Rutile(011)-a shows the Pt atom is adsorbed on the topmost $\text{Ti}_{3\text{C}}$ site, Rutile(011)-b shows the dimer of $\text{Ti}_{3\text{C}}\text{-O}_{2\text{C}}$ is the active site for the Pt atom. In Rutile(011)-c, the Pt atom is adsorbed on the topmost $\text{O}_{2\text{C}}$ sites. Rutile(110)-a presents the Pt atom are adsorbed on the single topmost $\text{O}_{3\text{C}}$ sites, and Rutile(110)-b presents the Pt atom are adsorbed on the bridge sites of the two nearest neighbor $\text{O}_{3\text{C}}$ atoms.

The stability of SACs largely depends on the adsorption location and oxygen vacancies (V_O). The oxygen vacancies on the surface of TiO_2 not only provide active sites for fixing metal atoms but also affect the catalytic performance. The Anatase(001) and (101) topmost oxygen vacancies computational models have been given by Aiura Y^[18], Gong et al.^[20] and Xue-Qing et al.^[21]. Cheng H et al.^[22], Petrik N G et al.^[23] and Petrik N G et al.^[24] presented the computational models for rutile(100), (011), and (110) surface with topmost oxygen vacancies. Taking into account that the introduction of oxygen vacancies will change the coordination numbers of Ti atoms, the metal atom will be introduced on top sites, bridge sites, and hollow sites near the Ti atom with decreasing coordination numbers or the nearest oxygen atom^[8,20–22], shown in Fig. 3 and Fig. 4. The Pt atom is loaded on the bridge sites of $\text{O}_{3\text{C}}$ which is adjacent to the topmost $\text{O}_{2\text{C}}$, as seen in Anatase(001)(V_O)-a. Anatase(001)(V_O)-b indicates that the Pt atom is still loaded on the topmost $\text{O}_{2\text{C}}$, but the nearest neighbor $\text{Ti}_{5\text{C}}$ of $\text{O}_{2\text{C}}$ has become $\text{Ti}_{4\text{C}}$. Anatase(101)(V_O)-a shows that two $\text{Ti}_{4\text{C}}$ near the oxygen vacancies co-adsorb the single Pt atom. Anatase(101)(V_O)-b shows that Pt atom are adsorbed on the topmost $\text{O}_{1\text{C}}$, but the nearest neighbor $\text{Ti}_{5\text{C}}$ of $\text{O}_{1\text{C}}$ has become $\text{Ti}_{4\text{C}}$ similarly, compared with Anatase(001)(V_O)-b. Unlike the TiO_2 surface of Anatase, the Pt atom on the Rutile surface is more likely adsorbed with Ti atoms with decreasing coordination numbers in Fig. 4. Rutile(100)(V_O)

illustrates the Pt atom loaded on hollow sites of the nearest Ti_{5C} trimer, Rutile(011)(V_O) shows that the Pt atom is fixed on the bridge sites of the two nearest Ti_{2C} atoms. Rutile(110)(V_O)-a shows the Pt atom is fixed on the bridge position of the nearest Ti_{3C} and Ti_{4C} atom, Rutile(110)(V_O)-b presents the Pt atom is adsorbed on the trimer of Ti_{3C} hollow sites.

4. Results And Discussion

We calculated the adsorption energy of all the models above to find the most stable energy in supporting information Table S1, and the models after structural relaxation are given in supporting information Picture 1 and Picture 2. The structure with the lowest adsorption energy after structural relaxation is considered the most stable structure. We calculated the adsorption energy ($E(ads)$) of oxygen vacancies and perfect surfaces for comparison in Fig. 5 and Fig. 6. These models are considered to be the most stable structures. We found that the adsorption energy we calculated always shows the same trends on these surfaces: the adsorption energy of the surface containing oxygen vacancies is significantly higher than that of the perfect surface. It is speculated that the oxygen vacancies change the electronic distribution state of the surrounding Ti atoms, which makes the binding force of Pt and Ti atoms stronger.

The d-band center energy of (001) and (101) surface of Anatase TiO_2 and (100), (011), (110) surface of Rutile TiO_2 have been calculated in supporting information Table S2. We plot the d-band center energy with the most stable adsorption energy on the surface in Fig. 7. We found from Fig. 7 that for the five types of TiO_2 surfaces, the movement of the center energy of the d-band also shows the same trend: for a surface containing oxygen vacancies, the d-band center energy of the Pt atom will be closer to the Fermi level. This shows that the surface containing oxygen vacancies may be more suitable for the substrate of Pt atom than the perfect surface for SACs.

The partial density of states of perfect surface and oxygen vacancies surface of Anatase (001),(101) and Rutile (100), (011), (101) are given in Fig. 8 and Fig. 9. We can see the change of the d-band energy of the Pt on a different surface. For the five types of surfaces, the d-band energy of Pt after introducing oxygen vacancies has increased significantly. At the same time, the energy hybridization between O atoms and Pt atom becomes weak, and the hybridization between Pt atom and Ti atoms increases. The interaction between Pt atom and Ti atoms may be the reason for increasing the d-band energy of Pt atom.

Otherwise, We calculated the d-band center energy of the Pt atom on the Pt metal bulk, which is -2.22eV, consistent with -2.23 eV which was calculated by Tianyi Wang et al.^[8]. We found that the d-band centers of Pt atom on selected TiO_2 surfaces are closer to the Fermi level than the d-band centers of Pt atom on the metal bulk. According to the d-band center theory of transition metals, the Pt atom on the surface containing oxygen vacancies is more conducive to adsorbing other atoms than the Pt atom on the metal bulk. Fig. 10. shows the relationship between the adsorption energy and the center of the d-band of Pt atom on different surfaces. under the line is the perfect surface, above the line is the oxygen vacancies

surface. Compared with the perfect surface, it is much easy to obtain larger adsorption energy or a higher d-band center for the containing oxygen vacancy surface.

Generally, the adsorption energy and cohesive energy were compared to evaluate the thermodynamic stability of SACs. The cohesive energy of Pt is -5.48 eV calculated in our work in supporting information Table S3, consistent with 5.53 eV which was calculated by Philipsen P H T ^[25]. Fig. 11 shows the relationship between adsorption energy and cohesive energy of different TiO₂ surfaces. We found that on the surface of Rutile(110) and Rutile(011) with oxygen vacancies, the adsorption energy of the Pt atom is higher than the cohesive energy of Pt metal. This means that its thermodynamic stability is much better than that of those perfect surfaces whose adsorption energy is much smaller than their cohesive energy which may not be stable enough as SACs except Rutile(110).

5. Conclusion

The calculation shows the effect of oxygen vacancy on the adsorption energy and d-band center energy of Pt atom on the surface of Anatase and Rutile TiO₂. On one hand, the introduction of oxygen vacancies will make the adsorption energy of TiO₂ for a single Pt atom increase, so that Pt atom can be more stably adsorbed on TiO₂. On the other hand, it will also cause the d-band center of the Pt atom toward the Fermi level, which will make it possible to have better catalytic performance. After introducing oxygen vacancies, the increase of adsorption energy makes the adsorption energy on some surfaces higher than the cohesive energy of Pt, which improves the thermodynamic stability of loading Pt atom on TiO₂ as SACs. The calculation results show that the (110) surface of Rutile TiO₂ with oxygen vacancies has a better balance between the adsorption energy and the center of the d-band among the five common surfaces calculated, and is more suitable for SACs.

Declarations

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Availability of data and material:

All data can be requested from the corresponding author.

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Figures

Figure 1

The computational models of a single Pt atom on the perfect surface of Anatase(001) and (101). Ti, O, and Pt are indicated as blue, red, and grey.

Figure 2

The computational models of a single Pt atom on the perfect surface of Rutile(100), (011), and (110). Ti, O, and Pt are indicated as blue, red, and grey.

Figure 3

The computational models of single Pt atom on oxygen vacancies(V_O) surface of Anatase(001) and (101). Ti, O, and Pt are indicated as blue, red, and grey.

Figure 4

The computational models of single Pt atom on oxygen vacancies(V_O) surface of Rutile(100), (011), and(101). Ti, O, and Pt are indicated as blue, red, and grey.

Figure 5

The adsorption energy ($E(\text{ads})$) of the most stable Pt/TiO₂ structure of Anatase(001),(101) and Rutile(100), (011), (101). Ti, O, and Pt are indicated as blue, red, and grey.

Figure 6

The adsorption energy ($E(\text{ads})$) of the most stable Pt/TiO₂ oxygen vacancies structure of Anatase (001), (101) and Rutile (100), (011), (101). Ti, O, and Pt are indicated as blue, red, and grey.

Figure 7

The d-band center energy of single Pt atom on perfect surface and oxygen vacancies surface of Anatase (001), (101) and Rutile (100), (011), (110). Unit is eV.

Figure 8

Partial Density of States of Anatase TiO_2 (001) perfect surface (a) and (101) perfect surface (b), compared with Anatase TiO_2 (001) oxygen vacancies surface (c) and (101) oxygen vacancies surface (d). The energy in the figure has subtracted the Fermi level.

Figure 9

Partial Density of States of Rutile TiO_2 (100) perfect surface(a), (011) perfect surface(b) and (110) perfect surface(c), compared with Rutile TiO_2 (100) oxygen vacancies surface (d), (011) oxygen vacancies surface(e) and (110) oxygen vacancies surface(f). The energy in the figure has subtracted the Fermi level.

Figure 10

The schematic diagram of the d-band center energy and the adsorption energy of the Pt atom on different adsorption surface modes. Surfaces containing oxygen vacancies are represented by V_o .

Figure 11

relationship between adsorption energy and cohesive energy of different surfaces. The red line indicates the cohesive energy ($E(coh)$) of Pt. Surfaces containing oxygen vacancies are represented by V_o .

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