

Structure and stability of Fe₄C bulk and surfaces: A density functional theory study

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Abstract

Density functional theory calculations have been performed on the structure and stability of Fe₄C bulk and the corresponding low-index surfaces. It is found that the structure with octahedral interstitial carbon (Fe₄C/oct) is more stable than that with tetrahedral interstitial carbon (Fe₄C/tet). For Fe₄C/oct, the most stable surface termination is the (100) surface with mixed carbon and iron ($T_{\text{Fe/C}}$). For Fe₄C/tet, the most stable surface termination is the dramatically reconstructed (110) surface with the newly formed $T_{\text{Fe/C}}$ surface layer. © 2007 Elsevier B.V. All rights reserved.

1. Introduction

Transition metal carbides have attracted considerable attention because of their excellent physical and chemical properties, e.g. extreme hardness, high melting point [1] and excellent electric as well as thermal conductivities [2]. Iron carbides are interesting materials for sensors, magnets, catalysts and alternative raw materials for steel productions [3]. It has been shown that iron carbide instead of metallic iron is used in carbon nanotube growth by the pyrolysis of organometallic precursors [4].

Recent studies indicate that pure face-centered cubic (fcc) γ -phase iron is thermodynamically unstable under normal conditions, and may be transformed into Fe₄C by incorporating carbon atoms into the lattices. In the fcc Fe lattice, there are two interstitial sites, i.e., tetrahedral and octahedral sites. Therefore, incorporating carbon atoms into these sites will lead to two different Fe₄C structures: (i) carbon atom in the tetrahedral interstitial site

(Fe₄C/tet), and (ii) carbon atom in the octahedral interstitial site (Fe₄C/oct).

There are several experimental and theoretical studies on Fe₄C/tet and Fe₄C/oct. Villars and Calvert [5] analyzed the detailed structural data for the intermetallic phases. Recently, Shevchenko et al. [6] further confirmed the existence of Fe₄C/tet and emphasized the parallels between atomic scale crystal growth and nanoparticle assembly. For Fe₄C/oct, Choo and Kaplow [7] studied a high carbon iron-based alloy (1.8 wt% C) virgin martensite aging at room temperature, and concluded that the formation of higher carbon region was probably due to the agglomerations of the ordered arrangements of Fe₄C with two different iron sites (with magnetic moments of 2–3 μ_B). Santos et al. [8] analyzed the electronic structure of Fe₄C by using the linear muffin-tin orbital method, and pointed out that the C atoms act as donors of electrons in the interstitial sites, while discrete variational calculations by Krause et al. [9] suggested that the C atoms act as acceptors of electrons. However, there are no theoretical studies on the Fe₄C surfaces. In this work, we present a theoretical study on the structure and stability of Fe₄C bulk and the corresponding low-index surfaces, aiming not only to get the information about the surface energy, structure and

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stability, but also to provide the references for further investigations into the catalytic activity in Fischer–Tropsch synthesis (FTS).

2. Methods and models

2.1. Methods

All calculations were carried out by using the Cambridge Sequential Total Energy Package (CASTEP) [10–12]. The exchange and correlation energies were calculated using the Perdew, Burke and Ernzerhof functional [13] within the generalized gradient approximation (PBE-GGA) [14]. Ionic cores were described by the ultrasoft pseudopotential [15], and the Kohn–Sham one-electron states were expanded in a plane wave basis set up to 340 eV. A Fermi smearing of 0.1 eV was utilized. Monkhorst–Pack mesh [16] of $(6 \times 6 \times 6)$ k -point sampling in the Brillouin zone was used for the Fe_4C bulk, and $(5 \times 5 \times 1)$, $(5 \times 4 \times 1)$ and $(4 \times 4 \times 1)$ k -point meshes were used for the (100), (110) and (111) surfaces, respectively. The pseudopotential with a partial core was used in spin-polarized calculation to include non-linear core corrections. Because of its large effect on magnetic systems, spin polarization was included in the calculation for Fe_4C to correctly account for its magnetic properties. A 10 Å vacuum region was also included between the slabs to prevent interactions between periodic images. The convergence criteria for structure optimization and energy calculation were set to medium quality with the tolerance for SCF, energy, maximum force, and maximum displacement of 2.0×10^{-6} eV/atom, 2.0×10^{-5} eV/atom, 0.05 eV/Å, and 2.0×10^{-3} Å, respectively.

2.2. Models

Two different structures of the Fe_4C cell are shown in Fig. 1. $\text{Fe}_4\text{C}/\text{oct}$ has two non-equivalent Fe sites, i.e., the corner site (Fe_1) without nearest neighbor C atoms and the face-centered site (Fe_2) with two C atoms in the first interstitial shell. This interstitial structure has a larger lattice constant (3.768 Å [17]) than fcc γ -Fe (3.600 Å). The structure of $\text{Fe}_4\text{C}/\text{tet}$ is cubic close packed and has only one Fe site with a lattice constant of $a = 3.878$ Å [5].

Figs. 2 and 3 show the low-index surfaces of $\text{Fe}_4\text{C}/\text{oct}$ and $\text{Fe}_4\text{C}/\text{tet}$, respectively. $\text{Fe}_4\text{C}/\text{oct}$ has three surfaces (Fig. 2), (100), (110) and (111) and each surface has two terminations. Both (100) and (110) have iron (T_{Fe}) as well as mixed iron and carbon ($T_{\text{Fe}/\text{C}}$) terminations, and (111) has pure iron (T_{Fe}) and pure carbon (T_{C}) terminations. $\text{Fe}_4\text{C}/\text{tet}$ also has three surfaces (Fig. 3), (100), (110) and (111). (100) has three terminations: the pure carbon termination (T_{C}) as well as terminations with pure Fe1 ($T_{\text{Fe}1}$) and pure Fe2 ($T_{\text{Fe}2}$). (110) has terminations with mixed iron and carbon ($T_{\text{Fe}/\text{C}}$), and with pure iron (T_{Fe}). (111) has terminations with pure carbon (T_{C}) and with pure iron (T_{Fe}).

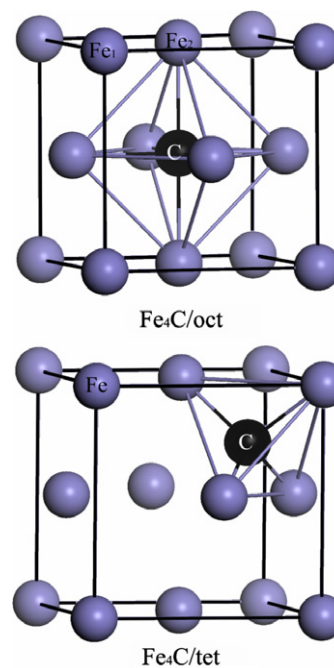


Fig. 1. The unit cell of $\text{Fe}_4\text{C}/\text{oct}$ and $\text{Fe}_4\text{C}/\text{tet}$.

In order to discuss these surfaces, the different slabs (1×1) with the same number of atoms (Fe_8C_2) (the Fe_{12}C_3 slab (1×1) was used for the (111) surface of $\text{Fe}_4\text{C}/\text{tet}$) were used to minimize the systematic errors as much as possible. For $\text{Fe}_4\text{C}/\text{oct}$, there are four layers for the (100), (110) and (111) surfaces and the top two layers are allowed to relax, while the bottom two layers are fixed in their bulk positions. For $\text{Fe}_4\text{C}/\text{tet}$, there are six, four and six layers for the (100), (110) and (111) surfaces, respectively. The top three, two and four layers of (100), (110) and (111) are relaxed, respectively, while the corresponding bottom layers are fixed.

To validate the methods and models, the convergence of the results was checked by increasing the plane wave kinetic energy cutoff (E_{cut}), the number of k -points sampling, vacuum thickness, and the number of layers on the $T_{\text{Fe}/\text{C}}$ termination of the $\text{Fe}_4\text{C}/\text{oct}$ (100) surface. The results in Table 1 show that the changes of the surface energy are less than 0.019 J/m^2 (or 0.85%), indicating that the methods and models used for the calculations are reliable.

3. Results and discussion

3.1. Bulk properties

Several physical parameters of Fe_4C are shown in Table 2. For fcc γ -Fe, the vacancy radii of the tetrahedral and octahedral sites are 0.404 and 0.745 Å, respectively. It is to note that these radii are smaller than the atomic carbon radius (0.760 Å [18]). Hence, inserting C atom into the lattice would expand the lattice constant, and a larger expansion would be expected in $\text{Fe}_4\text{C}/\text{tet}$ than in $\text{Fe}_4\text{C}/\text{oct}$. As shown in Table 2, the calculated lattice constants for

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