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Exploring the interaction of water with boron surfaces using density functional theory

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ABSTRACT

Boron-based materials have garnered significant interest in recent years as favorable candidates for storing hydrogen in various applications. This study focuses on examining the hydrolysis capabilities of boron surfaces through the analysis of water interaction with different boron surfaces via density functional theory (DFT) calculations. We include several forms of α-boron (111) (reconstructed (Rc) and unreconstructed forms (URc), defective boron), and a B_{28} subunit of β-rhombohedral boron. In addition to understanding the behavior of a single water molecule, we also look at the possible clustering effects of multiple water molecules on each surface. According to the findings, the degree of attachment between water molecules and boron surfaces relies heavily on the phase of the boron. The study revealed that defective α-boron and β-boron (B_{28}) exhibit a robust bonding with a single water molecule, as reflected in the high adsorption energies of -1.54 eV and -1.45 eV, respectively. Conversely, Rc α-boron and β-boron (B_{28}) exhibit feeble bonding with two water molecules, evidenced by their low adsorption energies of -0.62 eV and -0.69 eV, respectively. These results indicate that the process of water adsorption on boron surfaces is intricate and can differ based on the particular phase of boron.

1. Introduction

In recent years, elemental boron and boron-based compounds have attracted significant attention. Diverse applications have been proposed based on the extraordinary properties of boron (B), such as diamond-like hardness, superconductivity at high pressure, high melting point (2300°K), partially ionic bonding, and thermodynamic stability [1-8]. In addition to its elemental form, boron also appears in a wide variety of compounds and can show different behaviors in different materials [9,10].

Elemental boron has a surprising amount of complexity with many unusual allotropes, 16 in total [11,12]. However, to date, thermodynamic stability has been reported for only four boron allotropes: α-rhombohedral, β-rhombohedral, γ-boron, and T_{192}. [13]. There exist numerous configurations of solid boron, some of which include α-B_{12}, β-B_{105}, β-B_{106}, and γ-B_{28} [14,15].

The method of water adsorption on surfaces allows for theoretical description and prediction of these surfaces, as well as testing surface termination and adsorption energetics [16-21]. Water adsorption on boron surfaces has recently garnered significant interest owing to the unique properties of boron-containing materials and their prospective utility in diverse domains, including catalysis, energy storage, and electronics [22-27]. Comprehending the character of the interplay between boron surfaces and water molecules holds immense significance for advancing these applications [28-30].

The adsorption behavior of water molecules on various surfaces [17,31-36], including boron-based materials [37-39], has been effectively investigated using density functional theory (DFT). The adsorption of single and multiple water molecules on boron surfaces is a topic of great interest in the field of materials science due to its potential applications in various areas, including catalysis and energy storage [37-39]. The boron surface, in particular, is known for its unique electronic and structural properties, which can be altered by the presence of water molecules [37]. By adsorbing single and multiple water molecules on a boron surface, we can gain insight into the interactions between water and boron and how they affect the surface properties. Furthermore, the adsorption of water molecules can

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*Corresponding author: ergluesra@gmail.com also provide a way to enhance the reactivity of the boron surface, making it more useful for catalytic reactions [38]. Studying the adsorption of single and multiple water molecules on a boron surface is essential for developing new materials and advancing our understanding of surface chemistry [37-39]. Omidirad et al. investigated the charge-controlled mechanism of water molecule dissociation on vacancy-defected boron nitride nanosheets (BNNS) [37]. By utilizing DFT, the authors demonstrated that introducing a vacancy in 8x8 BNNS, in both neutral and charged states, leads to increased reactivity and energy of H_2O adsorption. This is attributed to the electron density increase in the vacancy wall, which facilitates the dissociation of water molecules. These findings shed light on the underlying physics of water dissociation on defected BNNS, and may have potential implications in various fields, including catalysis and energy conversion [37]. Feng et al. have investigated the potential of iron (Fe)-embedded boron nitride nanosheet as an efficient electrocatalyst for the oxygen reduction reaction (ORR) using DFT calculations. The study focuses on evaluating the Fe-embedded BN sheet as an electrocatalyst for ORR, along with the corresponding reaction mechanisms. The results of their DFT calculations reveal the significance of the B-vacancy site of the BN sheet as an anchoring point for Fe atom, ensuring their stability on defective BN sheet surfaces due to the strong hybridization of the Fe atom with the sp^2 dangling bonds of neighboring nitrogen atoms near the monovacancy site (with a high binding energy of 8.87 eV) [38].

Furthermore, the dissociative adsorption of water on boron surfaces is a topic of significant interest in materials science due to its potential applications in various areas, including hydrogen storage and catalysis [20]. The physical and chemical meaning of dissociative water adsorption on boron surfaces can be understood in terms of the electronic configuration of the boron atom. Boron has an incomplete valence shell, which makes it highly reactive and prone to forming covalent bonds with other atoms. When water molecules come into contact with a boron surface, the boron atoms attract the electrons from the oxygen atoms, leading to the dissociation of the water molecule. This process results in the formation of hydroxyl groups (OH) and hydrogen (H) atoms on the surface. These surface species play a crucial role in various catalytic reactions, including hydrogen evolution, CO_2 reduction, and oxygen reduction. Comprehending the significance, both in terms of physics and chemistry of dissociative water adsorption on boron surfaces is, therefore, crucial for designing efficient catalysts and developing new technologies in several fields, including energy conversion, environmental remediation, and electrochemistry [40,41].

Structural defects, intentionally and unintentionally created, can play an important role in determining the chemical properties of surfaces [42]. In general, the presence of vacant sites results in a reduction in the coordination number of vacancy generator atoms, leading to increased activity compared to other atoms on the surface [38]. These modified structures have the potential to enhance the efficiency of numerous chemical reactions, making them a promising area of exploration. Similarly, doping surfaces with metals such as Na has been an area of interest in recent years due to its potential applications in the field of electronics and energy storage [43,44]. The addition of Na atoms to boron-based surfaces can modify their electronic and chemical properties, leading to enhanced catalytic activity, improved electrical conductivity, and increased surface reactivity [43,45]. These unique properties make Na-doped boron-based surfaces promising candidates for a variety of applications [46,47].

In this work, we present a DFT exploration into the adsorption of single and multiple water molecules on various boron surfaces. As support, we have chosen the most common allotropes of boron, specifically α-boron and β-rhombohedral boron. α-boron is made up of B_{12} units and is relatively simpler. We, therefore, include reconstructed (Rc) and unreconstructed (URc), and defective forms of its (111) surface in our study. Conversely, β-rhombohedral boron has a complex structure that results in very large simulation cells. We thus restrict our studies to only a representative B_{28} subunit of β-rhombohedral boron. After an initial scan of the adsorption properties of one, two, and three H_2O molecules on the surfaces of these materials, we discuss the findings. The outcomes of our study offer valuable perspectives into the fundamental mechanisms of water adsorption on boron surfaces, which can contribute to the design and development of novel boron-based materials with improved performance in various applications.

2. Methods

All density functional theory calculations were implemented within a plane-wave using Vienna ab-initio Simulation Package (VASP) [48]. Perdew-Burke-Ernzerhof (PBE) [49] approximation was used for the exchange and correlation. The interaction between nuclei and valence electrons was modeled using the projected augmented wave approximation [50]. A plane-wave basis cutoff energy of 500 eV was applied in all calculations. The geometric optimization was performed via a conjugate-gradient algorithm with energy and force thresholds of 10^{-6} eV and 10^{-4} eV/Å, respectively. The DFT-D3 correction was utilized to model the interactions of long-range attractive van der Waals (vdW) [51]. The calculations were performed with Brillouin zone sampling with a Monkhorst-Pack [52] grid of 5x5x1 k-points for α-boron (111) surfaces, and only the Γ point was taken for the isolated B_{28} subunit of β-rhombohedral boron. B_{28} subunit was optimized in a 20x20x20 cubic simulation cell. The α-boron (111) surface and the water-adsorbed boron systems are modeled using the unit cell containing 36 boron atoms of hexagonal α-boron. The vacuum gap of 15Å was selected along the vertical direction to eliminate the interaction of periodicity. Zero temperature and zero pressure were performed during the calculations. During the course of the calculations, the adsorption energies of H_2O (or H_2) molecules on the surfaces were determined by Equation, where $E_{surface+H_2O}$, $E_{surface}$, and E_{H_2O} represent the total energy of the H_2O molecule adsorbed by the boron system, the boron surface, and an isolated H_2O molecule, respectively.

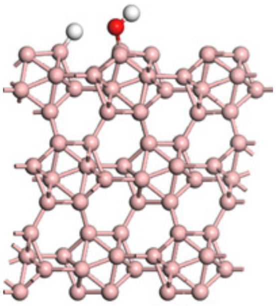
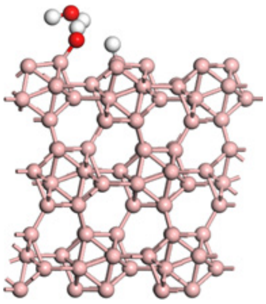
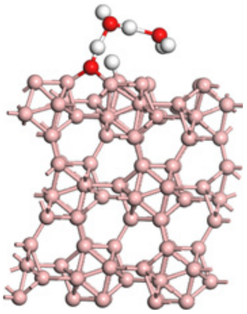
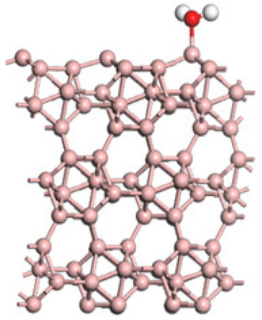
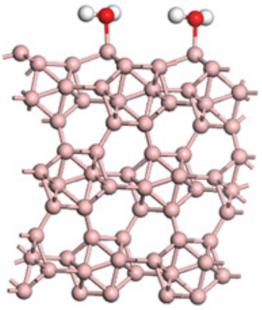
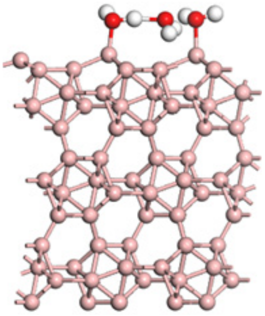
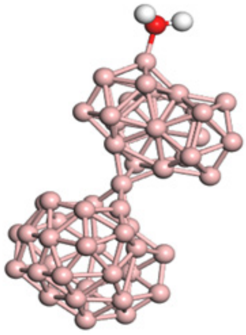
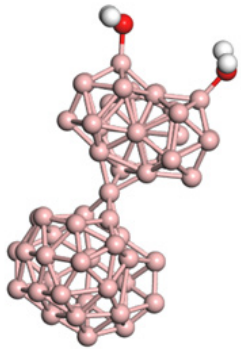
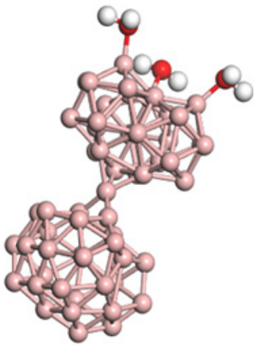
$$E_{ads} = E_{surface+H_2O} - E_{surface} - E_{H_2O} \tag{1}$$

Furthermore, we investigated the adsorption of multiple water (H_2O) molecules on a surface. To calculate the adsorption energies of the second and third H_2O molecules, we used a modified equation that takes into account the presence of the previously adsorbed molecules. Specifically, we replace the first and second terms in Eq.1 with the energy of the surface with two or three molecules, respectively, and the energy of the surface with a single molecule. This allows us to calculate the adsorption energy of the additional molecule in relation to the surface with the preceding H_2O molecules already adsorbed.

3. Results and Discussion

Table 1 summarizes the optimized geometries of one, two, and three water molecules adsorbed on the two α-boron (111) surfaces (URc, and Rc on the top and middle rows, respectively), and the B_{28} subunit of β-rhombohedral boron. In our calculations, the construction of a slab model for the URc boron (111) surface involved cleaving from the hexagonal α-boron's unit cell. This model includes a three-layered α-boron (111) slab containing 108 boron atoms and B_{12} subunits (Table 1). During the optimization process, the lowest layer was held constant, and the other two layers were permitted to move. After a scan of a few initial guesses, the adsorption geometry of a single water molecule was identified. Following this, two more molecules were adsorbed with a geometry optimization between each adsorption (Table 1). The geometry optimization for the single water molecule resulted in the breaking of the O-H bond on the URc α-boron (111) surface, causing the dissociative adsorption of the water molecule. This phenomenon refers to the breaking of water molecules into their constituent atoms upon contact with a boron surface.

Table 1. Optimized geometries of water clusters with one, two, and three H_2O on α-boron (111): URc (a), and Rc (b), as well as β-rhombohedral (B_{28}) (c) systems. The B, O, and H atoms are depicted by pink, red, and white spheres, in order.

Phase	$1H_2O$/B Surface	$2H_2O$/B Surface	$3H_2O$/B Surface
(a) **α-boron (URc)**			
(b) **α-boron (Rc)** **(111)-$I_{R,(z)}$ type**			
(c) **β-boron (B_{28})**			

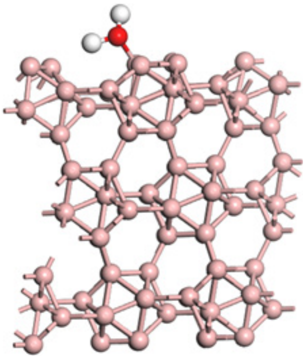
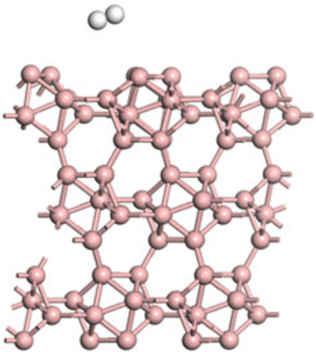
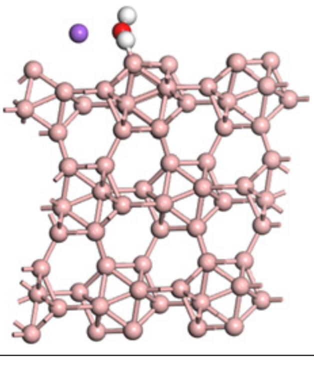
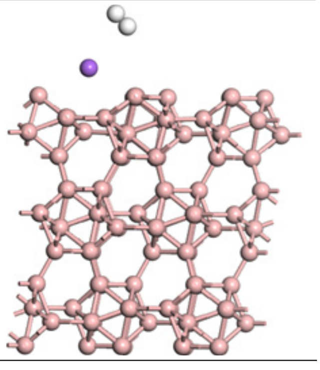
The water adsorption energies were calculated from Eq.1, and the results are listed in Table 2. The adsorption energies were calculated as -0.75 eV, -0.85 eV, and -1.23 eV for one, two, and three water adsorption boron surfaces, respectively. To represent the Rc α-boron (111) surface, some models from the literature were considered. Amsler et al. studied the surface reconstruction of α-boron (111) and found several low-energy surfaces in their study [53]. The (111)-$I_{R,(a)}$ which is a metallic Rc phase of α-boron (111), was reported to be the most stable configuration. Zhou et al. [54] showed that the reported (111)-$I_{R,(z)}$ type reconstruction surface is lower in energy than the (111)-$I_{R,(a)}$ type reconstruction phase of Amsler et al. [53]. In our work, the (111)-$I_{R,(z)}$ type surface was used to include different adsorption sites and chemical environments for the water molecule (Table 1). Once again, following geometry optimization, it was seen that the water molecules adsorbed by retaining their molecular form on the (111)-IR,(z) surface. The water adsorption energies were calculated, and the results for (111)-$I_{R,(z)}$ types Rc α-boron are given in Table 2. The adsorption energies were found to be 1.96 eV, -0.62 eV, and -1.12 eV for one, two, and three water molecules adsorbed by (111)-$I_{R,(z)}$ types Rc α-boron systems, respectively. Overall, URc surfaces were found to be more energetically favorable due to their lower adsorption energy.

Table 2. The calculated nH_2O adsorption energy of boron surfaces.

Boron Phase	E_{ads} (eV)		
	1H_2O	**2H_2O**	**3H_2O**
α-boron (Rc)	1.96	-0.62	-1.12
α-boron (URc)	-0.75	-0.85	-1.23
β-boron (B_{28})	-1.45	-0.69	-0.70
Defective α-boron (URc)	-1.54	-	-
Na_decorated α-boron (URc)	-0.70	-	-

The boron polymorph known as β-rhombohedral, which consists of B_{12} and B_{28} boron subunits, is then investigated (Table 1). As a first step of our water adsorption calculations two attached B_{28} cages, which are the building block of β-rhombohedral boron, were explored. One, two, and three water molecules were adsorbed on the top B_{28}. The water adsorption process was performed in two different initial optimization conditions for the B_{28} phase. As a first attempt, all the boron atoms were allowed to move freely during geometry optimization. To maintain the structural integrity of the subunits, and to prevent them from morphing into an amorphous entity, the bottom B_{28} and some lower atoms of the top B_{28} unit were fixed while most of the top unit was allowed to move freely. The optimized geometries of one, two, and three water molecules on the B_{28} systems are given in Table 1. The calculated adsorption energy results are given in Table 3. Our calculated values are -1.45 eV, -0.69 eV, and -0.70 eV for one, two, and three water molecules adsorbed B_{28} systems, respectively. In contrast with α-boron results, water molecules could remain in a molecular form, and, when two and three water molecules were adsorbed on the system (Table 1). All

Table 3. The one H_2O adsorbed geometries of URc α-boron (111): one boron defected (a), one Na decorated (b) systems. The B, Na, O, and H atoms are depicted by pink, purple, red, and white spheres, in order.

α-boron	1H_2O/B Surface	H_2/B Surface
(a) **Defective α-boron** **(URc)**		
(b) **Na_decorated** **α-boron (URc)**		

the results showed that the unreconstructed α-boron (111) surface is energetically more favorable than other boron surfaces for the water adsorption process, although dissociative water adsorption was observed in some instances.

Furthermore, we explored one defective boron and one Na-doped boron surfaces to form a contrast to the perfect surface that has so far been studied. Table 3 displays adsorption geometries on defective (with one B atom removed) and Na-doped α-boron (111) surfaces. First, by eliminating one surface boron atom, we created a boron vacancy on the α-boron (111) surface and place a single water molecule directly on the defect (Table 3). It was seen that water molecules did not break apart and kept their molecular form. Similarly, we decorated the pristine surface with one Na atom (Table 3). In this case, as well, we observed no dissociative adsorption (-0.70 eV), and the Na atom moved away from the surface. Finally, in order to understand the interaction of H_2 with imperfect surfaces, we studied the interaction between one H_2 molecule with the defective and the Na-decorated surface. H_2 adsorption energies were found to be -0.24 eV, and -0.11 eV for defective and Na-decorated boron systems, respectively. The optimized geometries of H_2 adsorbed systems are given in Table. 3.

As a result, the adsorption energies of water molecules on boron phases were investigated in this study to understand the nature of water adsorption on these surfaces. The results indicate that the strength of the bonding between water molecules and boron surfaces is highly dependent on the phase of the boron. Specifically, strong bonding is observed for one water molecule adsorbed on defective α-boron and β-boron (B_{28}), with adsorption energies of -1.54 eV and -1.45 eV, respectively. In contrast, weak bonding is observed for two water molecules adsorbed on Rc α-boron and β-boron (B_{28}), with adsorption energies of -0.62 eV and -0.69 eV, respectively. These findings suggest that the nature of water adsorption on boron surfaces is complex and can vary depending on the specific phase of boron. Further investigation is necessary to fully understand the mechanisms driving these differences and to optimize the use of boron surfaces in various applications, such as catalysis and energy storage.

4. Conclusions

In conclusion, our study using first-principle calculations has ensured significant perspectives into adsorption behavior of water molecules on different boron surfaces. We have shown that the surface morphology of boron plays a crucial role in defining the water adsorption energy and configuration. Our results suggest that the adsorption energy of water on boron surfaces is dependent on the surface orientation, and the URc α-boron (111) surface of boron shows the highest affinity for water adsorption. Our findings also indicate that the water molecule tends to form hydrogen bonds with boron atoms on the surface, leading to the formation of water-boron complexes. Furthermore, we have observed that the electronic properties of the boron surfaces significantly affect the adsorption behavior of water molecules. The presence of defects and impurities on the surface can cause modifications to the electronic structure of the surface, resulting in altered water adsorption properties. Overall, our study provides a theoretical understanding of the water adsorption behavior on boron surfaces, which could have important implications for various applications such as water purification, energy storage, and catalysis. Our results could also inspire further experimental studies aimed at exploring the water adsorption properties of different boron-based materials.

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