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Full Length Article

Adsorption and dissociation of CH_4 on graphene: A density functional theory study

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ABSTRACT

To investigate the mechanism of the heterogenous reactions during the Chemical vapor infiltration (CVI) process of carbon/carbon composites, the dissociation of CH_4 on graphene was calculated by density functional theory (DFT). Graphene was used as the adsorption surface in the course of the heterogenous reactions. Based on the energy analysis, the preferred adsorption sites of $CH_x(x = 0–4)$ and H on graphene were obtained. Then, the stable co-adsorption configurations of $CH_x/H(x = 0–3)$ on graphene were located. The calculation results show that CH_4, CH_3 and H prefer to be adsorbed at the top of a carbon atom of graphene, while CH_2, CH and C are favorable on the midpoint of a C—C bond of graphene. Transition state (TS) calculation shows that the dissociation of CH_4 into CH_3 and H is a rate-determining step. Additionally, by comparing the dissociation of CH_3 into CH_2 and H and the formation of C_2H_6 during the dissociation of CH_4, it is obvious that the CH_3 groups are more likely to produce ethane rather than dissociating into CH_2 and H.

1. Introduction

Carbon/carbon (C/C) composites materials are widely used in aerospace and other fields because of their excellent thermal and mechanical properties, like high specific strength, high specific modulus, good fracture toughness and wear resistance at high temperature [1–4]. Chemical vapor infiltration (CVI) is one of the most important methods to produce C/C composites [5–7], which usually uses hydrocarbons as carbon precursor, such as methane [8–10]. And methane will be dissociated under such high temperature and other specific conditions of CVI. During the formation of C/C composites, there are many kinds of molecules, radicals and carbon species formed by heterogenous reactions [11]. Therefore, it is essential to understand the heterogenous reactions involved in pyrocarbon deposition, which will help to optimize the CVI process of C/C composites.

A lot of work has been performed by researchers to study the mechanism of CVI process. Li et al. [12], proposed a model in which acetylene, ethylene and benzene were used as the carbon precursors to explain the elementary reaction mechanism of the CVI process. In this model, a lumped surface reaction mechanism was put forward, and the data of the surface reactions was acquired by combining the experimental results and simulated results. Becker and Huttinger [13] used active surface sites to analyze the deposition reactions including adsorptions, surface reactions and desorption. This is the first model to describe the pyrocarbon deposition and gas phase chemistry that is based on the Langmuir–Hinshelwood kinetics. Lacroix et al. [14], developed a heterogenous mechanism to describe the surface reactions of the pyrocarbon deposition using propane on carbon fibers. It showed that the simulation results were in good agreement with the experimental results for both the gas phase composition and deposition kinetics.

As mentioned above, although there are many detailed studies about the mechanism of the CVI process, there is no report on heterogenous reactions from the atomic level. Even though there are indeed lots of research about the adsorption and dissociation of the hydrocarbon molecules (like methane) on metals [15–20], while the deposition on carbon materials has never been considered. For example, Wang et al. [21] investigated the dehydrogenation of CH_4 on Rh(1 1 1), Rh(1 1 0) and Rh(1 0 0) surfaces, and elucidated the favorable adsorption sites and dehydrogenation mechanism of CH_4. Zhang et al. [22] investigated the adsorption and dissociation of CH_4 on Pt(*h k l*) surfaces using Density Functional Theory (DFT) method.

Recently, graphene has been widely studied for its fundamental aspects and other applications, such as the thermal transport property [23,24] and catalysis [25]. In this study, graphene was used as the adsorption surface during the heterogenous reactions. Because the atomic structures of the carbon fibers and the deposited pyrocarbon in the C/C composites are both turbostratic graphite structure [26–28],

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and graphene is a typical single layer graphite, to simplify the calculation, it is reasonable to consider graphene as the ideal microstructure of the adsorption surface. Methane was used as the carbon precursor gas. The sequential dehydrogenation of CH_4 on graphene was investigated and the formation of C_2H_6 during the dissociation of CH_4 was compared with the dissociation of CH_3 into CH_2 and H. Besides, the adsorption configurations of $CH_x(x = 0–4)$ and H on graphene and the co-adsorption configurations of $CH_x/H(x = 0–3)$ on graphene were calculated. Due to the complexity of the heterogenous reactions, this study discusses the adsorption and dissociation of CH_4 on graphene.

2. Computational details

2.1. Method

All the calculation of the density functional theory was performed using Dmol^3 [29,30] module implemented within the Materials Studio of Accelrys, Inc [31]. The electron exchange and correlation interactions were described by the Perdew-Burke-Ernzerhof (PBE) function within the generalized gradient approximation (GGA) [32]. The k-point meshes for Brillouin zone sampling were sampled with a 3 × 3 × 1 Monkhorst-Pack grid. The convergence criteria for structure optimization were set to 1.0×10^{-6} eV/atom, 1.0×10^{-5} eV/atom, 2.0×10^{-3} Ha/Å and 5.0×10^{-3} Å for the tolerance of SCF (self-consistent field), energy, maximum force, and maximum displacement, respectively. The double-numeric quality basis set with polarization functions (DNP) and all electron basis sets were used for all atoms. The smearing value was chosen as 0.005 and the spin unrestricted was selected.

The transition states structures and the reaction pathways were located by using the complete LST/QST method [33]. First, the linear synchronous transit (LST) maximization was conducted followed by an energy minimization in directions conjugate to the reaction pathway. Then, the TS approximation was used to perform quadratic synchronous transit (QST) maximization. After that, another conjugate gradient minimization was processed. Finally, a stationary point would be located when the cycle was carried out. The convergence criterion for TS calculations was set to 2.0×10^{-3} Ha/Å. The frequencies of the geometry optimization and TS search were both calculated with the same method, and the TS confirmation was performed on each transition state to ensure the validity of both reactants and products.

2.2. Model

In this study, a periodic 5 × 5 graphene supercell containing 50 carbon atoms was constructed. The lattice parameters were 12.30 Å, 12.30 Å and 20.00 Å in the a, b and c directions, respectively, which prevented interactions between periodic images. Three adsorption sites were considered for graphene in this work, namely, top of a carbon atom (Top), the midpoint of a C—C bond (Bridge), and the center of a hexagonal carbon ring (Center), as indicated in Fig. 1. It is accepted that the adsorption energy can be a criterion to evaluate the adsorption effect, which means that the adsorption effect would be better with the increase of the value of adsorption energy. The adsorption energy (E_{ads}) can be defined using Eq. (1):

$$E_{ads} = E_{graphene+\mathrm{CHx}(x=0-4)} - (E_{graphene} + E_{\mathrm{CHx}(x=0-4)}) \tag{1}$$

where $E_{graphene+\mathrm{CHx}(x=0-4)}$ is the total energy of the optimized graphene system on which the $CH_x(x = 0–4)$ is adsorbed, and $E_{graphene}$ and $E_{\mathrm{CHx}(x=0-4)}$ are the energies of the pristine graphene and the $CH_x(x = 0–4)$, respectively. The values of E_{ads} are all supposed to be negative. Besides, the equilibrium distance (d) is defined as the distance between the carbon atom of $CH_x(x = 0–4)$ and graphene plane (Top, Bridge or Center).

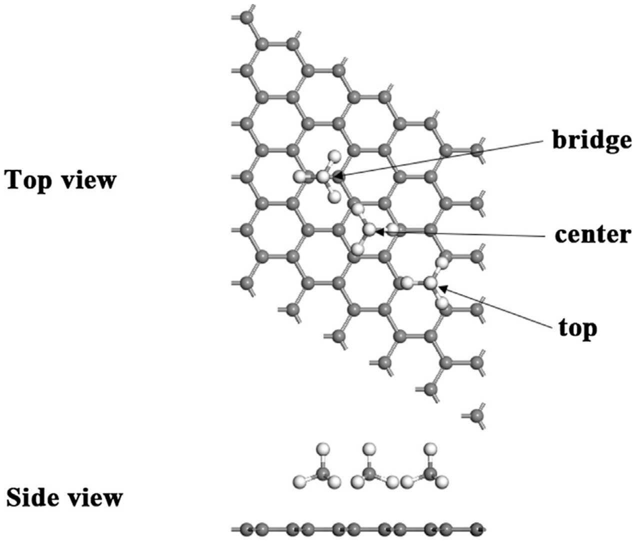

Fig. 1. Top view and side view of methane adsorbed on three sites of graphene: bridge site, center site and top site. C and H atoms are shown in the grey and white colors, respectively.

Table 1
The calculated adsorption energies (E_{ads}) and structural parameters for $CH_x(x = 0–4)$ on graphene.

	Site	E_{ads} (eV)	d (Å)
CH_4	Top	−0.33	3.358[a]
CH_3	Top	−0.46	1.585[a]
CH_2	Bridge	−2.94	1.515[b]
CH	Bridge	−2.20	1.482[b]
C	Bridge	−1.36	1.308[b]
H	Top	−1.52	1.128[a]

[a] For the distance from the C atom of $CH_x(x = 0–4)$ to the C atom of graphene right under the CH_x.

[b] For the distance from the C atom of $CH_x(x = 0–4)$ to the nearest C atom of graphene.

3. Results and discussion

3.1. Calculation of CH_4 molecule and graphene

At the very first beginning of this computational study, to ensure that the calculation method of this study is precise and credible, it is quite essential to figure out the optimized geometry structure of the CH_4 molecule and graphene, respectively. The C—H bond length and ∠H—C—H angle of CH_4 obtained from this calculation are $r_{(C\text{-}H)} = 1.097$ Å and $\theta_{(H\text{-}C\text{-}H)} = 109.471°$, which are in consistent with the experimental data of 1.096 Å and 109.4°, respectively [34]. And the results indicate that the C—C bond length of graphene is measured to be 1.42 Å, which is exactly the same as the experimental value of 1.42 Å for graphite and graphene. At the same time, the ∠C—C—C angle is equal to 120° and the optimized graphene retains the planar form. As a consequence, the above results clearly confirm the credibility of this calculation method.

3.2. Adsorption of $CH_x(x = 0–4)$ and H on graphene

Before investigating the mechanism of CH_4 dissociation on graphene, it is supposed to work out the individual bonding nature of all the related species adsorbed on graphene. Therefore, it is essential to study all the different adsorption sites of the species to get the most stable configurations of the $CH_x(x = 0–4)$ and H adsorbed on graphene. Then, the steadiest configurations of the $CH_x/H(x = 0–3)$ co-adsorbed on graphene can be obtained. After that, the dehydrogenation

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