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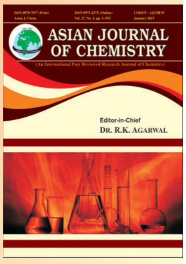

Quantum Chemical Calculations of Reaction Mechanism of Carbothermal Reduction of TiO_2 in Vacuum

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Density functional theory with generalized gradient approximation was used to preliminarily study the reaction mechanism of carbothermal reduction of TiO_2 on the material studies by quantum chemical calculations. The results show that in the beginning reaction of carbothermal reduction of TiO_2, the solid-solid reaction mainly occurs between TiO_2 and carbon. In the initial reaction stage of carbothermal reaction of TiO_2, the low-valence titanium oxide TiO_x ($x < 2$) and carbon monoxide gas will be easily produced and the probability of TiC_xO_{1-x} is very low. The gas-solid reaction between TiO_x ($x < 2$) and carbon monoxide occurred easily with the reaction proceeding and finally TiC was obtained.

Keywords: Carbothermal reduction, TiC, TiO_2, Quantum chemical calculations, Vacuum.

INTRODUCTION

TiC has been widely used in many fields such as wear resistant materials, aerospace materials and chemical industry materials attributing to its outstanding properties including high temperature resistance, wear resistance and corrosion resistance[1,2]. At present, TiC powders were prepared mainly by carbothermal reaction of TiO_2 method. There are many reports about TiC preparation process while the reaction mechanism is very few[3-6]. Several researchers[7-10] had speculated the reaction mechanism of carbothermal reaction of TiO_2 (Fig. 1). However, Fig. 1 is deduced from macroscopic and contains lack of continuity. The quantum chemical calculations can study in electronic level of the interaction between atoms and molecules. And it is very suitable for solving the problem of micro reaction mechanism and microstructure[11]. Xiao *et al.*[12] calculated the properties of $TiO_2(111)$ surface by the density functional theory. Menetrey *et al.*[13] investigated the adsorption performance of H, H_2O and CO to $TiO_2(110)$ surface with DFT-GGA method. Gianfranco *et al.*[14] studied the problem of $TiO_2(110)$ surface adsorbing CO with ab initio method. But the study about reaction mechanism of carbothermal reduction of TiO_2 has not been reported.

In this paper, the DFT-GGA calculation method was adopted and quantum chemical calculations about the reaction mechanism of carbothermal reduction of TiO_2 were preliminarily studied.

CALCULATION METHODS

$TiO_2(110)$ surface adsorption C and CO was optimized and charge density difference, energy band and density of states were calculated by DFT-GGA calculation method, exchange-correlation potential parameter selection PBE method[15] and Cheng *et al.*[16]. On this basis, the quantum dynamics simulation was conducted with the conditions as follows: the temperature is 1450 °C, the pressure is 50 Pa, the time is 1ps, the step length is 1 fs and the step number is 1000. All calculations were carried out under the grid $12 \times 12 \times 12$ and the parameters optimized as follows: the convergence standard of interactions of atoms is set to 0.5 eV/nm, the convergence standard of single atom is set to 2×10^{-5} eV/atom, the standard of internal stress of crystals is set to 0.1 GPa, the convergence standard of the maximum displacement of atoms is set to 2×10^{-4} nm. The $TiO_2(110)$ surface is dominant in the reaction so crystal (110) surface was selected to construct structural model (Fig. 2). The single cell of TiO_2 was cut out (110) surface and to build 3×2 super cell.

RESULTS AND DISCUSSION

Interaction between $TiO_2(110)$ and carbon: The optimal structure, electron density difference, total energy and Fermi energy of $TiO_2(110)$ surface adsorbing carbon were listed in Table-1. There are four adsorption types about $TiO_2(110)$ surface adsorbing carbon and they are oxygen sites of $TiO_2(110)$

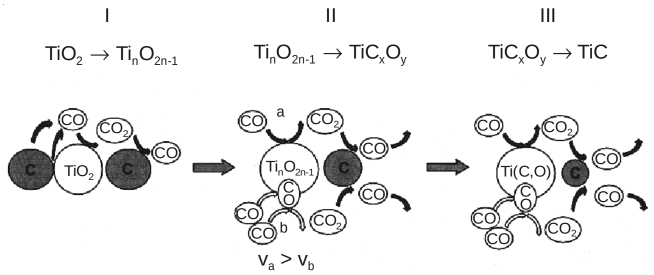


Fig. 1. Schematic reaction mechanism of the carbothermal reduction of TiO_2

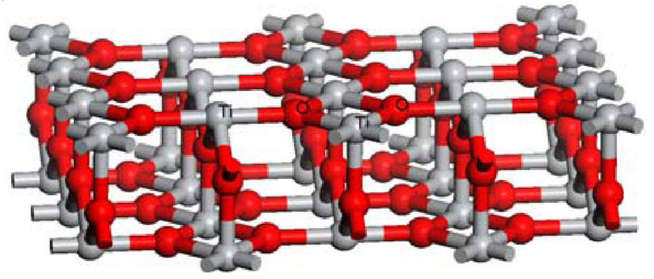


Fig. 2. Structural model of TiO_2(110) surface

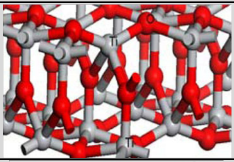
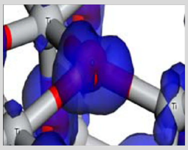
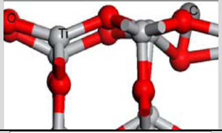
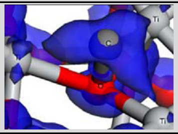
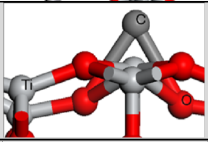
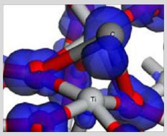
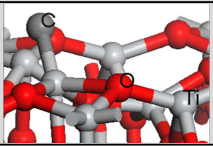
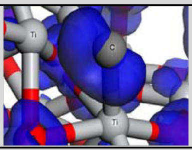
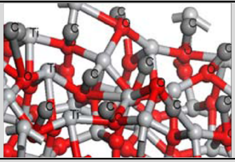
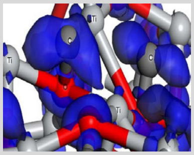
surface-adsorbing carbon, oxygen sites adsorbing bridging carbon, Ti sites adsorbing carbon and oxygen sites whole covering carbon, respectively.

According to the electron density difference diagram, the TiO_2(110) surface of Ti and O combining with covalent bonds. Therefore the bond lengths of Ti-O in the structure were optimized to be 1.944, 2.020, 2.077 and 1.828 Å and the average value was 1.967 Å.

When the oxygen site of TiO_2(110) surface adsorbing carbon, it can form ionic bond with three Ti and the bond lengths were 2.177, 2.176 and 2.199 Å, respectively. Meanwhile, carbon and oxygen formed covalent bond and the bond length was 1.476 Å. When the oxygen site of TiO_2(110) surface adsorbing bridging carbon, it can form ionic bond with two Ti and the bond lengths were 1.871 and 1.872 Å and C and O formed covalent bond and the bond length was 2.600 and 2.580 Å. When the Ti site of TiO_2(110) surface adsorbing carbon, it can form ionic bond with two Ti and the bond lengths were 1.868 and 2.030 Å. The calculation results shown that TiO_2(110) surface interacting with carbon to form bonding and the bond is the most obvious when the O site interacts with carbon forming three Ti-C ionic bonds. Calculated by the energy to be seen the energy from small to large' s order is O site adsorbing carbon, Ti site adsorbing C and O site adsorbing bridging C illustrating the TiO_2(110) surface of O site adsorbing carbon site structure is the most stable and the interaction is the strongest.

Based on the above analysis, the O site of TiO_2(110) surface complete coverage twelve carbon was calculated at last. In the optimized structure diagram the twelve C formed ionic bonds with near three Ti, respectively. The bond lengths of C-Ti bond formed by the two central carbon are 2.111, 2.347, 2.029 and 2.147, 2.284 , 1.989 Å. The C and O forms covalent bond and the average bond lengths is 1.581 Å. The calculations show that when the O site of TiO_2(110) surface complete coverage carbon, the carbon interacts with (110) surface obviously to form Ti-O and C-Ti bonds. The total energy of optimization structure is -56093.870746 eV which is the smallest in four adsorbing

TABLE-1
OPTIMAL STRUCTURE, ELECTRON DENSITY DIFFERENCE, TOTAL ENERGY AND FERMI ENERGY OF TiO_2(110) ADSORB C

TiO_2(110) adsorb C	Optimized structural diagram	Electron density difference diagram	Total energy (eV)	Fermi energy (eV)
TiO_2(110)			-54254.895118	2.397
O^a Adsorb C			-54420.848357	1.979
O Adsorb bridge C			-54419.554580	1.847
Ti^b Adsorb C			-54420.014102	1.838
O Adsorb nC			-56093.870746	1.990

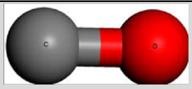
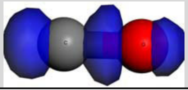
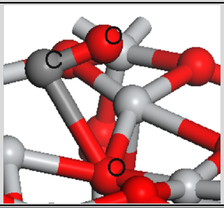
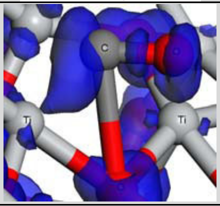
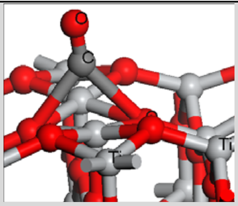
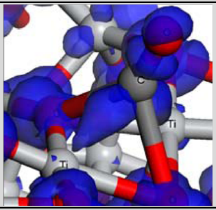
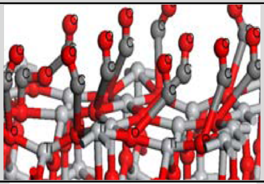
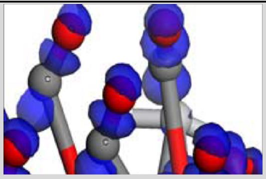
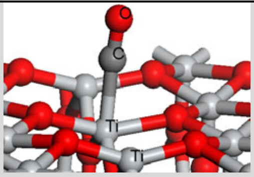
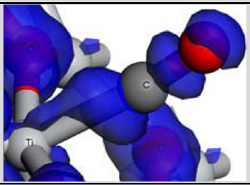
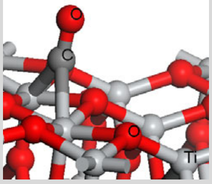
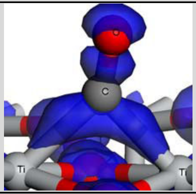
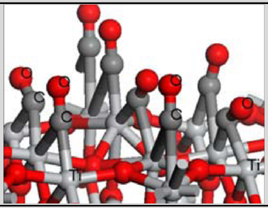
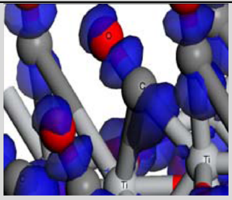
[a] O is the atom O of TiO_2(110); [b] Ti is the atom Ti of TiO_2(110)

carbon types and the most stable in the structure and the strongest of the interaction.

Interaction between TiO_2(110) and CO: The optimal structure, differential electron density, total energy, Fermi energy and bond length of TiO_2(110) surface adsorbing CO were shown in Table-2. There are six types of TiO_2(110) surface adsorbing CO as follows: oxygen sites of TiO_2(110) surface adsorbing CO, oxygen sites adsorbing the bridging CO, oxygen sites complete coverage CO, Ti sites adsorbing CO, Ti sites adsorbing the bridging CO and Ti sites complete coverage the bridging CO. It is easy for TiO_2(110) surface to adsorb carbon of CO rather than O. So the structure model was constructed with TiO_2(110) surface adsorbing carbon of the CO. Based on the differential electron density diagram of CO can know that CO molecules combined with covalent bonds and the bond length is 1.153 Å.

When the O site of TiO_2(110) adsorbing CO, the bond length of CO is 1.330 Å and C forms ionic bonds with three Ti and the bond lengths are 1.959, 2.162 and 2.299 Å, respectively. When the O site of TiO_2(110) adsorbing the bridging CO, the bond length of CO is 1.202 Å and C forms ionic bonds with two Ti and the bond lengths are 2.255 and 2.256 Å. When the O site of TiO_2(110) complete coverage CO, the average bond length of CO is 1.191 Å. Meanwhile, every carbon bonds with nearby Ti atom and the average bond length is 2.134 Å

TABLE-2
OPTIMAL STRUCTURE, ELECTRON DENSITY DIFFERENCE, TOTAL ENERGY, FERMI ENERGY AND BOND LENGTH OF TiO_2(110) ADSORB CO

TiO_2(110) adsorb CO	Optimized structural diagram	Electron density difference diagram	Total energy (eV)	Fermi energy (eV)	Bond length[a] (Å)
CO Molecule			-589.365204	-3.604	O–C 1.153
O[b] Adsorb CO			-54858.897007	2.033	O–C 1.330 C–O 2.525
O Adsorb bridge CO			-54857.476134	2.018	O–C 1.202 C–O 2.407; 2.516
O Adsorb nCO			-61352.881819	2.594	O–C 1.191 C–O 2.713
Ti[c] Adsorb CO			-54857.696739	2.090	O–C 1.184 C–Ti 2.045
Ti[c] Adsorb bridge CO			-54857.907111	1.998	O–C 1.202 C–Ti 2.258 2.246
Ti[c] Adsorb bridge nCO			-58403.860074	2.207	O–C 1.199 C–Ti 2.247 2.078

[a] O-C is the bond length of CO; C-O is the bond length of C to the O of TiO_2(1 1 0) surface; C-Ti is the bond length of C to the Ti of TiO_2(1 1 0);
[b] O is the atom O of TiO_2(1 1 0) surface; [c] Ti is the atom Ti of TiO_2(1 1 0) surface

due to the effect of potential field of CO. When the Ti site of TiO_2(110) adsorbing CO the bond length of CO is 1.184 Å. Carbon bonds with only one Ti forms ionic bond and the length is 2.045 Å. When the Ti site of TiO_2(110) adsorbing the bridging CO the bond length of CO is 1.202 Å. C bonds with only two Ti forms ionic bond and the length is 2.246 Å and 2.258 Å, respectively. When the Ti site of TiO_2(110) complete coverage the bridging CO, the bond length of CO is 1.199 Å. Carbon bonds with only two Ti forms ionic bonds and the length is 2.247 and 2.078 Å, respectively.

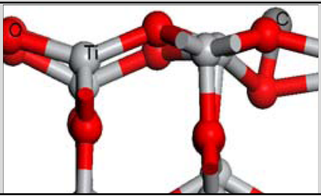
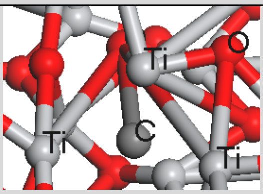
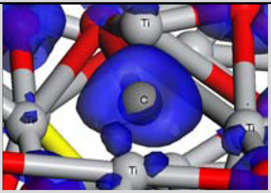
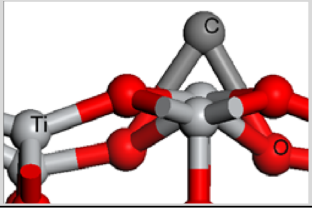
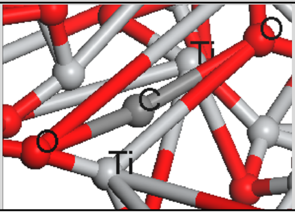
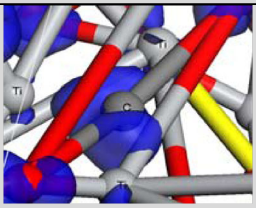
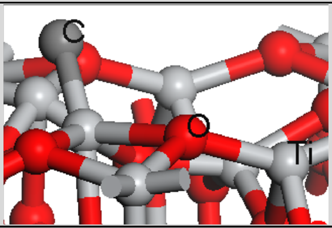
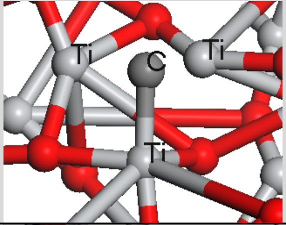
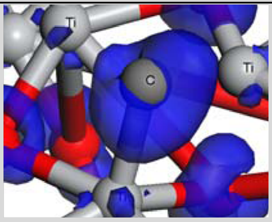
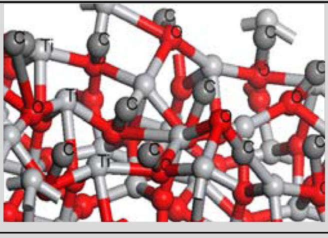
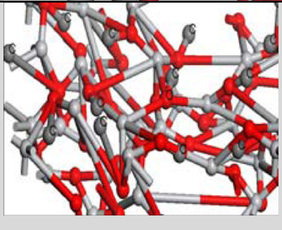
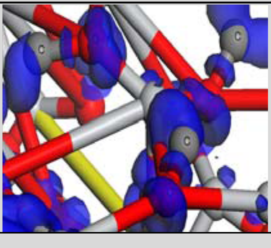
Quantum dynamics simulations of TiO_2 (110) and C: The optimal structure, simulation structure and differential electron density of TiO_2(110) surface adsorbing C were described in Table-3. When the O site of TiO_2(110) adsorbing carbon, after the quantum dynamics simulation the structure of TiO_2 changed and carbon adsorbed on (110) surface moving internal obviously. In the simulation animation, carbon moves from above of TiO_2(110) surface to inner and bonding with interior atoms. After 1ps, the carbon atom formed ionic bonds with four Ti and the bond length were 2.082, 2.387, 1.961 and 1.897 Å. The bond length of C and O was 2.797 Å which was longer than C-O of CO molecules (1.153 Å).

When the O site of TiO_2(110) adsorbing the bridging carbon, after the quantum dynamics simulation the structure of TiO_2 changed and the carbon adsorbed on (110) surface moving internal. In the simulation animation, carbon moves from above of TiO_2(110) surface to inner and bonding with interior atoms which is less significant than adsorbing carbon. After 1ps, the carbon atom formed ionic bonds with three Ti and the bond length were 1.977 Å, 2.055 and 2.101 Å. The bond length of C and O was 3.203 Å which was also longer than C-O of CO molecules (1.153 Å).

When the Ti site of TiO_2(110) adsorbing carbon, after the quantum dynamics simulation the structure of TiO_2 changed and the carbon adsorbed on (110) surface without moving internal. In the simulation animation, the carbon moves above the TiO_2(110) surface always and bonded with nearby atoms. After 1ps the carbon atom formed ionic bonds with three Ti and the bond length were 2.171, 1.832 and 1.926 Å.

In summary, after the quantum dynamics simulations calculation the interaction between sites of O and Ti of TiO_2(110) and carbon is the more obvious. The O site adsorbing C is the most obvious. The carbon moves internal of the TiO_2(110) surface and bonded with Ti. As shown in Table-4, the total energy of crystal cell is larger than before quantum dynamics simulations and the fermi energy becomes from positive to negative. The conclusions indicated that the structure of TiO_2 and carbon change unstable and generate other substance but no CO gas. The simulation calculations of complete coverage of carbon is needed further studied.

TABLE-3
OPTIMIZED STRUCTURE, DYNAMICS STRUCTURE AND ELECTRON DENSITY DIFFERENCE OF TiO_2(110) SURFACE ADSORBING CARBON

TiO_2(110) adsorbing C	Optimized structural diagram	Dynamics simulation-structural diagram	Dynamics simulation-electron density difference diagram
O[a] Adsorbing C			
O Adsorbing bridging C			
Ti[b] Adsorbing C			
O Adsorbing nC			

[a]O is the atom O of TiO_2(110) surface; [b]Ti is the atom Ti of TiO_2(110) surface

TABLE-4
TOTAL ENERGY AND FERMI ENERGY OF TiO_2(1 1 0) SURFACE ADSORBING C BEFORE OR AFTER DYNAMICS SIMULATION

TiO_2(110) adsorbing C	Optimized structure-Total energy (eV)	Optimized structure-Fermi energy (eV)	Dynamics simulation-Total energy (eV)	Dynamics simulation-Fermi energy (eV)
O[a] Adsorbing C	-54420.848357	1.979	-54401.095176	-0.401
O Adsorbing bridging C	-54419.554580	1.847	-54399.889969	-0.454
Ti[b] Adsorbing C	-54420.014102	1.838	-54400.883678	-0.459
O Adsorbing nC	-56093.870746	1.990	-56078.130340	-0.505

[a]O is the atom O of TiO_2(1 1 0) surface ; [b]Ti is the atom Ti of TiO_2(1 1 0) surface

When the O site of TiO_2(110) complete coverage twelve carbon, the structure of C TiO_2 changed after dynamics simulation. In the simulation animation, the carbon adsorbed on (110) surface moving internal obviously. After 1ps there are nine carbon atoms formed covalent bonds with O and the bond length were 1.527, 1.342, 1.424, 1.346, 1.258, 1.430, 1.489, 1.281 and 1.275 Å. The C-O is close to CO molecule indicating that there are nine C will generate gas CO. The remainder three carbon will bond with Ti and melt into TiO_2 structure to form TiC_xO_y. In Table-4, the total energy of crystal cell of the O site of TiO_2(110) complete coverage carbon becomes larger and the Fermi energy changes from positive to negative illustrating that the structure of TiO_2 and carbon changes unstable than before simulation and maybe generates CO and TiC_xO_y.

Conclusion

The quantum chemical calculations showed that the solid-solid reaction between TiO_2 and C at the early carbothermal reduction reaction of TiO_2. The interaction is very strong between carbon and TiO_2(110) surface and the bonds form between C and O with Ti. But the interaction is not obvious CO and TiO_2(110) surface. The simulation results indicated that the major products are TiC_x($x < 2$) and CO gas at the early period of carbothermal reaction and the generation probability of TiC_xO_{1-x} is small. With the reaction proceeding, it is easy for the solid-gas reaction between TiC_x($x < 2$) and CO gas and the intermediate produce was reduced gradually at last the TiC was obtained.

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