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Full Length Article

Theoretical investigation on the adsorption and dissociation behaviors of $TiCl_4$ on pyrolytic carbon surface

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ABSTRACT

We present a theoretical investigation of the reaction mechanism of $TiCl_4$ dissociation on pyrolytic carbon surface and discuss the influence of H atom on adsorption and dissociation behaviors of $TiCl_4$ by using density functional theory. The adsorption behaviors of $TiCl_x$ (x = 4-0) and the interactions between pre-adsorbed H atom and $TiCl_x$ are studied by calculating adsorption energies E_{ads} and interaction energies H_{Ti}, respectively. The pre-adsorbed H atom significantly facilitates the adsorption of $TiCl_x$ on pyrolytic carbon surface. Specially, $TiCl_3$ adsorption on pyrolytic carbon surface converts from an endothermic process into an exothermic process due to the present of pre-adsorbed H atom. The calculation results of H_{Ti} show that the interactions between pre-adsorbed H atom and $TiCl_x$ are attractive. The dissociation of $TiCl_4$ on pre-adsorbed H pyrolytic carbon surface is an exothermic process, and $TiCl_4 \rightarrow TiCl_3$ is the limited step. The dissociation barriers of each step are less than 1.5 eV except for TiCl → Ti, which does not need to overcome any barriers, that is to say, once TiCl is adsorbed on pre-adsorbed H surface the reaction of TiCl → Ti spontaneously occurs. It thus can be concluded that the dissociation of $TiCl_4$ on pyrolytic carbon surface is a favorable process as long as H_2 molecular have decomposed into atomic H and adsorbed on pyrolytic carbon surface, and the intermediate species ($TiCl_3$, $TiCl_2$ and TiCl) play an important role on the titanium CVD deposition. We also study the adsorption behavior of H atom and the dissociation behavior of H_2 molecular on pyrolytic carbon surface.

1. Introduction

Pyrolytic carbon (PyC), the disordered nanocrystalline graphitic material formed through gas phase dehydrogenation (or pyrolysis) of hydrocarbons and subsequent deposition on surfaces, is a very important kind of carbon materials [1–5]. PyC are extensively used in many potential applications owing to its good thermal and electrical conductivity as well as high durability and chemical and wear resistance [6–11]. In particular, due to the dominating sp^2 bonding, biocompatibility, and chemical inertness, PyC has been used as an alternative material for lithium-ion battery [12] and bioelectrochemical systems (BESs) [13–19] instead of graphite, graphene, and carbon nanotube (CNT). Moreover, catalyst free synthesis of PyC permits coating of metal and dielectric substrates of any shape [20,21]. It is well-known that pure titanium film is usually used as a transition layer in carbon-based materials [22–25]. Otherwise, due to its excellent properties, such as good mechanical properties, low elastic modulus, corrosion resistance, a low level of toxicity, and a high level of biocompatibility [26–33], titanium also has been used in chemical industries and BESs [34,35]. Therefore, PyC/Ti coating is expected as a novel potential material in BESs.

Chemical vapor deposition (CVD) is an advanced manufacturing technique for surface coating, which represents a straightforward technique for depositing homogeneous nanocrystalline films with good step coverage, even on complex shapes. Thin films and coatings made by CVD methods usually show better adhesion and higher internal stress than by other techniques [36]. In addition, CVD methods can produce single layer, multilayer, composite, nanostructured and functionally graded coating materials with well controlled dimension and unique structures at low deposition temperatures and in a short time [37]. It is thus potentially important to understand the mechanism of CVD process. CVD growth generally involves the following key steps: (1) active gaseous precursor dissociation; (2) atom diffusion on the substrate; (3) formation of the nucleation islands; and (4) growth of islands. It is obvious that the first dissociation process is the precondition for the coating growth and the decomposition products directly determine further coating growth mechanism. Although common stable titanium halides including TiX_4, TiX_3, and TiX_2 (X = Cl, Br, and I) have been used as the precursors for titanium deposition by CVD

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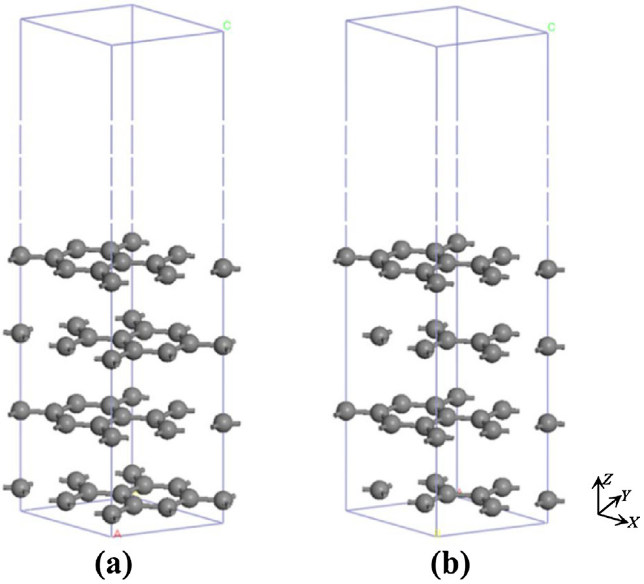

Fig. 1. Schematic structures of graphite (0001) (a) and the constructed PyC surface (b) 2 × 2 supercell.

method [38,39], their high boiling points make them hard to be vaporized and therefore not easy to be introduced into the reaction chamber except for $TiCl_4$. So, in this work using $TiCl_4$ as precursor, we present a systematic study on the possible dissociation mechanism of $TiCl_4$ on PyC surface during titanium CVD deposition by employing density functional theory (DFT).

According to the previous experimental and theoretical reports, when $TiCl_4$ is used as titanium precursor in a CVD process, it is possible that small amounts of one or more gaseous subchlorides (TiCl, $TiCl_2$ or $TiCl_3$) are produced during the process of titanium atoms from $TiCl_4$ [40–46]. It is worthy to mention that when $TiCl_2$ and $TiCl_3$ as precursors to form pure titanium thin films by CVD method can disproportion to form $TiCl_4$ and Ti at 450–700 °C [39]. The obtained $TiCl_4$ can be reused as the precursor for titanium deposition. On the other hand, H_2 is usually used as the reactant gas when $TiCl_4$ as the precursor. Thus, in order to understand how H_2 influencing and controlling the quality of titanium coating, a fundamental insight into the mechanism of $TiCl_4$ dissociation under H_2 co-existence is important. Here, we firstly discuss the adsorption and dissociation of H_2 molecule on PyC surface, and then determine the adsorption behaviors of $TiCl_4$ and its intermediate species, $TiCl_x$ (x = 3-1), on the clean and H-preadsorped PyC surface by calculating the adsorption energies. Finally, the influences caused by the co-existence H to $TiCl_x$ (x = 4-0) and dissociation behaviors of $TiCl_x$ are discussed.

2. Computational detail

2.1. Method

The calculations are performed within DFT formalism with a plane wave basis set and using pseudopotentials [47,48] to describe the ionic potentials. The generalized gradient approximation (GGA) of PBE (Perdew-Burke-Ernzerhof) functional is employed to describe the exchange-correlation functional [49]. The plane wave code CASTEP [50,51] and Dmol3 [52,53] are used. The Kohn-Sham equations [54] are solved by a self-consistent field (SCF) procedure, and the SCF convergence criterion is set to 1.0×10^{-6} eV/atom. Geometry optimization and adsorption energy are calculated in CASTEP code. Calculations are performed using a 500 eV cut-off energy and a 6 × 6 × 1 *k*-point sampling grid. Geometries are optimized by using the Broyden-Fletcher-Goldfard-Shanno (BFGS) algorithm [55] until energy, maximum force, and maximum displacement are converged to 1.0×10^{-5} eV/atom, 0.01 eV/Å, and 0.002 Å, respectively.

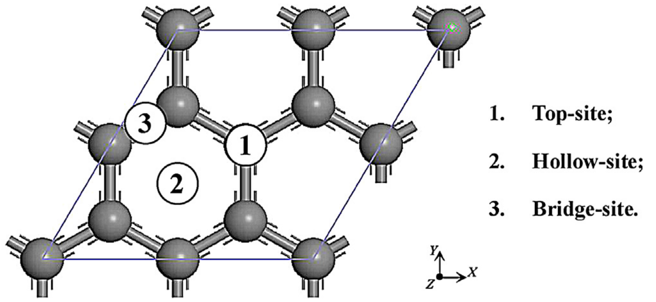

Fig. 2. Top views of PyC surface and three possible adsorption sites. The grey balls denote carbon atoms.

The minimum energy pathway (MEP) in the present work is calculated by the linear synchronous transit (LST/QST) [56,57] and nudged elastic band (NEB) [56] methods, as implemented in Dmol3 code. To accurately calculate MEP, the double numeric quality basis set with polarization functions (DNP) and GGA-PBE exchange-correlation functional are both used. We set the convergence thresholds to be 10^{-5} Ha, 0.001 Ha/Å, and 0.005 Å, for energy, force, and displacement, respectively. 6 × 6 × 1 *k*-point sampling grid is also used to calculate the MEP. To get reliable results, we set the real-space global orbital cut-off radius to be as high as 5.2 Å and the smearing of electronic occupations to be 0.005 Ha. In addition, for each structure along the MEP, the vibrational frequencies are computed at the same level to confirm that a transition state has one and only imaginary frequency. Considering the effect of van der Waals (vdW) interactions between the PyC surface and the adsorbates, a semiempirical DFT-D2 force-field approach which includes vdW interaction, is employed in all calculations.

2.2. Model

According to the previous reports, PyC belongs to the family of turbostratic carbons (TCs) due to slipped or randomly oriented basal planes of crystallites. The carbon atoms in TCs are also bonded by sp^2 hybrid orbits in a plane which, in analogy with the (0001) plane of graphite, is called the basal plane. The basal plane has a high strength just as in graphite due to the strong covalent bonding of carbon atoms. However, in TCs, the basal plane are not stacked along *c*-axis in a regular ···ABABAB··· manner, they will be rotated with respect to each other about [0001] through arbitrary instead [58]. The bonding between the basal planes is of weak vdW type. The random stacking of the basal planes in TCs will result in that interplane spacing is not a fixed constant but is variable, with an average value that is slight larger than the interplane spacing in graphite (3.345 Å).

Firstly, the surface is obtained by cutting graphite along [0001] direction and four-layer slab is chosen. Secondly, the second and forth layers are moved along the direction parallel to the surface until the basal planes are stacking as ···AAA··· manner. Finally, a vacuum layer as large as 20 Å is used along the *c*-axis normal to the surface to avoid periodic interactions. A (2 × 2) supercell is used to model the coverage of a 1/8 monolayer. Fig. 1 shows the structures of graphite (0001) and the constructed PyC surface 2 × 2 supercells. To make sure whether the constructed surface model is reasonable, the (2 × 2) supercell is fully optimized to check the interlayer distances. After fully relaxation, the interlayer distances of the surface model are 3.399, 3.401, and 3.400 Å, respectively, slightly larger than the interplane spacing of graphite, in agreement with the pre-