Theoretical study of the adsorption properties of porous boron nitride nanosheets

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ARTICLE INFO

ABSTRACT

This paper analyzes the values of adsorption activation energy, binding energy and charge distribution between the molecules and an h-BN hexagonal boron nitride monolayer, and considers the dependence of the energy characteristics of chemisorption on the type of molecules. We provide a comparison between the processes of interaction of the single molecules and their water associates with the ordered and porous cluster surfaces. This paper addresses the physical and chemical principles of water purification from organic contamination using hexagonal boron nitride with vacancy and multivacancy defects.

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1. Introduction

Experimental and theoretical studies of an h-BN hexagonal boron nitride monolayer, and some layered structures based on it, at the moment are of great interest due to its unique properties, as well as a variety of possible applications. Mono- and few-layered h-BN nanosheets have a wide energy band gap [1], high thermal conductivity [2], high mechanical and elastic properties [1] and strong oxidation resistivity [3,4]. In addition, h-BN-related nanostructures have good adsorption properties due to a partially-ionic character of BN chemical bonds [5], and a high surface area [2,5].

One of the major goals in environmental protection is high-efficiency cleaning of water resources from various contaminants. Some high-porous layered nanomaterials based on hexagonal boron nitride have been recently developed, they have excellent adsorption properties for a wide range of oils, solvents, and dyes [6]. These materials have been successfully used to clean the contaminated water thanks to a combination of superhydrophobicity, porosity, and swelling ability. Lately, nanosheet-structured boron nitride spheres have been synthesized [7]. It is shown that these nanostructures have a high adsorption capacity and can be used for removing oil, dyes, and heavy metal ions from water.

In this regard, there is certain interest in a theoretical study on the processes of interaction of organic molecules with the hexagonal boron nitride monolayer surface. It is known that hydrocarbons can contaminate the surface of mono- and few-layered h-BN [8], as well as multilayered heterostructures based on hexagonal boron nitride and graphene [9]. Such contamination can happen, for example, when the sample is being prepared under ambient conditions. In [10] it is shown that organic particles can be completely removed from the h-BN film surface by heat treatment in Ar/O$_2$ atmosphere at 500 °C.

Here we report a theoretical study on the adsorption properties of boron nitride nanosheets containing various vacancies, also involving quantum-chemistry methods. Vacancies on the h-BN surface have been previously studied experimentally by ultrahigh-resolution transmission electron microscopy [11]. Monovacancies have been found mainly on boron, as well as some unusual triangle-shaped multi-atom vacancies with nitrogen-terminated zigzag edges. Pursuant to ab $initio$ calculations [12,13], boron and nitrogen monovacancy defects in an h-BN monolayer introduce electronic states in the energy-gap region. The energetics and electronic structure of the multiatomic vacancies have been studied in [14] using the density-functional theory (DFT). It has been found that the energetics and the atomic structure of the vacancies depend on their charge states and the

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environmental concentrations of boron and nitrogen atoms. h-BN porous nanosheets of two different structures, including the new stable phase (named inorganic graphenylene), were examined by the authors of [15] by means of *ab initio* calculation. They showed that the partial BN pairs replacement by carbon atoms significantly reduces the band gap.

Probabilities for creating different types of vacancies under ion irradiation were calculated by molecular dynamic simulations in [16]. It was shown that the total number of defects does not necessarily increase with ion energy. The *ab initio* simulations on the adsorption of molecular hydrogen on the defective h-BN sheet have proved that the vacancies reduce the barriers for H_2 dissociation in comparison to an ordered layer [17]. In [18], based on *ab initio* calculations and molecular dynamics simulations, it was shown that the hexagonal BN structures with appropriate triangular pores possess excellent H_2/CH_4 selectivity.

In this paper, we studied the adsorption of water, ethanol, ethylene glycol, and toluene molecules on the ordered h-BN sheet surface and a vacancy-containing sheet surface. We used the approach developed previously in our studies of graphene fluorination in hydrofluoric acid aqueous solutions [19].

2. Methodology

We used the $B_{48}N_{48}H_{24}$ clusters as a model system to simulate the one-layer hexagonal boron nitride nanostructures. Pore modeling was carried out by removing one atom (or several ones) from the central part of the cluster. Quantum-chemical simulation was performed using the semi-empirical schemes included in the MOPAC2012 software package [20]; unrestricted Hartree–Fock self-consistent field calculations and the PM6 approximation were done. The PM3 and PM6 approximations are suitable for modeling the hydrogen bonds because they include an extra term in the energy calculation, which may be considered as the van der Waals's attractive energy [20]. The dangling bonds at the cluster edges were saturated with hydrogen atoms. Determination of the optimized cluster geometry corresponding to system energy minimum was carried out by the Baker's Eigen Following (EF) method. In the system stationary points, the gradients on the atoms did not exceed 3 kcal/Å. Cluster geometry and total energy, atom bonds orders, value of the electron density, atom orbital populations, molecular localized orbitals were calculated.

To simulate the processes of adsorption and desorption of molecules and fragments, we used the reaction coordinate calculation. Reaction coordinate is a parameter that changes (increases or decreases) its value a fixed number of times with a certain step as a result of calculation. This parameter may be the distance between the atoms, or the angle between the bonds. In our case, the parameter was selected as r – the distance between the atom (B or N) in hexagonal BN and the atom (O, C, or H) within the adsorbate molecule. At each step of the calculation, the value changes, and the system geometry is optimized (total energy minimum is searched). The result is an adsorption curve which is the dependence of the system total energy on the reaction coordinate (Fig. 1a). The curve allows to calculate the value of the adsorption activation energy E_a and the bond energy E_b (heat of adsorption). In the simulation of dissociative molecular adsorption, we used two reaction coordinates. The distance between an atom of one dissociation fragment and the cluster was chosen as the first coordinate, while the second one was the distance between the atoms of fragments chemically bonding to the boron and nitrogen in h-BN during adsorption. For example, for ethanol adsorption on the multivacancy in h-BN by the $C_2H_5(OH) \leftrightarrow C_2H_5O + H$ reaction, we selected the B–O and O–H distances. Thus, we calculated the potential energy surface (the total energy dependence on the two reaction coordinates) to determine the minimum activation energy

of the process. Fig. 1b illustrates that the ethanol molecule from its initial state S1 approaches h-BN, maintaining its integrity up to a $\sim$ 2.3 Å distance between the boron atom of h-BN and the oxygen atom of the ethanol molecule. Then the hydrogen atom separates from the OH fragment, while the O–H distance increases and the total energy of the system drops. In the final state S2, dissociation fragments are bonded with boron and nitrogen atoms.

The value of the binding energy E_b of an atom (a molecule) to the cluster is calculated by the formula:

$$E_b = E_{sys} - (E_{BN} + E_A),$$

where E_{BN} and E_A are full energy of a pure $B_{48}N_{48}H_{24}$ cluster and an isolated atom (molecule), E_{sys} is (cluster + adsorbed particle) system total energy.

As test calculations, we simulated a number of adsorption processes: a single oxygen atom adsorption and a single hydrogen atom adsorption on the B and N atoms of the cluster (according to [4,17,21]). We used the PM6 and PM3 approximations for the calculations. For the adsorption of atomic hydrogen on the boron and nitrogen atoms, we obtained the $E_b = -0.01$ eV and $E_b = +0.36$ eV values, respectively, while applying the PM6 technique. For the oxygen atom adsorption, we obtained $E_b = -2.29$ eV (the PM6 technique). We used the bridge site (the oxygen atom moved between the atoms of boron and nitrogen over the B–N bond) as an initial approximation. Optimization has revealed that the oxygen atom forms two chemical bonds with atoms of boron and nitrogen. The calculated geometric and energy characteristics are in good agreement with the results of *ab initio* calculations performed in Refs. [4,17,21]. It should be noted that when using the PM3 approximation, we obtained overestimated values for the binding energy of the hydrogen atom with the cluster: $E_b = -0.16$ eV and $E_b = -0.12$ eV for adsorption of H on the B and N atoms, respectively, $E_b = -2.18$ eV for adsorption of O. Thus, we used the obtained clusters and the PM6 method for further simulation of vacancy defects, and for the processes of particle adsorption on the hexagonal BN surface.

In this paper, we make an attempt to find out the physical and chemical principles of water purification from various contaminants using porous h-BN, so we have chosen ethanol, ethylene glycol, and toluene molecules as adsorbates. Simulating water solutions of ethanol, ethylene glycol, and toluene is associated with certain methodological difficulties. Adsorption of molecules from the gas phase (vacuum) and aqueous solution would have different mechanisms, energy characteristics, and could result in different final states of the "surface-adsorbate" system. It is known that aqueous solutions contain some associates of the solute molecules with water molecules. We chose the following models for the associate of ethanol and ethylene glycol molecules with water: $C_2H_5(OH) + H_2O$ and $C_2H_4(OH)_2 + 2H_2O$, wherein each hydrogen atom of the alcohol molecule hydroxyl group (OH) forms a hydrogen bond with the oxygen atom of the water molecule. We have not considered a toluene molecule associate with H_2O molecules. Furthermore, pure water and aqueous solutions carry various associates of water molecules which may affect the solute molecules binding to the surface of h-BN.

As a model, we have selected a molecular associate consisting of seven H_2O molecules held by eight hydrogen bonds. In this associate, two water molecules form 3 bonds each, and five molecules form 2 bonds each with the neighboring molecules. Such geometrical model corresponds to one of the perfect polyhedra constructed of water molecules specified by computer simulation in [22]. Thus, our simulation of molecular adsorption from aqueous solutions was carried out in the framework of modeling the adsorption of adsorbate molecule associates with water molecules, therefore, the study in this paper should be viewed as an estimate one.