Prediction of Structural and Electronic Properties of C and Cl\textsubscript{2} Adsorbed on the Rutile TiO\textsubscript{2} (110) Surface

Fan Yang, Liangying Wen,*, Qin Peng, Yan Zhao, Shengfu Zhang,*, and Zhongqing Yang

ABSTRACT: The study of the adsorption mechanism of C and Cl\textsubscript{2} on the TiO\textsubscript{2} (110) surface is of great significance for the formulation of the technological parameters in the fluidized chlorination process. Based on the first-principles calculations of density functional theory, the co-adsorption models of C and Cl\textsubscript{2} on the rutile TiO\textsubscript{2} (110) surface under different ratios were established. The adsorption structure, adsorption energy, charge density, and density of states were calculated and analyzed to reveal the reaction mechanism of C and Cl\textsubscript{2} adsorbed on the rutile TiO\textsubscript{2} (110) surface under different ratios. The results showed that with the increase of the ratio of C atoms in the reaction process, the complete adsorption possibility of Cl atoms on the surface of TiO\textsubscript{2} (110) increased. Both Ti\textsubscript{6c} and C atoms were electron providers, while O\textsubscript{3c} and O\textsubscript{2c} were electron acceptors. The bonding interactions between C and O\textsubscript{2c} or C and Cl atoms were stronger, and the stabilities were higher. When C bonded with O\textsubscript{2c} and two Cl atoms, respectively, the overlapping peak width of C and O\textsubscript{2c} atoms was greater at the high energy level, and the electron delocalization was enhanced, and more electrons were transferred around the two Cl atoms. When C bonded with O\textsubscript{2c} and one Cl atom, respectively, the electron activity at the low energy level was higher, and the stability of the chemical bond was lower.

1. INTRODUCTION
Titanium dioxide has been widely used in the production of high-quality white paint because it can prolong the paint service life and increase the brightness of paint color. The fluidized chlorination has become an important method to produce titanium dioxide in the industry because of its low waste discharge and high production efficiency. C can promote the adsorption of Cl\textsubscript{2} on the surface of TiO\textsubscript{2}. In the actual chlorination reaction, C is usually added in the form of petroleum coke, which is called carbochlorination. In the fluidized chlorination process, titanium oxide and petroleum coke solid particles are suspended in chlorine gas atmosphere and there are adsorption reaction occurrences. The materials in the fluidized state have the characteristics of accelerating the mass and heat transfer of the gas–solid phase and enhancing the production. At present, it has become the main technology of titanium dioxide production enterprises in the world. The density functional theory has been used to explore the microscopic mechanism of the chlorination reaction of rutile TiO\textsubscript{2} (110) in fluidized chlorination from the atomic point of view. In recent years, many scholars have studied the adsorption behavior of different gas molecules and solid-phase particles on the surface of rutile TiO\textsubscript{2} (110). Wen et al. studied the adsorption behavior of C\textsubscript{4} and Cl\textsubscript{3} on the TiO\textsubscript{2} (110) surface and found that the C\textsubscript{4} cluster could promote the Cl\textsubscript{2} molecule to dissociate into two Cl atoms. Wei et al. studied the adsorption behavior of H\textsubscript{2}S on the TiO\textsubscript{2} (110) surface and found that the adsorption behavior of H\textsubscript{2}S on the surface of rutile TiO\textsubscript{2} (110) was closely related to its coverage. When all of the bridge oxygen vacancies were covered by H\textsubscript{2}S molecules, the maximum degree of spontaneous dissociation of H\textsubscript{2}S could be achieved. Although many scholars have studied the adsorption behavior of different gas molecules and solid-phase particles on the surface of rutile TiO\textsubscript{2} (110), the co-adsorption reaction of C and Cl\textsubscript{2} on the surface of TiO\textsubscript{2} (110) has been rarely reported. In the process of fluidized chlorination, the excess of Cl\textsubscript{2} is inevitable. Therefore, to explore the reaction mechanism of fluidized chlorination, it is of great significance to study the co-adsorption behavior of C and Cl\textsubscript{2} on the TiO\textsubscript{2} (110) surface under different ratios.

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In this work, the TiO$_2$ (110) surface of rutile was studied, and the first-principles calculations method of density functional theory was used to predict the adsorption structures and the electronic properties of C and Cl$_2$ adsorbed on the TiO$_2$ (110) surface under different ratios. Through the analysis of adsorption structure, adsorption energy, charge density, and density of states, the adsorption mechanism and reaction behavior of C and Cl$_2$ adsorbed on the surface of TiO$_2$ (110) under three different ratios were explored, providing a deeper theoretical basis for the further study of the reaction process of carbochlorination of TiO$_2$.

2. RESULTS AND DISCUSSION

2.1. Structure Analysis. When the Cl$_2$ molecule is adsorbed on the TiO$_2$ (110) surface, there is no obvious interaction between the Cl$_2$ molecule and the TiO$_2$ (110) surface. When C atom is adsorbed on TiO$_2$ (110) surface alone, C bonds with the O atom on the surface. Figure 1 shows the structures formed by C and Cl$_2$ adsorbed on the surface of TiO$_2$ (110) with the ratio of 1:2. One Cl$_2$ molecule is dissociated in the structure of Figure 1a. After dissociation, two Cl atoms form bonds with C atom, and the bond length of C−Cl is 1.689 Å. C forms a C−O$_2$c(r) double bond with the surface O$_2$c(r), and the bond length is 1.265 Å. Other adsorption structures have a similar dissociation phenomenon of the Cl$_2$ molecule. In the structure of Figure 1c, the C atom takes O$_2$c(r) off the adsorption surface and forms the CO molecule, and the length of the chemical triple bond formed between C and O$_2$c(r) is 1.171 Å.

When C and Cl$_2$ are adsorbed on the surface of TiO$_2$ (110) with the ratio of 1:2, only one Cl$_2$ molecule is dissociated, and the two Cl atoms after dissociation are adsorbed on the surface of TiO$_2$ (110) together with C atom, forming three adsorption structures such as a, b, and c. In Figure 1, the adsorption energies of structures a, b, and c are −8.452, −8.402, and −8.478 eV, respectively, and the adsorption processes are all chemisorption, showing that the structural stability of two Cl atoms bonding with Ti atoms is relatively higher, followed by the structural stability of two Cl atoms bonding with C atoms, and the structural stability of two Cl atoms bonding with Ti and C atoms is relatively lower.

Figure 2 shows the structures formed by C and Cl$_2$ adsorbed on the surface of TiO$_2$ (110) with a ratio of 2:2. The two Cl$_2$ molecules in Figure 2d are all dissociated into Cl atoms, and the dissociated Cl atoms are all bonded with C atoms, and the bond lengths are 1.694, 1.694, 1.693, and 1.693 Å, respectively. Both C atoms form C−O$_2$c bonds with O$_2$c on both sides, and the bond length is 1.271 Å. After bonding with C atom, the O$_2$c on both sides are obviously raised from the surface, and the distances moved up are 0.477 and 0.476 Å, respectively. Other adsorption structures have a similar adsorption phenomenon of C and Cl$_2$ molecules on the TiO$_2$ (110) surface. In the structure of Figure 2f, after C atoms bond with O$_2$c on both sides, O$_2$c is taken away from the surface and the CO molecule is formed and separated from the surface.

When C and Cl$_2$ are adsorbed on the surface of TiO$_2$ (110) with the ratio of 2:2, it is possible for the Cl$_2$ molecules to be completely adsorbed. Compared with Figure 1, with the increase of the C content, the possibility of Cl$_2$ molecule dissociation and bonding with the adsorption surface increases, indicating that the increased ratio of C can promote the dissociation of the Cl$_2$ molecule, and it is conducive to the complete adsorption of Cl$_2$ on the surface of TiO$_2$ (110) and improves the reaction degree of the adsorption process. In Figure 2, the adsorption energies of d, e, f, and g are −16.449, −16.051, −14.698, and −13.901 eV, respectively. The adsorption energies of structures d and e are all less than those of structures f and g, indicating that the stability of the adsorption structure formed by the dissociation of two Cl$_2$ molecules is higher than that formed by the dissociation of a single Cl$_2$ molecule.

Figure 3 shows the structures formed by C and Cl$_2$ adsorbed on the surface of TiO$_2$ (110) with the ratio of 2:3. The Cl$_2$ molecules in the structure of Figure 4h are all dissociated into
Cl atoms, and then some Cl atoms are recombined to form Cl₂ molecules. Finally, two Cl atoms are adsorbed on the surface of TiO₂ (110), and four Cl atoms are recombined to form two Cl₂ molecules. The distance between Cl atoms in the original Cl₂ molecules is extended to 4.643, 4.772, and 4.324 Å, respectively. The two Cl atoms that are not involved in the recombination after dissociation form bonds with the C atoms on both sides, with bond lengths of 1.771 and 1.760 Å, respectively. C atoms form C–O₂c bonds with O₂c on both sides, with bond lengths of 1.301 and 1.299 Å, respectively. In Figure 3, other adsorption structures have a similar adsorption phenomenon of C and Cl₂ molecules on the TiO₂ (110) surface. In the structure of Figure 3i, the CO molecule is formed and separated from the surface, resulting in a decrease of the coordination number of Ti6c(m) on the right side of the surface.

When C and Cl₂ are adsorbed on the surface of TiO₂ (110) with the ratio of 2:3, the Cl₂ molecules are completely dissociated. However, Cl atoms after dissociation are not completely adsorbed on the surface of TiO₂ (110), and there is a phenomenon that new Cl₂ molecules sometimes are reformed. In other words, when the adsorption reaction between C and Cl₂ occurs with the ratio of 2:3, the Cl₂ molecules are more easily dissociated, but the adsorption rate is relatively lower. Compared with Figures 1 and 2, it can be seen that with the increase in the ratio of C atom in the reaction process, the possibility of complete adsorption of the Cl atom on the TiO₂ (110) surface increases. In Figure 3, the adsorption energies of h, i, and j are −13.949, −14.651, and −17.943 eV, respectively. The adsorption processes are all chemisorption. The adsorption energy of structure j is lower than that of structures h and i, indicating that the adsorption structure with the C-Cl bond and the Ti5c-Cl bond is more stable.

According to the analysis, when the ratio of C and Cl₂ is 1:2, the structures formed are of low stabilities. Therefore, in the actual process of fluidized chlorination, the reaction of C and Cl₂ under the ratio of 1:2 is more conducive to the process of fluidized chlorination.

### 2.2. Charge Analysis

Table 1 shows the charge density analysis of C and Cl₂ adsorbed on the TiO₂ (110) surface with the ratios of 1:2 and 2:2, where a, b, and c correspond to the structures of a, b, and c in Figure 1, respectively, and d, e, f, and g correspond to the structures of d, e, f, and g in Figure 2, respectively. In Table 1, the charge transfers of atoms and molecules such as Ti6c(m), O3c(r), O2c(r), C, C*, Cl₂, and

Table 1. Mulliken Charge Analysis of C and Cl₂ Adsorbed on the TiO₂ (110) Surface with the Ratio of 1:2 and 2:2

|   | a     | b     | c     | d     | e     | f     | g     |
|---|-------|-------|-------|-------|-------|-------|-------|
| Ti6c(m) | q(e)  | 10.72 | 10.68 | 10.72 | 10.73 | 10.67 | 10.73 | 1.30  |
| Δq(e) | 1.28  | 1.32  | 1.28  | 1.27  | 1.33  | 1.27  | 1.30  |       |
| O3c(r) | q(e)  | 6.71  | 6.68  | 6.66  | 6.70  | 6.66  | 6.67  | 6.70  |
| Δq(e) | −0.71 | −0.68 | −0.66 | −0.70 | −0.66 | −0.67 | −0.70 |       |
| O2c(r) | q(e)  | 6.51  | 6.55  | 6.47  | 6.52  | 6.55  | 6.47  | 6.57  |
| Δq(e) | −0.51 | −0.55 | −0.47 | −0.52 | −0.55 | −0.47 | −0.57 |       |
| C     | q(e)  | 3.87  | 3.88  | 3.53  | 3.90  | 3.88  | 3.54  | 3.91  |
| Δq(e) | 0.13  | 0.12  | 0.47  | 0.10  | 0.12  | 0.46  | 0.09  |       |
| C*    | q(e)  | 3.90  | 3.89  | 3.54  | 3.91  |       |       |       |
| Δq(e) | 0.10  | 0.11  | 0.46  | 0.09  |       |       |       |       |
| Cl₂   | q(e)  | 13.78 | 14.18 | 14.41 | 13.82 | 14.16 | 14.48 | 14.00 |
| Δq(e) | 0.22  | −0.18 | −0.41 | 0.18  | −0.16 | −0.48 | 0.00  |       |
| Cl₂*  | q(e)  | 14.00 | 14.01 | 14.00 | 13.82 | 14.11 | 13.99 | 13.98 |
| Δq(e) | 0.00  | −0.01 | 0.00  | 0.18  | −0.11 | 0.01  | 0.02  |       |

*a*O₃c(r) and O₂c(r) are O₃c and O₂c atoms located on the right side after the reaction, respectively. C* is the C atom located on the left side after the reaction. Cl₂ and Cl₂* in the adsorption structures correspond to the marks in Figures 1 and 2, respectively. q(e) is the total amounts of electrons, and Δq(e) are the amounts of electrons gain and loss after the reaction.
Table 2 shows the charge density analysis of C and Cl2 adsorbed on the TiO2 (110) surface with the ratio of 2:3, from the surface of TiO2 (110) to form the CO molecule, \( \sum \text{Cl}_2 \) obtains more electrons.

2.3. Analysis of Difference Charge Density. Figure 4 shows the difference charge density maps for the adsorption structures of C and Cl2 on the surface of TiO2 (110) with the ratio of 1:2. The blue region and yellow regions represent the electron-accumulated region and the electron-depleted region, respectively. The yellow region around the C atom is more obvious, indicating that the C atoms lose some electrons in the adsorption process. The structures of b and c both contain Ti5c–Cl bonds, and the surrounding areas of these bonds are electron-accumulated regions, indicating that there is an obvious interaction between Ti5c and Cl after adsorption.

Figure 5 shows the difference charge density maps for the adsorption structures of C and Cl2 on the surface of TiO2 (110) with the ratio of 2:2. The yellow regions around C and C* atoms are more obvious, indicating that both C and C* atoms lose electrons in the adsorption process. Electron accumulation is found around the Cl atoms bonded with Ti5c in the structures of e and f, indicating that the Cl atoms have obvious interaction with the TiO2 (110) surface.

Figure 6 shows the difference charge density maps for the adsorption structures of C and Cl2 on the surface of TiO2 (110) with a ratio of 2:3. The yellow regions around C and C* atoms are more obvious, indicating that both C and C* atoms lose electrons in the adsorption process. In Figure 6j, the blue regions around the Ti5c–Cl and C–Cl bonds in the structures are the electron-accumulated regions, and the blue region around the Ti5c–Cl bond is larger, indicating that more electrons gather here and the interaction between Ti5c and Cl atoms is stronger.

2.4. Density of State Analysis. Figure 7 shows the partial density of states of C atom and O2c when C and Cl2 adsorbed on the surface of TiO2 (110) with different ratios, where a, b, d, and g correspond to the structures a and b in Figure 1 and structures d and g in Figure 2, respectively, and h and j correspond to the structures h and j in Figure 3, respectively. In the co-adsorption process of C and Cl2 on the TiO2 (110) surface, C and O2c(r) will form bonds. In most adsorption structures, the C atom will form a C–O bond with the Cl atom, and then an adsorption structure containing the O2c(r)–C–Cl bond will be formed. Therefore, it is of great significance to study the density of states of C–O2c(r) and C–Cl bonds in the adsorption process of C and Cl2 on the TiO2 (110) surface. In the structures of a, d, and j, C atoms are bonded with two Cl atoms at the same time. Here, only the

![Figure 5. Difference charge density maps for the adsorption structures of C and Cl2 on the surface of TiO2 (110) with the ratio of 2:2. The structures d, e, f, and g correspond to the structures d, e, f, and g in Figure 2, respectively. The isosurface level is 0.05 electrons/Å³. The top is the front view, and the bottom is the side view.](https://dx.doi.org/10.1021/acsomega.0c03368)
front Cl atoms bonded with C in the front view of each structure are analyzed for the density of states.

In Figure 7a, on the left side of the Fermi energy level, σ bond is contributed by C 2s and O 2p orbitals at −11.79 eV, and the π bond is contributed by C 2p and O 2p orbitals at −9.63 and −8.21 eV, respectively. The intensity of the overlapping peaks at these low energy levels is higher, indicating that there is a strong bonding interaction between C and O2c(r). There are overlapping peaks at −11.79 eV contributed by C 2s and Cl 3s orbitals, and overlapping peaks at −9.29 and −8.21 eV contributed by C 2p and Cl 3p orbitals, and the intensity of the overlapping peaks are higher, indicating that there is a strong bonding interaction between C and Cl atoms. The bonding interactions between C and O2c or C and Cl atoms for other density of states in Figure 7 are similar to those in Figure 7a. According to the analysis of the density of states of C and Cl2 adsorbed on the surface of TiO2 (110) with different ratios, the peaks of the density of states of C atom are mainly around −12.5 to −4.0 and −1.5 to 1.0 eV, which has the characteristics of polarization. Compared with C atom, the peaks of the density of states of O2c is more dispersed, and the peaks are lower at −1.5 to 1.0 eV, indicating that the electron activity around O2c is higher, and more electrons at higher energy level are transferred around C atom, which is conducive to the formation of the C–O2c bond. In the structures a, d, and j of Figure 7, the C atom forms bonds with O2c and two Cl atoms, respectively. In the structures of b, g, and h of Figure 7, the C atom forms bonds with O2c and one Cl atom, respectively. In the diagrams of a, d, and j, the peak polarization of the C atom is more obvious, and the overlapping peak widths of C and O2c are larger at the high energy level, indicating that the electron nonlocality of the C atom and O2c is stronger at the high energy level. That is to say, more electrons are transferred around the two Cl atoms. Compared with the diagrams of a, d, and j, the peaks of C and O2c or C and Cl atoms in the diagrams of b, g, and h migrate significantly to the higher energy levels at the left side of the Fermi energy level, indicating that the electron activities between C and O2c or C and Cl atoms are higher at the lower energy levels. The bonding interactions between C atom and O2c or C and Cl atoms in the diagrams of b, g, and h are weaker than that between C atom and O2c or C and Cl atoms.
in a, d, and j, and the stabilities of the C–O2c bond and the C–Cl bond are relatively lower.

3. CONCLUSIONS

Based on the first-principles calculations method of the density functional theory, the chlorination adsorption structures and electronic properties of C and Cl2 adsorbed on the TiO2 (110) surface with different ratios were predicted, and the following results were obtained.

(1) With the increase in the ratio of C atom in the adsorption reaction process, the possibility of complete adsorption of Cl atom on the TiO2 (110) surface increases. When C and Cl2 are adsorbed on the surface of TiO2 (110) with the ratio of 2:2, it is possible for the Cl2 molecules to be completely adsorbed; and this ratio of C and Cl2 is conducive to the complete adsorption of Cl2 on the surface of TiO2 (110).

(2) In the chlorination adsorption process of C and Cl2 on the TiO2 (110) surface with different ratios; Ti5c(m), C, and C* are electron providers, and O3c(r) and O2c(r) are electron acceptors.

(3) In the chlorination adsorption process, the bonding interactions between C and O2c(r) or C and Cl atoms are stronger and the bond stabilities are higher.

4. CALCULATION METHOD AND MODELS

Based on the density functional theory, the adsorption process of C and Cl2 on the surface of rutile TiO2 (110) was calculated by Castep13–19 module in Material Studio. To ignore the interaction between the inner electrons in the calculation process, the ultrasoft pseudopotential of the plane wave was used to describe the interaction between the ionic cores and the valence electron.

Generalized gradient approximation—Perdew–Burke–Ernzerhof (GGA-PBE) was used in the calculation of the exchange-correlation functional.20–22 Figure 8 shows the optimized structure of the TiO2 (110) surface, and the surface contains Ti5c (fivefold coordinated Ti atom), Ti6c (sixfold coordinated Ti atom), O2c (twofold coordinated O atom), and O3c (threefold coordinated Ti atom). The calculation model adopted a 2 × 2 supercell, which was composed of nine atomic layers. Before calculation, the bottom six atomic layers were fixed, while the other atoms were all relaxed. To avoid the interactions between the atoms of the neighbor, the vacuum space of the bulk was set to 15 Å. The 2 × 1 × 1 K-point was set by the Monkhorst–Pack method, and the energy cutoff was 400 eV. The convergence tolerance energy, max force, and max displacement were 1.0 × 10−5 eV/atom, 0.03 eV/Å, and 0.001 Å, respectively. To represent the interaction between molecules in the adsorption process, van der Waals forces between molecules were considered in the calculation. An excessive amount of Cl2 is inevitable in the fluidized chlorination process. An appropriate amount of C is conducive to the adsorption of Cl2 on the surface of TiO2 (110), so as to improve the efficiency of the fluidized chlorination reaction. To study the influence of C content on the adsorption process of Cl2 on the surface of TiO2 (110), the adsorption behaviors of C and Cl2 with ratios of 1:2, 2:2, and 2:3 were modeled and calculated.

The stability of the adsorption system can be characterized by $E_{\text{ads}}$ and it can be obtained by eq 1 as follows.

$$E_{\text{ads}} = E_{X+\text{TiO}_2} - (E_X + E_{\text{TiO}_2})$$  \hspace{1cm} (1)

where $E_{X+\text{TiO}_2}$ is the surface energy of X (X = C + Cl2) adsorbed on the TiO2 surface, $E_X$ is the energy of X (X = C + Cl2), and $E_{\text{TiO}_2}$ is the energy of the TiO2 clean surface.

AUTHOR INFORMATION

Corresponding Authors

Liangying Wen — School of Materials Science and Engineering and Chongqing Key Laboratory of Vanadium—Titanium Metallurgy and Advanced Materials, Chongqing University, Chongqing 400044, P. R. China; orcid.org/0000-0002-7897-8952; Email: cquwen@cqu.edu.cn

Shengfu Zhang — School of Materials Science and Engineering and Chongqing Key Laboratory of Vanadium—Titanium Metallurgy and Advanced Materials, Chongqing University, Chongqing 400044, P. R. China; orcid.org/0000-0002-0858-7286; Email: zhangsf@cqu.edu.cn

Authors

Fan Yang — School of Materials Science and Engineering and Chongqing Key Laboratory of Vanadium—Titanium Metallurgy and Advanced Materials, Chongqing University, Chongqing 400044, P. R. China

Qin Peng — School of Materials Science and Engineering and Chongqing Key Laboratory of Vanadium—Titanium Metallurgy and Advanced Materials, Chongqing University, Chongqing 400044, P. R. China

Yan Zhao — School of Materials Science and Engineering and Chongqing Key Laboratory of Vanadium—Titanium Metallurgy and Advanced Materials, Chongqing University, Chongqing 400044, P. R. China

Zhongqing Yang — School of Power Engineering, Chongqing University, Chongqing 400044, P. R. China; orcid.org/0000-0001-5432-8704

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c03368
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