



## Full Length Article

CO adsorption, dissociation and coupling formation mechanisms on Fe<sub>2</sub>C(001) surfaceXiaohu Yu<sup>a,\*</sup>, Xuemei Zhang<sup>a</sup>, Yan Meng<sup>a</sup>, Yaoping Zhao<sup>a</sup>, Yuan Li<sup>a</sup>, Wei Xu<sup>a</sup>, Zhong Liu<sup>b,\*</sup><sup>a</sup> Institute of Theoretical and Computational Chemistry, Shaanxi Key Laboratory of Catalysis, School of Chemical & Environment Sciences, Shaanxi University of Technology, Hanzhong 723000, China<sup>b</sup> Key Laboratory of Salt Lake Resources and Chemistry, Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining 810008, China

## ARTICLE INFO

## Article history:

Received 28 August 2017

Received in revised form 25 October 2017

Accepted 31 October 2017

Available online 1 November 2017

## Keywords:

DFT

Iron carbide

Fischer-Tropsch synthesis

CO adsorption

Dissociation

Coupling

## ABSTRACT

By means of density functional theory calculations and atomic thermodynamics, we systematically investigated the CO adsorption on the Fe<sub>2</sub>C(001) surface at different coverage. It has been found that CO prefers to adsorb on the surface iron atom at low coverage (1–8 CO); CO prefers to adsorb at the bridge site of Fe and C atoms at high coverage (9–12 CO). Eight CO molecules binding on the Fe<sub>2</sub>C(001) surface is favorable thermodynamically as indicated by the stepwise adsorption energy. The phase diagram shows that addition of more CO molecules up to a number of 8 is thermodynamically favorable, and that the incremental energy gained by adding one more CO molecule is almost constant up to 4 CO molecules, decreases up to 8 CO molecules, after which it becomes thermodynamically unfavorable to add more CO molecules. Probability distribution of different single-CO adsorbed states on the Fe<sub>2</sub>C(001) surface as function of temperature shows that CO dissociation and coupling are least preferred, indicating that carbide mechanism is not dominant in the iron-based Fischer-Tropsch synthesis reaction. The projected density of states (PDOS) was used to analyze the CO adsorption mechanism.

© 2017 Elsevier B.V. All rights reserved.

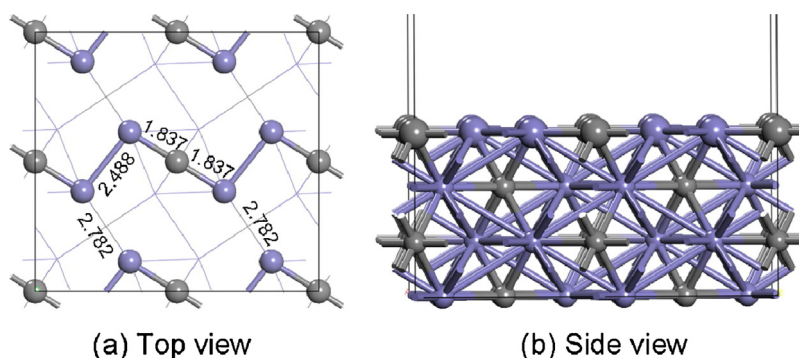
## 1. Introduction

Iron carbide is an important active phase in iron-based catalysts in Fischer-Tropsch synthesis (FTs) process [1,2], which has become increasingly important especially for liquid fuel production under the background of shortage of oil supply in the world. In the process of FTs reactions, the iron-based catalyst is exposed to the syngas (CO + H<sub>2</sub>) environment that maintains the stable existence of iron carbides [1,2]. It is well known that activation with carbon monoxide and syngas in FTs typically results in complicated conversion of Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub> and, finally, to one or more iron carbides: CO adsorption on iron carbide surface hydrogenated by the adsorbed hydrogen atom, followed by the coupling with CH<sub>x</sub> and formed longer hydrocarbon. The initial step for CO adsorption on the iron carbide surface has been widely investigated in experiments. However, there are few theoretical investigations aiming at a comprehensive understanding the interaction between CO and iron carbide surfaces [3–6].

It was reported [7] that there exist Fe, Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>4</sub>C, Fe<sub>3</sub>C, Fe<sub>2</sub>C, Fe<sub>5</sub>C<sub>2</sub>, Fe<sub>7</sub>C<sub>3</sub> in freshly activated or used Fe-based FTs catalysts, and the phase formation and transformation of iron carbides usually change with different temperature in fused catalysts. In addition, it was found [8] that Fe<sub>2</sub>C and Fe<sub>2.2</sub>C phases are formed simultaneously at low temperature (115 °C), however only the Fe<sub>2</sub>C phase is formed at 150–185 °C; the Fe<sub>5</sub>C<sub>2</sub> phase is formed in the range 220–400 °C; and stable the Fe<sub>3</sub>C phase is formed at 450 °C. However, there are only a few theoretical studies on the adsorption of small molecules on Fe, Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>4</sub>C, Fe<sub>3</sub>C and Fe<sub>5</sub>C<sub>2</sub> surfaces [3–5,9–16] and no report on the Fe<sub>2</sub>C surfaces. Cao et al. [3] reported that CO prefers to adsorb on the three-fold iron site of (001), (110), and (100) on the Fe<sub>5</sub>C<sub>2</sub> surfaces. Liao et al. [4] reported that CO favors the three-fold site of (100) and the four-fold site of (001), but the two-fold site and three-fold site of (010) at low coverage for CO adsorption on the Fe<sub>3</sub>C surfaces. Recently, Ramo and Jenkins [5] studied the small molecules adsorption on the Fe<sub>3</sub>C(010) surface and found that CO prefers to adsorb at bridge site of two iron atoms which agrees well with Liao et al.' results [4]. Deng et al. [6] researched CO adsorption on the Fe<sub>4</sub>C surfaces and found that CO adsorbs at different sites of different surfaces. Huang et al. [17] studied CO adsorption on the magnetite (111) surface using standard density functional theory (DFT) and it was found that the on-top

\* Corresponding authors.

E-mail addresses: [yuxiaohu950203@126.com](mailto:yuxiaohu950203@126.com) (X. Yu), [liuzhong@isl.ac.cn](mailto:liuzhong@isl.ac.cn) (Z. Liu).



**Fig. 1.** (a) Top and (b) Side views of the  $\text{Fe}_2\text{C}(001)$  surface. (iron atoms in blue, carbon atoms in grey). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

configurations are most stable on both  $\text{Fe}_{\text{tet}1}$  and  $\text{Fe}_{\text{oct}2}$  terminations. In addition, the CO adsorption on the  $\text{Fe}_{\text{oct}2}$  termination is more stable than on the  $\text{Fe}_{\text{tet}1}$  termination. Yu et al. [18] systematically studied CO adsorption on the  $\text{Fe}_3\text{O}_4$  surfaces using DFT+U, and found that more than one CO can bind on one surface iron atom on both  $\text{Fe}_{\text{tet}1}$  and  $\text{Fe}_{\text{oct}2}$  terminations of  $\text{Fe}_3\text{O}_4(111)$  and A layer of  $\text{Fe}_3\text{O}_4(110)$ , only one CO can bind on one surface iron atom on other surfaces, and different adsorption mechanisms can be explained by spatial effect.

The orthorhombic  $\text{Fe}_2\text{C}$  phase was chosen in this work since its stability is more stable than hexagonal  $\text{Fe}_2\text{C}$  by 0.16 eV on the basis of former computed cohesive energies [19]. In addition,  $\text{Fe}_2\text{C}(001)$  surface was selected to study the interaction with  $\text{H}_2$  molecules since it is one of main facet of  $\text{Fe}_2\text{C}$  [19], and surface structures and properties of  $\text{Fe}_2\text{C}$  have been predicted [19] theoretically. In order to get the detailed mechanism for CO adsorption on  $\text{Fe}_2\text{C}$  surfaces, extensive DFT calculations were carried out to investigate CO adsorption on the  $\text{Fe}_2\text{C}(001)$  surface at different coverage in the present work. Boltzmann statistics was used to analyze the probability distribution of different adsorption states of single CO as function of temperature. The phase diagram of CO adsorption on the  $\text{Fe}_2\text{C}(001)$  surface is analyzed using atomic thermodynamics. In addition, we discussed the overall trends of the adsorption energy as a function of coverage and analyzed the CO adsorption mechanisms using the projected density of states (PDOS).

## 2. Method and surface model

### 2.1. Computational method

All calculations were performed by using the frozen-core all-electron projector-augmented wave (PAW) method within spin polarized DFT as implemented in the Vienna Ab-initio Simulation Package (VASP) [20–22]. The exchange and correlation energies of the electrons were described by the generalized gradient approximation (GGA) [23] functional parametrized by Perdew, Burke, and Ernzerhof (PBE). A 400 eV cutoff energy was used to control the number of plane waves and a 645 eV cutoff energy was used to control the number of the augmentation wavefunctions. Projector-augmented-wave (PAW) potentials [24] with valence configurations of  $3p^63d^64s^2$ ,  $2s^22p^4$  and  $2s^22p^2$  were used to describe the Fe, O, and C atoms, respectively. The Brillouin zone integrations were performed using Monkhorst-Pack (MP) grids [25], and a Gaussian smearing  $\sigma$  was 0.2 eV. Structure optimizations were conducted until the energy was smaller than  $10^{-4}$  eV and the Hellmann-Feynman force on each atom was less than 0.02 eV/Å. For integration within the Brillouin zone, specific k-points were selected using a  $7 \times 7 \times 7$  MP grid for the bulk  $\text{Fe}_2\text{C}$  and a  $3 \times 3 \times 1$  MP grid for  $\text{Fe}_2\text{C}(001)$  surface. These settings were able to gener-

ate a lattice constant ( $a = 4.651 \text{ \AA}$ ,  $b = 4.258 \text{ \AA}$ ,  $c = 2.801 \text{ \AA}$ ) for bulk  $\text{Fe}_2\text{C}$ , which agrees well with the experimental value ( $a = 4.704 \text{ \AA}$ ,  $b = 4.318 \text{ \AA}$ ,  $c = 2.830 \text{ \AA}$ ) [26] and former theoretical result [19].

### 2.2. Surface model

Top and side views of  $p(2 \times 2)$  supercell of the  $\text{Fe}_2\text{C}(001)$  surface are shown in Fig. 1a. The four-layer slabs are used to describe the  $\text{Fe}_2\text{C}(001)$  surface, with the top two layers and adsorbed CO are allowed to fully relax, and two bottom layers are fixed in bulk position. A 15 Å vacuum gap was used to separate from  $\text{Fe}_2\text{C}(001)$  surface images which is periodically repeated in the z direction perpendicular to the surface. In all calculations, the CO molecules were adsorbed on one side of the  $\text{Fe}_2\text{C}(001)$  surface. The leading dipole moment errors induced CO molecules adsorption on the  $\text{Fe}_2\text{C}(001)$  surface were corrected by using dipole moment methods as implemented in the VASP code [20–22].

For the  $\text{Fe}_2\text{C}(001)$  surface with  $n$  adsorbed CO molecules, we defined the total CO adsorption energy as:

$$\Delta E(\text{CO})_n = E(n\text{CO}/\text{Fe}_2\text{C}(001)) - E(\text{Fe}_2\text{C}(001)) - nE(\text{CO}) \quad (1)$$

where  $E(n\text{CO}/\text{Fe}_2\text{C}(001))$ ,  $E(\text{Fe}_2\text{C}(001))$  and  $E(\text{CO})$  are the energies of the adsorbed system, clean  $\text{Fe}_2\text{C}(001)$  surface, and an isolated CO molecule in gas phase, respectively, and  $n$  is number of adsorbed CO molecules. The stepwise adsorption energy is defined as:

$$\Delta \Delta E(\text{CO}) = \Delta E(\text{CO})_n - \Delta E(\text{CO})_{n-1}. \quad (2)$$

The average adsorption energy is defined as:

$$\Delta E = \Delta E(\text{CO})_n/n \quad (3)$$

From above definition, it is clear that a more negative adsorption energy indicates the stronger adsorption. A cubic unit cell of  $10 \times 10 \times 10 \text{ \AA}^3$  was used to calculate CO, and the calculated bond distance of CO molecule is 1.14 Å, which agrees well with previous theoretical result (1.14 Å) [27] and the experimental result (1.13 Å) [28].

## 3. Results and discussion

In this work, the CO adsorption was defined as CO molecule binding on the surface iron atoms, the CO mixed adsorption was defined as CO molecules binding on the surface iron and carbon atoms, the CO coupling was defined as CO molecule binding on the surface lattice carbon atom and forming a C–CO-like structure, and the CO dissociation was defined as CO molecule dissociates to carbon and oxygen atoms binding on the  $\text{Fe}_2\text{C}(001)$  surface. The total adsorption energies of the most stable CO adsorption, coupling, mixed and dissociation formation configurations are shown in Table 1.

Download English Version:

<https://daneshyari.com/en/article/7836315>

Download Persian Version:

<https://daneshyari.com/article/7836315>

[Daneshyari.com](https://daneshyari.com)