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Theoretical study on hydrogen storage capacity of expanded h-BN systems

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ABSTRACT

In this work, the hydrogen storage capacity of the expanded hexagonal Boron Nitride (eh-BN) systems has been presented. We have employed a new equation of state (EOS) for hydrogen gas to figure out the hydrogen density distribution profiles in the eh-BN systems. In this regard, the environmental conditions (i.e., temperature and pressure) are considered in the prediction procedure using DFT single point calculations. The eh-BN systems with different layer spacings are studied by PBE method with consideration of the long range dispersion corrections. On account of the in-plane polar bonds, a series of adsorption positions are considered. Additionally, the adsorption energy and hydrogen density profiles are reported. Furthermore, the relation between uptakes and the interlayer spacings with the effects of the environmental conditions are also provided. The limit of the physical hydrogen storage capacity in a perfect eh-BN system at 243 K and 10 MPa is founded to be 2.96 wt.%.

1. Introduction

As one of the most promising clean energy source, the compact storage and safe delivery are the main challenges for the application of the hydrogen energy. The short-term goal of the designed novel hydrogen storage materials is to reach the gravimetric density limit of hydrogen, i.e., 5.5 wt.% and 0.04 g/cm^3 at ambient temperature and pressure by the year 2017, which is targeted by the U. S. Department of Energy. In the automobile industry, to fuel a typical vehicle, the hydrogen storage system is required to contain at least 7.5 wt.% and 0.07 g/cm^3 hydrogen fluid at the acceptable limit $T = 243$ K and $P = 10$ MPa [1]. Another notable criterion includes the system recyclability. The hydrogen molecule should also be able to be desorbed from the storage system under ambient conditions. Hence, the adsorption energy of a single hydrogen molecule in an effective storage system should lie between the physisorbed and chemisorbed states. More precisely, this adsorption energy needs to be around 0.1–0.3 eV per H_2 molecule [2–4].

Initially, the perfect graphene was considered as the most promising hydrogen storage material owing to its large surface area and light weight. It has already been confirmed that the perfect monolayer graphene do not have strong hydrogen storage capability ascribe to its surface inertia. However, graphene is still a rational model to test and verify the theoretical methods for gas storage prediction due to its intrinsically simple structure and high symmetry. The monolayer h-BN has nearly identical geometrical configuration as graphene. On the other hand, the B-N bond is a sort of in-plane polar bond. In this situation, the distribution of the hydrogen molecules on the h-BN surface is more complicated than that on graphene. Therefore, a purposeful test for theoretical method with monolayer h-BN model is worthwhile. Moreover, the polar B-N bond was expected to bring greater hydrogen storage capacity than the C-C band in graphene. For this reason, many nanostructures based on the h-BN have also been studied as molecule adsorption materials [5–7]. Zhao et al. [5] claimed that a 7.69 wt.% hydrogen storage capacity was found in the graphene/boron nitride heterobilayer system through the theoretical studies at LDA level. Another even higher theoretical uptake value, around 8.7 wt.%, was found in the Li-decorated hybrid boron nitride and graphene domains by Hu et al. [6], also at LDA level. Oxygen-doped BN nanosheets were studied by Lei and co-workers [8], experimentally and theoretically. The system had 5.7 wt.% capacity for hydrogen storage under 5 MPa at room temperature. Recently, Kumar et al. [9] presented the importance of the bond exchange spillover mechanism in the h-BN nanostructures as hydrogen storage materials. A 7.4 wt.% uptake was predicted in the h-BN nanostructures at GGA level with dispersion correction in their work. At once, Zhang et al. [10] studied the

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Li-doped porous BN material for hydrogen generation and storage. The authors reported a 7.5 wt.% theoretical uptake derived from the around 0.16 eV adsorption energy in such systems. However, the theoretical predictions via DFT calculations always seem to be overly optimistic because of the missing thermodynamic information.

The most theoretical studies on the hydrogen material design are based either on the DFT calculations at ground state, or on the statistical mechanic methods, e.g. the molecular dynamics (MD) or Monte-Carlo (MC) simulations [11]. The advanced QM/MD-μVT simulation [12] is until now still expensive and time-consuming. Morris' group, following the works of Patchkovskii [13] and Cabria [14], combined the DFT single point calculations and the thermomechanical boundary conditions by using an effective continuum model together to predict the hydrogen and methane uptakes in nanoporous carbons [15–18]. This method can provide the hydrogen storage capacity with full thermodynamic information only via a series of DFT single point calculations. The time for the thermodynamic simulations can be saved in this way. A new EOS for hydrogen fluid is introduced in our previous work [19] to improve the prediction accuracy of this combination method. The determination of the fugacity coefficients of the hydrogen fluid is the key point in a similar prediction research. We believe that with the help of our EOS, the fugacity coefficients of the hydrogen fluid can be estimated with full physical meanings, and show very good agreements with the experimental results at reasonable temperatures and pressures.

The eh-BN is a simple and effective theoretical model of the nanoporous h-BN material. In the present work, the relation between the storage capacity and the interlayer spacing (i.e., the pore size) is discussed to find the storage limit of the eh-BN systems at certain temperature and pressure. This work is organized as follows: In Section 2, the models of the hydrogen molecule and eh-BN systems will be introduced. The simulation method and parameter arrangement will be presented there, too; In Section 3, the main simulation results will be presented and discussed. The adsorption energy map and the pressure profiles inside the eh-BN systems will be shown. The relation of the hydrogen uptakes to the interlayer spacings of the eh-BN will be discussed; A short conclusion will be given in Section 4.

2. Methodology

As a premise, the gas storage system in this research is assumed to be in equilibrium. As known, one of the most important equilibrium condition is that the chemical potential should be a continual function at the spatial boundary, i.e., the chemical potentials in the external free gaseous phase and in the adsorbed phase should have the identical values on the boundary line. Therefore, the following equation should be ensured in the adsorbed phase and the free gaseous phase:

$$P_{in} = \frac{\phi_{ext}}{\phi_{in}} P_{ext} \exp\left[-\beta E_{in}^{ads}\right], \tag{1}$$

where the subscripts *in* and *ext* denote the adsorbed phase inside the material system and the external free gaseous phase, respectively. β is the inverse of $k_B T$, where k_B is the Boltzmann constant. The adsorption energy is marked as E_{in}^{ads} in Eq. (1). The fugacity, $f = \phi P$, is introduced in the calculation as an effective pressure to describe the chemical thermodynamic process. The fugacity coefficient ϕ can be fixed at particular temperature T and pressure P by

$$\ln \phi(T,P) = \frac{1}{RT} \int_0^P \left(V_m(P') - \frac{RT}{P'}\right) \mathrm{d}P', \tag{2}$$

where V_m denotes the molar volume of the gas, and R is the Avogadro constant. The molar volume V_m can be numerically determined with the aid of the virial expansion of the EOS for a real gas:

$$\frac{PV_m}{RT} = 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \frac{D(T)}{V_m^3} + \cdots, \tag{3}$$

where $B(T), C(T)$ and $D(T)$ are the second, third and fourth virial coefficients, respectively. According to our previous work [19], until the fourth virial term is taken into account, the accurate fugacity coefficients of the normal hydrogen gas can be obtained compared with the experimental values. Details for how to determinate these virial coefficients can be found in our previous work [19].

A Gaussian type effective potential is introduced by Feynman and Hibbs (FH) in their book [20] to get rid of the quantum derivation between the experimental results and the Lennard-Johns (LJ) simulations. The Taylor expansion until second order for FH-effective potential [21] is employed to describe the body-body interaction between the hydrogen moleculs, as follows:

$$U_{LJ}^{FH}(r) = U_{LJ}(r) + \frac{\beta\hbar^2}{24 m_r}\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}}{\mathrm{d}r}\right) U_{LJ}(r) \tag{4}$$

where m_r is the reduced mass of the LJ pairs. In this work, m_r is set to 1.6744×10^{-27} kg [22] for the diatomic hydrogen molecule, which is treated as an entity. The LJ-parameters used here are set exactly to be the same as in the previous work [19]. Naturally, the adsorbed and free hydrogen molecules are in two different states. However, the difference is very small owing to the essence of the physical adsorption. The electron density maps of an adsorbed H_2 molecule at certain typical positions on a monolayer h-BN are illustrated in Fig. 1. Note that the atomic configurations of the adsorption systems are fully relaxed during the calculations. According to our calculations, the largest deviation of the Mulliken charges between the adsorbed and free hydrogen molecules will not be larger than 4.7%. The change of the Coulomb interaction owing to this charge perturbation will be smaller than a percent. Considering the tiny variance, our simulations are performed with the free hydrogen model. We assume also that the hydrogen fluid keeps to be the normal form under our study conditions. The effect of the spin isomers ratio can be covered in the estimation errors.

If the hydrogen storage system is considered as a continuum model, the adsorption energy of a single hydrogen molecule in the eh-BN system can be introduced in Eq. (1) as E_{in}^{ads}, which is defined as follows:

$$E_{in}^{ads} = E_{tot}(X + H_2) - E_{tot}(X) - E_{free}(H_2), \tag{5}$$

where the X denotes the hydrogen storage material system, and $E_{tot}(X)$ represents the total energy of the material system, $E_{free}(H_2)$ points out the energy of a free hydrogen molecule, $E_{tot}(X + H_2)$ is the total energy of the material system X with an adsorbed hydrogen molecule. Note that the basis set superposition error (BSSE) is already taken into account in our calculations. Here, the energy quantities are obtained from the calculations performed by the CRYSTAL14 computer code [23]. Three all electron Gaussian basis sets of triple-zeta valence with polarization quality (TZVP) are applied for boron, nitrogen and hydrogen atoms, which are developed by Peintinger et al. [24]. It is worth mention that the adsorbed hydrogen molecules may have different spatial forms, e.g., standing or lying on the h-BN surface. Nonetheless, the physical adsorption energies of the hydrogen molecule with different spatial forms have the differences less than 10 meV. Therefore, the spatial forms of the hydrogen molecule will not affect our prediction results. On the other hand, the change of the molecule orientation in a dynamic system is caused by the dynamic energy (in other words, the tem-