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Migration and desorption of hydrogen atom and molecule on/from graphene

Hoai T. Nguyen [a], Lam K. Huynh [a, d], Thanh N. Truong [b, c, *]

[a] Institute for Computational Science and Technology, Ho Chi Minh City, Viet Nam
[b] Department of Chemistry, University of Utah, Salt Lake City, UT, USA
[c] Hoa Sen University, Ho Chi Minh City, Viet Nam
[d] International University, Vietnam National University, HCMC, Quarter 6, Linh Trung Ward, Thu Duc District, Ho Chi Minh City, Viet Nam

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ABSTRACT

Migration and desorption of hydrogen atom and molecule on/from graphene are crucial for understanding mechanism of the hydrogen storage in graphene and graphene synthesis. All possible hydrogen atom migration, hydrogen atom and hydrogen molecule desorption from single layer graphene have been studied systematically by using functional density theory B3LYP/6-31G(d). Our results show that the hydrogen atom desorption is energetically favorable with the lowest desorption barrier of 149.3 kJ mol^{-1} from stable hydrogen adsorption sites, while the migration is restricted due to high barriers which are greater than 191.0 kJ mol^{-1}. Hydrogen molecular desorption is possible only from edge adsorbed hydrogen atom due to its comparable barrier of 149.9 kJ mol^{-1}. Other hydrogen molecular desorption pathways are less likely due to small population of the reaction species.

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1. Introduction

The migration and desorption of hydrogen atom and molecule on graphene are central to a number of important processes involving graphene such as the transformation between hydrogenated graphene (HG or graphane), graphene synthesis or graphene as a hydrogen storage material. For instance, in graphene synthesis it can be made from graphite via top-down approaches (e.g., exfoliation methods). However, graphene produced by these approaches require multi-steps and thus offer low yields, high production cost, and are unable to perform mass production and thus unsuitable for commercial electronic applications [1–3]. Alternative strategy to graphene synthesis is using bottom-up approaches (e.g., chemical vapor deposition (CVD), epitaxial growth on silicon carbide, and other methods). These methods produce good quality material, but require rather harsh growth conditions [1]. To improve production conditions, it is possible to produce graphene from hydrogenated graphene. Wang et al. [4] proposed a new route to prepare CVD monolayer graphene based on the interconvertibility between graphane-like film and graphene. Graphane-like films can be prepared via plasma-enhanced chemical vapor deposition. High quality monolayer graphene are formed by thermal dehydrogenation of these graphane-like films to 500 °C. The advantage of this process against other CVD processes is its lower deposition temperature. A more recent work of Smith et al. [5] succeeded in producing fully hydrogenated graphane for the first time by hydrogenation of graphene at high pressure and temperature. They also confirmed the ability of removing hydrogen from hydrogenated graphene by annealing at 200 °C.

In addition, understanding the migration and desorption of hydrogen atom and molecule on graphene is critical for effective use of graphene as materials for hydrogen storage [6–8]. In hydrogen fuel cells the issue of storage and transport of hydrogen is a worrisome problem for actual applications [9]. Many efforts have been made to overcome that limitation and develop a better design for hydrogen storage, hydrogen batteries and hydrogen fuel cells. High hydrogen storage capacities were reported for carbon nanostructures via spillover mechanism. Hydrogen spillover is a mechanism where dissociation of hydrogen molecule and chemisorption, migration of hydrogen atom take place on the surface of metal-doped carbon structures [8,10]. In light of this, fundamental understanding of the adsorption/desorption hydrogen molecules and migration mechanism of hydrogen atom on graphene surface is of particular importance.

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* Corresponding author. Department of Chemistry, University of Utah, 315 South 1400 East, rm 2020, Salt Lake City, UT, USA.
E-mail address: truong@chem.utah.edu (T.N. Truong).

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Despite theirs importance, to the best of our knowledge to date, these mechanisms have not been studied in details. Several experiments confirmed such hydrogen adsorption/desorption processes. In particular, Elias et al. [7] utilized characterization techniques such as atomic imaging and electrical transport measurements to verify graphene can be converted to graphane. Limited information is available from previous density functional theory calculations. For instance, electronic structure, total energy, structural distortions and magnetism of hydrogenated graphene were theoretically investigated by Boukhvalov et al. [6]. The authors proposed that stable configurations of hydrogenated graphene can be produced from hydrogen chemisorption on the two different carbon sites. However, they did not take into account the differences between graphene edge and interior carbon sites. Chandrachud et al. [11] investigated the change in physical properties namely the transformation from a semi-metal graphene to an insulator graphane or a semiconductor hydrogenated graphene, and thus extends the applications of graphene in certain electrical devices where semiconductors and insulators are needed. From DFT calculations, Han et al. [8] reported that the chair-like all-paired configuration of hydrogenated graphene can satisfy the thermodynamic requirement for room-temperature hydrogen storage. Besides, there is a high migration barrier for hydrogen along graphene surface, thus limits hydrogen spillover mechanism. However, their results only accounted for the hydrogen migration on interior sites of graphene. It should be noted that graphene edge sites may play a significant role in this mechanism.

In this research, by using density functional density, we have carried out extensive and systematic study of the migration and desorption of hydrogen atom and molecule on graphene at the atomistic level. The aim of this study is to improve the understanding of these processes. The paper particularly focuses on studying possible pathways for the hydrogen adsorption/desorption and the migration of hydrogen atoms on both the edge and interior carbon sites of graphene. The results of this study can be used as a basis for constructing kinetic model for simulations on the hydrogen migration and desorption on/from single layer graphene.

2. Computational details

The migration and desorption of hydrogen atom and molecule on graphene was investigated using a six six-member ring carbon model as shown in Fig. 1. The letters label different carbon sites for later discussion. Note that this model contains all types of carbon edge sites, namely a, b, k, l are armchair sites, c is the tip-shape site, d, e and f are zigzag sites, g, h, i, and j are interior sites. Density functional theory B3LYP [12], combined with the 6-31G(d) basis set was used in all cases. Full geometry optimizations and vibrational analyses were performed at all stationary points to confirm their nature, namely equilibrium point with no imaginary frequency or transition state with one imaginary frequency whose mode corresponding to the reaction coordinate. In addition, intrinsic reaction coordinate (IRC) [13,14] calculations were performed for each transition state to verify its corresponding reactants and products. All calculations were done using the Gaussian 09 program [15].

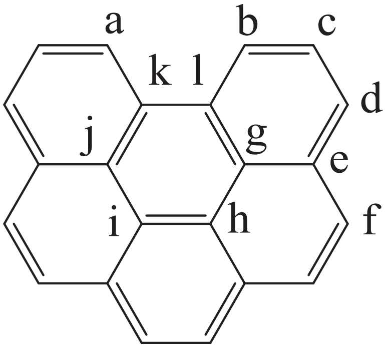

Fig. 1. 2D representation of graphene model. The letters label different carbon atom sites.

3. Results and discussion

The hydrogen migration and desorption on/from graphene surface involves three main processes: H atom migration, H atom desorption, and H_2 desorption. Since H atom desorption and H atom migration are on the same global potential energy surface and thus it is more convenient and informative to discuss them together.

3.1. Hydrogen atom migration and desorption on graphene surface

Potential energy profiles for hydrogen migration on a graphene surface is important for understanding the spillover mechanism which was employed when exploring the use of graphene as hydrogen storage materials [8,10]. The hydrogen spillover mechanism involves three steps: 1) the dissociation of hydrogen molecule takes place on the surface of metal nanoparticles; 2) these hydrogen atoms move from metal nanoparticles to graphene surface; and 3) hydrogen atoms migrate along the graphene surface [10]. The understanding of hydrogen migration and desorption on/from graphene contributes to the understanding of this mechanism. Since hydrogen atom can adsorb on different edges or basal/interior sites of graphene and thus potential profiles for migrations amongst these sites would vary.

In this study, we consider all possible migration pathways from a stable hydrogen atom adsorbed sites along the armchair, zigzag edges and basal plane sites (see Fig. 2). In particular, with the site notations given in Fig. 1, these migrations are:

$$\mathrm{Hxy}:[\mathrm{C_x}]\mathrm{H_2}+[\mathrm{C_y}]-\mathrm{H}\rightarrow[\mathrm{C_x}]-\mathrm{H}+[\mathrm{C_y}]\mathrm{H_2} \quad (1)$$

x and y are carbon sites.

The optimized structures of the stable species are shown in Fig. 2, while the transition state structures are given in Fig. 3. The calculated total electronic and relative energetics for all species are available in Supplementary (Table S1) and the energy profiles relative to the most stable hydrogen adsorbed site Hb are displayed in Fig. 4. In these Table and Figures, Hx denote stable sites, Hx→y denotes the transition state structure for migration of a hydrogen atom from site x to site y.

First, structures and relative stabilities of different species Hx are briefly discussed. It has been experimentally observed that hydrogen was added to interior sites of the graphene lattice as well as along edges [16]. These sites can be either hydrogenated carbon sites or non-hydrogenated carbon sites. Hydrogenated carbon sites are carbon edge sites which bind to a hydrogen atom >CH such as the a, b, c, d, and f sites while non-hydrogenated carbon sites >C- are mostly the interior carbon sites which have no hydrogen termination such as the e, j, k, and l sites. When a hydrogen atom is adsorbed on a carbon site, the site transforms from a sp^2 to sp^3 configuration and thus it pulls the carbon atom out of the graphene plane and disrupts the resonance structure of the conjugated π-bonds in the graphene plane. The distortion is more so for non-hydrogenated carbon sites and as a consequence, the structures (Hj, Hl, Hk, He models) are less stable or have higher relative energies than others (Ha, Hb, Hc, Hd, Hf). In particular, adsorption of H atom on a hydrogenated carbon sites b and d has the least