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Glassy materials as a hydrogen storage medium: Density functional calculations

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The adsorption of molecular hydrogen on a glassy material and its relatives is studied with a use of pseudopotential density-functional method. The binding energy and distance of adsorbed hydrogen is particularly calculated. It is found that the desorption temperature of hydrogen in layered boron oxide is significantly higher than that in carbon nanotubes as much as twice, which is attributed to heteropolar bonding in boron oxide. The effect of water addition to boron oxide on hydrogen adsorption is also investigated. Our results indicate that water may reduce the surface area of boron oxide but has little effect on the hydrogen adsorption energy. We also calculated an optimum pore size for hydrogen diffusion into boron oxide. The current study demonstrates a pathway to the finding of a class of materials for hydrogen storage media that can hold hydrogen at ambient conditions through physisorption.

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I. INTRODUCTION

Hydrogen has been considered as a clean and efficient energy source.[1–3] However, the lack of proper ways to store hydrogen has been a serious bottle-neck to the large-scale use of hydrogen as an energy medium. Previous approaches to storing hydrogen in forms such as compressed hydrogen, liquid hydrogen, or metal hydrides have serious drawbacks of low capacity, safety problems, or impractical release temperatures to name a few. In recent years storing hydrogen in nanostructured materials through physisorption has been of great research interests as a potential way to achieve a high hydrogen storage capacity at ambient conditions (Refs. 2 and 3 and references therein). Materials at nanoscale have advantages over their bulk forms such as large surface area and potentially strong chemical reactivity (and hence a strong binding energy with hydrogen). For example, in the last several years there have been active studies for hydrogen storage medium on single-walled carbon nanotubes, which have all their atoms at the surface. However, the desorption temperature and the storage capacity have been reported[4–7] to be well below the claimed values of early measurements.[8–10]

The capacity of a hydrogen storage material through physisorption is proportional to its specific surface area (SSA),[11–13] and the desorption (or release) temperature of hydrogen (T_D) is determined by the strength of the interaction between hydrogen and the material's surface, called the heat of adsorption. A straightforward way to estimate the heat of adsorption is to calculate the binding energy of hydrogen on the surface of the material. Activated carbons, which are known as highest surface-area materials, can have an SSA of up to $2600\ \mathrm{m}^2/\mathrm{g}$.[14,15] However, it has proven difficult to increase the heat of adsorption of hydrogen in activated carbons, and hence the desorption temperature is as low as cryogenic temperatures (~ 77 K). Recently, Jhi *et al.*[16] and Jhi and Kwon[17] showed that noncarbon light-element nanostructured compounds could be potential hydrogen storages with higher desorption temperatures than carbon-based materials.

The adsorption of molecular hydrogen on surfaces is in nature a physisorption due to a strong H-H bond and closed-shell electronic configuration of the molecule. As the strength of the interaction between hydrogen and adsorbent materials increases, molecular hydrogen tends to dissociate into atomic hydrogen and subsequently diffuse into the adsorbents, which is typically observed in metal hydrides. The heat of adsorption then increases so significantly to more than 1 eV that the release of hydrogen occurs at very high temperature ($T_D \sim 300\ ^\circ\mathrm{C}$ for MgH_2 for example). Therefore, the finding of proper materials that have moderate hydrogen binding energy (but still in physisorption range of $0.2-0.3$ eV as estimated from the van't Hoff equation[18]) with a sufficient surface area (of a few thousands m^2/g) is a key to the development of hydrogen storage operating at ambient conditions.

We searched for compounds that consist of light elements and form (locally) layered structures similar to graphite because such materials are expected to have high surface areas and avoid strong chemical reactions with hydrogen but retain substantial molecular binding. In this paper, we report our study of glassy layered materials, namely, boron oxide and related materials, as potential hydrogen storage media through pseudopotential density functional calculations. We chose boron oxide because it can have layered structures locally and ionic bonding and because it can form a porous glassy network, which gives a potential for high surface area and relatively strong adsorption energy.

Borox oxide is a very important industry mineral and has a very rich chemistry as carbon.[19,20] The structure of vitreous B_2O_3 has been a subject of intense studies.[21] Although the structure of boron oxide is not completely understood at the atomic level, a widely accepted view is that vitreous B_2O_3 consists of mixed random networks of boroxol rings and BO_3 triangles. The random network has locally a two-dimensional layered structure, which then constitutes a three-dimensional glass structure connected by nonbridge oxygens.[21–25] In vitreous B_2O_3, boron atoms are threefold coordinated by oxygen atoms and centered at the basic unit of BO_3 triangles as shown in Fig. 1. Three BO_3 triangles can join to form a boroxol ring (B_3O_6), whose existence is supported by Raman and NMR measurements.[26–29] Just as the

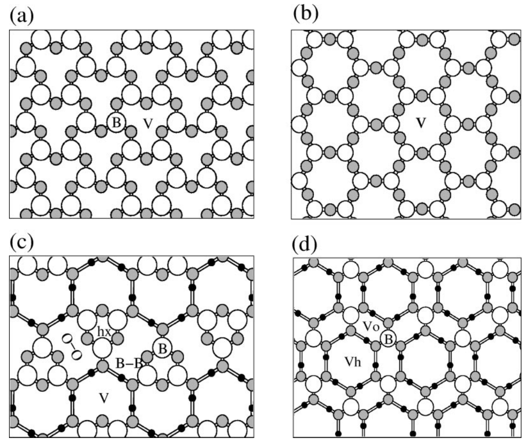

FIG. 1. Schematic view of boron oxide and related Structure. (a) I-B_2O_3 with B-O-B angle of 120° and (b) II-B_2O_3 with B-O-B angle of 180°. Boron atoms are denoted by empty circles and oxygen atoms by gray ones. The center of a void site is marked as V. (c) HBO_2 planar structure with various void sites for hydrogen binding. B and V denote boron atom and a void site, respectively. Other void sites for hydrogen adsorption simulation, such as hx, B-B, and O-O are also shown. B-B and O-O denote the middle of two adjacent boron and oxygen atoms, respectively. (d) H_3BO_3 lattice structure with two types of voids, Vo and Vh, shown. Hydrogen atoms in HBO_2 and H_3BO_3 in (c) and (d) are denoted by small filled circles. They are forming hydrogen bonds with nearby oxygen atoms.

BO_3 triangles combine to form hexagonal boroxol rings, so do the rings interconnect to create latticed honeycomb-like networks of interconnected hexagonal rings. These various structural configurations thus represent local regions of order in the amorphous glassy composition.

The addition of water to boron oxide (B_2O_3) creates boric acid (H_3BO_3, known more specifically as orthoboric acid) and also a structural intermediate between these two species, metaboric acid (HBO_2), depending on local conditions of temperature and the amount of water. Boric acid and metaboric acid, however, are not glassy. We also studied the adsorption of hydrogen on the boric acids to check the effect of water contamination in boron oxide. Boric acids exist in a layered crystalline form similar to that of graphite. As water is removed from boric acid or meta-boric acid by heating or evaporation, boron oxide is reformed. Thus, a composition of boron oxide can vary smoothly from B_2O_3 to H_3BO_3 depending on water content.

II. COMPUTATIONAL METHODS

Figure 1 depicts the structures used in the present calculations. In order to study the binding property of hydrogen on B_2O_3, we adopt the layer model of Borrelli and Su[30] to construct two-dimensional crystalline structures that consist of BO_3 triangles with a B-O-B angle of 120° [I-B_2O_3, Fig. 1(a)] and 180° [II-B_2O_3, Fig. 1(b)] among many possible configurations of B_2O_3. The B-O-B angle can continuously change from 120° to 180° by rotating the BO_3 triangles in the plane. The B-O bond length was chosen to be about 1.37 Å which is close to the average bond length measured in experiment.[21] The distance between B_2O_3 layers was taken to be 20 Å to minimize the layer-layer interaction. The regular two-dimensional lattice structures can exist as localized regions within larger three-dimensional amorphous or random network structures which can also contain pores or voids of various sizes. In this depiction, it can be seen that each boron atom connects to three oxygen atoms, and each oxygen atom bridges two boron atoms. We believe that the hydrogen binding energy is not sensitive to the global structure of B_2O_3, and the results here can represent the adsorption energy of hydrogen on B_2O_3 as long as glassy boron oxide has similar local configurations chosen in this study. Figures 1(c) and 1(d) show a part of layers of HBO_2 and H_3BO_3, respectively, used in present calculations. Hydrogen atoms (in black dots) from water are making hydrogen bonding with oxygen atoms (in gray circles). A supercell of 8 BO_3 triangles was used for adsorption simulation of hydrogen on B_2O_3. Similar sizes of supercells were chosen for boric acids.

We performed a series of total energy calculations using the pseudopotential density functional method[31] in order to study the binding of hydrogen on boron oxide and boric acids. Exchange-correlation of electrons was treated with the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof,[32] which is believed to be better than the local density approximation (LDA) in describing gas adsorptions. It has been questioned, though, whether the GGA (or LDA) could describe correctly van der Waals (vdW) interactions due to their long-range nature. Recently there have been several attempts to incorporate the vdW interactions into the density functional theory (for example, see Refs. 33–36 and references therein), but none of them have yet reached the level of a consistent and reliable methodology. While some *ad hoc* approaches have been used to produce potentials for describing the physisorption (Refs. 37–39 and references therein), further development of exchange-correlation functionals for the vdW interaction is required for consistent and accurate computations. It should be noted that binding energies calculated here can be understood in the framework of a given exchange-correlation functional, providing a guidance for search of new hydrogen storage materials.

Atomic orbitals with double zeta polarization are used to expand single-particle wave functions[40] with the cutoff energy of 80 Ry for real space mesh. We used 0.01 Ry of the confinement energy shift, which defines the cutoff radii of the atomic orbitals. Binding energy curves were obtained by performing successive calculations of total energy at varying distance between the hydrogen molecule and the adsorbents. Full relaxations of atomic positions were carried out with the center of mass of hydrogen being fixed until their Hellmann-Feynman forces are less than 0.001 Ry/a_B with a_B being the Bohr radius.

III. RESULTS AND DISCUSSION

We selected several sites for adsorption simulation and then calculated the binding energy and distance of hydrogen molecule. For boron oxide, we chose the top of oxygen, bo-

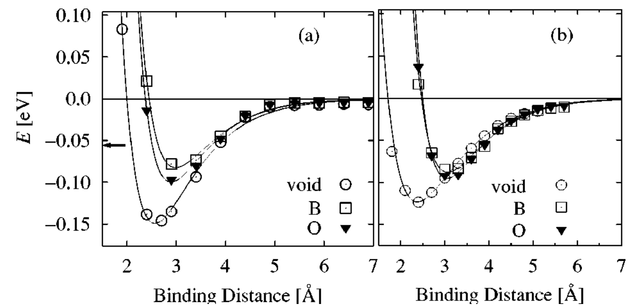

FIG. 2. Binding energy curves of H_2 on various sites of (a) I -B_2O_3 and (b) II-B_2O_3: on top of void site (empty circles), boron (empty squares), and oxygen atoms (solid triangles). The binding energy of hydrogen on carbon (∼0.06 eV) is indicated by an arrow for comparison. The maximum binding energy obtained here is about 0.15 eV when hydrogen adsorbs on top of void sites [see Figs. 1(a) and 1(b)].

ron atoms, and the center of void as depicted in Fig. 1. Figure 2 shows the binding energy curves of hydrogen adsorption on various sites of B_2O_3. According to our calculations, the strongest binding occurs at the top of the void site, which is attributed to larger contacts between hydrogen and the atoms in the B_2O_3 plane. The binding energy was obtained to be about 0.15 eV after fitting the energy curves with the Morse function. The adsorption energy on top of boron and oxygen atoms is similar to each other with its value ranging about 0.08−0.1 eV. Binding energies on II-B_2O_3 are similar to those on I-B_2O_3 [Fig. 2(b)]. Once hydrogen molecules adsorbed on the void sites, the intersite diffusion of hydrogen occurs through a hopping over oxygen atoms according to our results. Our calculations show that the binding energy of hydrogen on boron oxide is significantly higher than that on graphite as indicated by an arrow in Fig. 2(a). As the hydrogen molecule comes closer to the boron oxides surface, we observed a small but net electric dipole moment in hydrogen, which is compared to the zero dipole moment at large distances between hydrogen and adsorbents. The dipole is due to the redistribution of charge in hydrogen rather than physical charge transfer between adsorbents and hydrogen. The interaction between (closed-shell) hydrogen molecule and solid surfaces is usually in physisorption range, and the induced dipole (and/or higher) moment(s) of hydrogen thus is crucial for the binding. As a rule of thumb, the induced dipole moment can be large if local electric fields are strong. The ionic bonding is thus expected to be more effective for inducing electric dipole in hydrogen. The desorption temperature of hydrogen on boron oxide was estimated to be as much as about 150 K from the van't Hoff equation.[41] Note that the desorption temperature of hydrogen on activated carbon is quite low, close to the liquid nitrogen temperature (∼77 K). Experimentally, T_D of hydrogen in boron oxide was measured to be about 110 K (Ref. 17), which is in fairly good agreement with our results considering that the measured temperature corresponds to the binding energy averaged over various sites and structures.

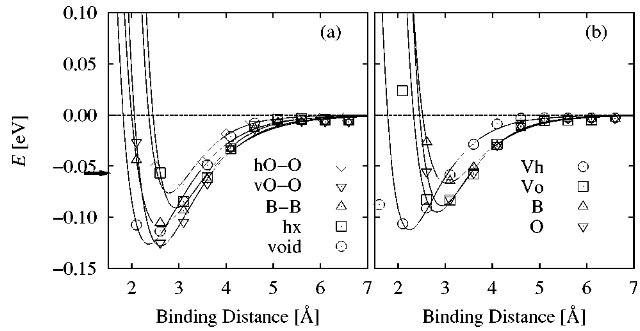

FIG. 3. Binding energy curves of H_2 on various sites of (meta) boric acids. (a) Four types of void sites are particularly considered for the adsorption, as denoted by O-O site (middle of two adjacent oxygen atoms) with two different hydrogen molecular orientation, horizontal (hO-O, diamonds) and vertical (vO-O, down triangles) to the HBO_2 surface, respectively, and B-B site (middle of two adjacent boron atoms, upside triangles), hx (squares), and V (circles). (b) Similar calculations for H_2 adsorption on H_3BO_3. On top of Vh (circles), Vo (squares), boron atom (up triangles), and oxygen atom (down triangles) in H_3BO_3. The maximum binding energy is about 0.12 eV when hydrogen adsorbs on top of Vh site [see Figs. 1(c) and 1(d)]. The hydrogen binding energy on carbon is also shown by an arrow for comparison.

The contamination of water converts boron oxides into (meta) boric acids, which have layered structures, as mentioned above. Similar calculations as for B_2O_3 were carried out to study the binding property of hydrogen on various sites of boric acids. The binding energies of hydrogen on boric acid and meta-boric acid are found similar to those on boron oxide overall (Fig. 3). In all cases, the binding energy is largest at the top of void sites, where the binding distance is shortest (∼2.3 Å). We note that the actual distance between the hydrogen molecule and the nearest oxygen atoms in the void sites is about 3 Å, which is close to the equilibrium distance of hydrogen molecular binding on top of oxygen as shown in Figs. 2 and 3(b). Therefore oxygen atoms surrounding the void sites are providing a shallow potential well with a larger contact area that is enhancing the binding at the sites. Our results indicate that the effect of water contamination of boron oxide on hydrogen adsorption may not be the reduction of binding energy but rather the conglomeration of particles or the destruction of pore structures, which can result in less surfaces available for hydrogen binding.

Since BO_3 triangles can connect to each other at random, it is possible that boron oxide can contains rings of large diameter (pore structures). Hydrogen can diffuse through the rings to access inner surface of boron oxides. The presence of atomic-scale pores in activated carbon and other materials is well known,[42] and it is thus reasonable to believe that boron oxide of large surface-area can be prepared by methods which yield such pores as well. We studied the diffusion of hydrogen molecules through such pores to find optimal pore size for diffusion as well as adsorption. The adsorbing simulations were performed on artificially constructed circular boron oxide rings of various size, with inner intra-atomic diameters that define pores sizes of 3.4, 4.6, and 6.5 Å, respectively. The 6.5 Å-diameter ring consists of ten BO_3 triangles, and similar-sized rings are observed in B_2O_3.[21] Figure 4 shows the calculated binding energy curves with the energy at 0 Å defining the diffusion barrier. The energy bar-

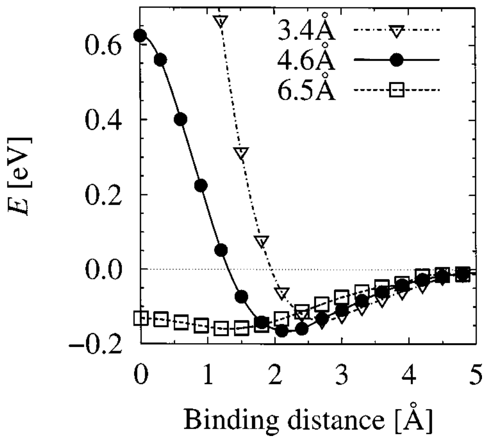

FIG. 4. Energy curves for hydrogen adsorption and diffusion through various sized pores, which are constructed by connecting BO_3 triangles. Smaller diameter pores look similar to the void sites in Figs. 1(a) and 1(b).

rier required for the diffusion through the pores is very large for the pores of a diameter of 3.4 Å, but nearly nonexistent at 6.5 Å. At 4.6 Å, the diffusion barrier is about 0.8 eV which substantial kinetic energies provided by, for example, applying high pressure are necessary to overcome. The size-dependent diffusion barrier suggests that operating pressure can be tuned by controlling the distribution of the pore size. The heat of adsorption of hydrogen sorbing to these structures, once the 6.5 Å diameter threshold is attained, is equal to or greater than that on planar boroxol ring lattices. These computations demonstrate that pores with diameters of 6.5 Å or more, within a host medium comprising boron oxide and its derivatives, provide an effective passageway for hydrogen access into such a medium. Such pores can be more significant in terms of hydrogen storage capacity because hydrogen molecule is much smaller in diameter than nitrogen molecule, which is used for surface area measurement, and hence can access those nano- or micro-pores with less kinetic barriers.

In summary, we showed that glassy materials, namely, a family of boron oxides, can be a good hydrogen storage with desorption temperature of upto 150 K. Our computational results of hydrogen diffusion onto boron oxide pore structures demonstrate that pores of a diameter larger than 6.5 Å provide free accessibility for hydrogen passage, as well as a heat of adsorption that is equal to or greater than that on a planar structure. Therefore maintaining and containing large void structures or pores are essential to enhance the hydrogen binding as well as for higher surface area. Our study demonstrates that ionic compounds with a sufficient high surface area can be a better hydrogen storage than carbon-based materials.

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