Lithium Decorated Borane Clusters (BnHnLi6, n=5-7) as Promising Materials for Hydrogen Storage: A Computational Study

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Research Article

Keywords: DFT, Borane clusters, adsorption, AIMALL, Molecular Dynamics Simulations

Posted Date: September 20th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-671186/v1

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Abstract

In this study, we have investigated the hydrogen adsorption potential of lithium decorated borane clusters \( (B_nH_nLi_6, \ n = 5–7) \) using density functional theory calculations. The principle of maximum hardness and minimum electrophilicity confirmed the stability of the hydrogen adsorbed complexes. The outcomes of the study reveals that, the hydrogen molecules are adsorbed in a quasi-molecular fashion via Niu-Rao-Jena type of interaction with average adsorption energy falling in the range of 0.10-0.11eV/H\_2 and average Li-H\_2 bond length is in the range of 2.436–2.550Å. It was found that the hydrogen molecules are physisorbed at the host clusters at low temperature range 0K- 77K with gravimetric density up to 26.4 wt% which was well above target set by U.S. Department of Energy (US-DOE). ADMP-MD simulations showed that almost all the H\_2 molecules are desorbed at higher temperature form 373K-473K without distorting the host clusters which indicates the studied clusters can be promoted as promising reversible hydrogen storage.

1. Introduction

Rapid consumption of fossil fuel and their restricted supply have not only depleted the natural source of energy to a shocking amount but also engendered many environmental problems such as global warming, greenhouse issues, and air-pollution etc \([1–4]\). Hence, during the past couple of decades tremendous effort has been devoted to explore clean, efficient and cost-effective alternative energy sources that should be non-polluting and non-hazardous in nature. In this regard, hydrogen being the most abundant element in the earth can be considered as one of the prominent energy carriers that can be projected as the future fuel \([5, 6]\). In addition, the combustion of the hydrogen fuel yields water and non-toxic by-products which insure it to be one of the most environment friendly gas available \([7–9]\). However, the major bottleneck of utilizing it is to find an efficient storage system that can trap hydrogen in a large specific area and with high gravimetric and volumetric densities (4.5 wt% and > 30 gH\_2/L by 2020) as proposed by US Department of Energy (US-DOE) \([10, 11]\). In addition, to achieve cost-effective reversible hydrogen storage and to release hydrogen at ambient conditions, hydrogen binding energy should be in the intermediate range of physisorption and chemisorption process \([12, 13]\). Moreover, fast adsorption and desorption kinetics of hydrogen at ambient conditions are also taken into account while considering the storage materials. Therefore, for the practical onboard application, tremendous research efforts have been put for designing materials for effective hydrogen storage.

Nanostructured clusters are of particular interest in hydrogen storage due to their riveting reaction kinetics, thermodynamics and catalytic behavior and which possess high diffusivity and surface to volume ratio as compared to their bulk counterparts \([14, 15]\). Since last few years hydrogen storage in carbonaceous nano-clusters have been widely reported in literature. Alongside of carbon based compounds, boron nanostructured clusters, having numerous structural analogies with carbonaceous clusters, were also investigated by different researchers. For example, hydrogen storage capacity of lithium decorated B\_60 was theoretically investigated by Wang et al. who reported that the hollow cage
could trap maximum up to 28 H\textsubscript{2} through van der Waals interactions with an average binding energy of 0.33 eV/H\textsubscript{2} leading to a gravimetric density of 8.19 wt\% [16]. Zhang et al. performed molecule dynamics simulations to study the hydrogen storage in the Ca doped B\textsubscript{40} and found that the clusters could store up to 30 H\textsubscript{2} molecules with an average adsorption energy of 0.17 eV/H\textsubscript{2} via orbital hybridisation and charge polarisation mechanism that leads to 8.11 wt\% of gravimetric density. Molecular dynamic simulation reveals that the adsorbed hydrogen molecules could be released very quickly at room temperature. [17]. Scandium decorated B\textsubscript{38} clusters was theoretically explored by Liu et al. who reported that Dewar-Kubas mechanism between Sc atom and adsorbed H\textsubscript{2} molecules was responsible for adsorption of 6H\textsubscript{2} on each Sc atom with a moderate adsorption energy of 0.22 eV/H\textsubscript{2} resulting a gravimetric density of 7.57 wt\% [18]. Juan et al. theoretically predicted the hydrogen storage efficiency of Ca doped hexagonal B\textsubscript{36} clusters with van der Waals corrections and found that this cluster could adsorb 4.97 wt\% of hydrogen with an average binding energy of 0.36 eV/H\textsubscript{2} that could easily desorb at near ambient temperatures [19]. Similar kind of observations were also reported by Ye et al. and Leu et al.[20, 21]. Tang et al. have shown that maximum of 16 number of H\textsubscript{2} molecules were captured by alkali, alkaline-earth and transition metal doped smallest boron cage (B\textsubscript{28}) via strong Dewar-Kubas with a moderate average adsorption energy (0.2–0.6 eV/H\textsubscript{2}) resulting in 7.99 wt\% gravimetric density [22]. Wang et al. studied the H\textsubscript{2} interaction with Li decorated B\textsubscript{24} cluster and who reported that through charge polarization mechanism the cluster could capture 9.24 wt\% hydrogen molecules with 0.10 eV/H\textsubscript{2} of average adsorption energy [23]. Recently, our investigation on Sc doped small boron clusters for hydrogen storage capacity using molecular dynamics simulations revealed that these clusters could accommodate maximum of 9.43 wt\% with average adsorption energy in the range 0.08–0.10 eV/H\textsubscript{2} and which are desorbable at ambient conditions [24]. Besides, a lot of boron based materials have also been investigated for hydrogen storage by many other authors [25–27].

Besides, hydrogen storage in boranes (B\textsubscript{m}H\textsubscript{n}) which are synthetic class of boron hydrides possessing non-classical 3-centre-2-electron bonding, were also reported by many authors. For instance, Using first principle calculation Ghosh et al. studied the hydrogen uptake in lithium doped closo borane and found that the designed material could bind molecular hydrogen through charge-dipole interaction with average binding energy of 2.2 Kcal/mol giving rise to gravimetric density up to 7.3 wt\% [28]. The hydrogen adsorption capacity of lithium decorated diborene and diboryne was also explored by Ghosh et al. who reported that these clusters could capture H\textsubscript{2} molecules through ion quadruple and ion induced dipole interaction resulting in a gravimetric density up to 23\% and 24\% respectively [29]. Chaudhuri et al. investigated the hydrogen capturing ability of Li, Sc, and Be decorated B\textsubscript{6}H\textsubscript{6} using first principle calculation and found that these complexes could be considered as a promising candidate for hydrogen storage at low temperatures with a gravimetric density up to 12.5 wt\% [30]. Similarly, Ali et al. explored the interaction of hydrogen molecules with B\textsubscript{6}H\textsubscript{6}\textsuperscript{2–} complex and reported the adsorption energy close to 3.5 Kcal/mol per H\textsubscript{2} which was the optimal adsorption energy required for reversible hydrogen storage at
ambient temperature [31]. A similar study was also reported by Wan and co-workers. [32]. In addition, hydrogen storage in other borane and carborane based clusters are reported by many others [33–36].

In the present study we have investigated hydrogen storage in inorgano-metallic complexes, \((B_nH_nLi_6, n = 5–7)\).

### 2. Computational Details

The geometry optimization of the structures with and without \(H_2\) molecules has been carried out using Minnesota 06 (M06) hybrid functional implemented with 6-311 + + G(d,p) basis set within the framework of Density Functional Theory (DFT). M06 functional has been considered to be an efficient method to successfully investigate the non-covalent interactions. Therefore, it has proven to perform well in hydrogen storage investigations because the process of hydrogen storage involves many kind of non-covalent interactions [37]. No optimizations were accomplished with any imaginary harmonic frequencies. All the calculations were performed using computational chemistry program Gaussian 09 and Chemcraft was used to create 3D molecular complexes [38]. To investigate the stability as well as the reversibility of adsorbed hydrogen molecules on the lithium decorated borane clusters, the optimized structures were subjected to Atom-centered Density Matrix Propagation (ADMP) molecular dynamics simulations at different temperatures. The time step for the ADMP-MD simulations was set at 1fs with maximum 1000 steps were specified for each trajectory. Furthermore, to explore the nature of interaction between the hydrogen molecules and sorption centers of the host cluster we have employed the Bader's Quantum Theory of Atoms in Molecules (QTAIM) [39]. The partial density of states (PDOS) were calculated and analyzed using GaussSum program [40].

The stability and reactivity of the lithium decorated borane clusters and their \(H_2\) trapped analogues were examined by calculating their, global reactivity descriptors, e.g hardness (\(\eta\)), electrophilicity (\(\omega\)) and electronegativity (\(\chi\)) [41–44].

Now, hardness (\(\eta\)) is computed by the ionization potential (I) and electron affinity (A) using Koopmaan's Theorm [45].

\[
\eta = \frac{I-A}{2} \quad (1)
\]

Similarly, the electrophilicity index can be defined as 1

\[
\omega = \frac{\chi^2}{2\eta} \quad (2)
\]

where
The kinetic stabilities of the complexes were determined by calculating the energy gap ($E_g$) between their highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs).

The average hydrogen adsorption energy without zero point energy correction ($E_{ads}$), are obtained using the following equation:

$$E_{ads} = \left[ \left\{ E_{Host} - nE_{H2} \right\} - E_{Complex} \right]$$  \hspace{1cm} (3)

Here $E_{Complex}$, $E_{H2}$ and $E_{Host}$ is the total electronic energies without zero point energy correction of hydrogenated complex and hydrogen molecule and host cluster respectively.

The hydrogen storage gravimetric density was determined using following equation:

$$H_2(\text{wt}%) = \frac{M_{H2}}{M_{H2} + M_{Host}} \times 100$$  \hspace{1cm} (4)

Where $M_{H2}$ indicates the mass of total number of adsorbed H$_2$ molecules and $M_{Host}$ indicates the mass of lithium doped borane cluster

### 3. Results And Discussion

We optimized the geometries of bare $B_nH_nLi_6$, $n = 5–7$ clusters employing M06/6-311++G(d,p) level of theory and the structural parameters computed are found in good agreement with earlier reported data by Boldyrev et al. [46]. Figures 1 and 2 show the optimized ground state geometries of bare $B_nH_nLi_6$ and H$_2$ adsorbed compounds respectively. Hydrogen molecules were added sequentially till no further hydrogen molecules could be adsorbed in an allowed range of Li-H$_2$ distance as per the standard of US-DOE. A maximum of eighteen number of hydrogen molecules get adsorbed by the studied $B_nH_nLi_6$ i.e $B_5H_5Li_6$, $B_6H_6Li_6$ and $B_7H_7Li_6$ clusters. As expected the adsorption centers mostly lie on Li atoms leading to small elongation in Li-Li bond length in the range of 0.01Å -0.03Å. However, from the table, it can be observed that, there is almost no change in B-B bond lengths after the H$_2$ adsorption. Hence, the insignificant geometrical changes in host clusters after the H$_2$ adsorption signifies the process to be physisorption kind. The average distance between the sorption center (Li) and hydrogen molecule was found to be in the range of 2.042Å -3.637Å. Hydrogen molecules are found to bind with the lithium adsorbents in a quasi-molecular fashion leading to H-H bond elongation in the range of 0.75–0.77 Å. Because Li has large second ionization energy, therefore H$_2$-Li interaction occurs due charge polarization giving rise to Niu-Rao-Jena kind of bonding [47–49].
Stability of the hydrogenated clusters is an important aspect to focus on while studying hydrogen storage mechanism. We have calculated the global reactivity descriptors such as; hardness ($\eta$) and electrophilicity index ($\omega$) which provide a quantitative measure of the stability of the clusters. According to the principle of *maximum hardness and minimum electrophilicity index* proposed by Parr et al., molecules with a high value of hardness ($\eta$) and low value of electrophilicity ($\omega$) gives rise to stable configuration [50, 51]. We computed the reactivity parameters at M06/6-311++G(d,p) level of theory and the values are provided in Table 2. It has been observed that, the $\eta$ value increases while $\omega$ value decreases with sequential adsorption of H$_2$ molecules in all studied complexes indicating the stability of the systems. For example, in the case B$_7$H$_7$Li$_6$-18H$_2$ the hardness is found to increase by 7% being maximum for B$_7$H$_7$Li$_6$-18H$_2$ whereas $\omega$ value decreases by 18% being minimum for the same cluster. Similar observation is also observed in other studied compounds. Therefore all the hydrogen decorated complexes considered here are considered stable. The above fact can be reassured by analysing their HOMO-LUMO energy gaps ($E_g$) which is found to consistently increases with the number of hydrogen molecules for all the clusters (Fig. 3). So the kinetic stabilities of the clusters increase up to the adsorption of 18 number of H$_2$ molecules imparting the whole systems a non-reacting atmosphere for further addition of H$_2$.

To study the hydrogen adsorption mechanism of lithium decorated borane clusters, the average adsorption energies ($E_{ads}$) are calculated using the Eq. 2↑ and the values are plotted in the Fig. 4. It can be observed from plot that the H$_2$decorated clusters display an decreasing $E_{ads}$ with increasing H$_2$ molecule at a adsorption site (Li) which is obvious due to steric repulsion among the H$_2$ molecules. However, if we look into the H$_2$ adsorption on the cluster as a whole, an almost odd-even effect is observed. This might be due to a non local effect of H$_2$ interaction on one site on the H$_2$ binding on the other. The calculated adsorption energy found in the ideal range of 0.10 eV/H$_2$ to 0.16 eV/H$_2$ which is the required range of physisorption mechanism.
Table 1
Average bond lengths between Boron atoms (B-B), Boron Hydrogen (B-H), Center of the complex and central Lithium (C-M), Center of the complex and peripheral Lithium (C-P), Lithium Hydrogen (Li-H) and Hydrogen Hydrogen (H-H) in Å.

| Complexes         | B-B (Å) | B-H (Å) | C-M (Å) | C-P (Å) | Li-H (Å) | H-H (Å) |
|-------------------|---------|---------|---------|---------|----------|---------|
| B$_5$H$_6$Li$_6$  | 1.692   | 1.255   | 3.367   | 3.024   |          |         |
| B$_5$H$_6$Li$_6$-18H$_2$ | 1.692 | 1.252   | 3.367   | 3.044   | 2.436    | 0.75    |
| B$_6$H$_6$Li$_6$  | 1.675   | 1.258   | 2.990   | 3.341   |          |         |
| B$_6$H$_6$Li$_6$-18H$_2$ | 1.674 | 1.254   | 2.962   | 3.331   | 2.552    | 0.75    |
| B$_7$H$_7$Li$_6$  | 1.666   | 1.256   | 2.635   | 3.619   |          |         |
| B$_7$H$_7$Li$_6$-18H$_2$ | 1.666 | 1.253   | 2.608   | 3.622   | 2.550    | 0.75    |

Table 2
Calculated Hardness ($\eta$) Electrophilicity Index ($\omega$), and HOMO – LUMO Energy Gap ($E_g$) of lithium doped boranes as well as hydrogen trapped complexes.

| Complexes         | $\eta$ | $\omega$ | $E_g$ (Å) | wt% |
|-------------------|--------|----------|-----------|-----|
| B$_5$H$_6$Li$_6$  | 1.692  | 1.255    | 3.367     | 3.024 |
| B$_5$H$_6$Li$_6$-18H$_2$ | 1.692 | 1.252    | 3.367     | 3.044 |
| B$_6$H$_6$Li$_6$  | 1.675  | 1.258    | 2.990     | 3.341 |
| B$_6$H$_6$Li$_6$-18H$_2$ | 1.674 | 1.254    | 2.962     | 3.331 |
| B$_7$H$_7$Li$_6$  | 1.666  | 1.256    | 2.635     | 3.619 |
| B$_7$H$_7$Li$_6$-18H$_2$ | 1.666 | 1.253    | 2.608     | 3.622 |

Hirshfeld charge analysis has been carried out to study the charge distribution mechanism during the hydrogen adsorption in lithium decorated borane clusters. The variation of average Hirshfeld charges on B, Li and H atoms with the number of H$_2$ per clusters are presented in the Fig. 5. It is observed that the average Hirshfeld charge on lithium atom increases with increase in hydrogen content indicating that the Li atom gets more positively ionic in comparison to H$_2$ molecules due to induced polarization. However,
increase of H₂ molecules about the Li center slightly decreases its positive charge distribution. Because there is no noticeable change in average charge distribution over H₂ and B atoms, the superposition of charge distribution of all H₂ molecules tends to induce negative charge on Li, thereby decreasing the degree of its positive charge distribution. This confirms a Niu-Rao-Jena type of interaction among Li and H₂ molecules.

In order to reveal the bonding characteristic and frontier molecular orbital, partial density of state (PDOS) of the host clusters as well as hydrogen adsorbed system has been investigated. We set the value of full width half maxima value at 0.3 eV. The PDOS of B and Li atoms in host and hydrogen adsorbed clusters are shown in Fig. 6. For every studied cluster, a very weak overlap between B and Li atom observed which suggests ionic-like bonding between B and Li which is in good agreement with the QTAIM results. It can be observed that, as compared to the host clusters there exist some new peaks in hydrogenated clusters and near Fermi level, LUMO of H₂ has comparatively less contribution than Li LUMO which suggests that prominent charge transfer between them is unlikely to happen. Therefore the H₂-Li bonding is most probably due to polarization (Niu-Rao-Jena kind of interaction).

Table 3
Electron density in (ρ) a.u., ∇²ρ, Total energy density (H_{BCP}) in a.u at BCP of (Li,H) and (Li,B).

| Complexes         | ρ_{Li-H} | ∇²ρ_{Li-H} | ρ_{Li-B} | ∇²ρ_{Li-B} | H_{BCP_{Li-H}} | H_{BCP_{Li-B}} |
|-------------------|---------|-----------|---------|-----------|---------------|---------------|
| B₃H₆Li₆-18H₂      | 0.0065  | 0.0377    | 0.0305  | 0.1345    | 0.0018        | 0.0006        |
| B₆H₆Li₆-18H₂      | 0.0066  | 0.0444    | 0.0274  | 0.1238    | 0.0023        | 0.0012        |
| B₇H₇Li₆-18H₂      | 0.0161  | 0.0844    | 0.0204  | 0.0878    | 0.0022        | 0.0014        |

The nature of the interaction between the adsorbed H₂ molecule and the Li decorated borane clusters have been investigated by performing topological analysis using Bader’s Quantum Theory of Atoms in Molecules (QTAIM) [52]. In order to describe the relative decrease or increase of charge accumulation at the bonding sites, we computed topological parameters such as electron density (ρ), and its Laplacian ∇²ρ at the BCPs along with total energy density (H_{BCP}) that can give a qualitative knowledge about nature of bonding interaction[53, 54]. The negative H_{BCP} is an indicator of shared-kind bonding. In Table 3 we provide the computed topological parameters, which were calculated using QTAIM. From Table 3, it is found that for the Li doped borane clusters, ρ < 0.20 a.u. and positive ∇²ρ with positive H_{BCP} at bond critical points (BCPs) of (Li, H) inferring that H₂ molecule is more likely to have somewhat closed-shell type interaction with Li atoms corresponding to van der Wall type of bonds. Moreover, the positive value of H_{BCP} (in the ranges of 0.0012 a.u. − 0.0031 a.u. for Li-H) also suggest that, in all studied clusters, kinetic energy density dominates over the potential energy density [53, 54].

In order to explore the thermodynamic stability and desorption of H₂ molecules at different temperatures, hydrogen adsorbed complexes are subjected to ADMP molecular dynamics simulations. The relaxed geometries obtained at M06/6-311++G(d,p) level of theory have been used for initial structures for the
ADMP simulations. The thermostatic simulations were carried out at 1 atm pressure and at seven different temperatures viz: 0, 77, 100, 200, 300, 373 and 473 K for 1ps time-scale. The potential energies trajectories during the simulations were presented in Fig. 7 and the corresponding snapshots at different time steps are provided in the Supplementary Information. From Fig. 7 it can be observed at 0K and 77K hydrogen adsorbed systems are stable enough and almost all hydrogen molecules remain adsorbed on Li sites resulting in gravimetric density in the range of 22.5 wt% – 26.4 wt% which fairly good as per the standard of US-DOE. Upon increasing the temperature to 100K, first H₂ molecule starts desorbing from the host cluster starts around 200fs. Further increasing the temperatures it is found that, at 373K and 473K only two hydrogen molecules are weakly attached to the host clusters. The ADMP simulation reveals that, the systems are stable at lower temperature and releases maximum of hydrogen molecules at the higher temperatures for all the systems. Moreover, it is noteworthy to say that, during the simulations insignificant deformation in the host clusters makes them potential reversible storage medium for future application.

3. Conclusion

Lithium decorated borane clusters (BₙHₙLi₆, n = 5–7) have been investigated for hydrogen storage medium using first principle calculation. On full saturation, the clusters can adsorb maximum up to 18 H₂ molecules in quasi molecular form through Niu-Rao-Jena type of bonding with average adsorption energy range of 0.10–0.11 eV/H₂ and average Li-H₂ distance 2.436–2.550 Å. The hydrogen adsorbed compounds followed the maximum hardness and minimum electrophilicity principle signifying their better stabilization. The calculated HOMO-LUMO energy gap increased with the increasing number of H₂ molecules also reconfirming their kinetic stability. The analysis of the QTAIM results revealed the the nature of the interaction between Li-H to be weak van der Waals type. The MD simulations shows that the H₂ molecules are physisorbed at 0K and 77K, giving rise to gravimetric density up to 26.2 wt% which was well above the target set by US-DOE. At higher temperature such as 373K and 473Kthe host clusters almost all hydrogen molecules without any structural distortion. The above discussion supports the fact that the studied clusters could be promoted as a potential hydrogen storage medium.

Declarations

Acknowledgements:

We acknowledge the financial support from Science & Engineering Research Board (SERB), DST, India under grant no. EMR/2014/000141. Authors also acknowledge Indian Institute of Technology (Indian School of Mines), Dhanbad for providing support and other research facilities.

Ethical Approval:

We hereby declare that all the authors are aware of and approve of the submission.
Consent to Participate:
We hereby declare that they have consent to participate

Consent to Publish:
We hereby declare that we are agree to publish the manuscript

Authors’ Contributions:
Shakti S Ray: Conceptualization, Software, Formal analysis, Investigation, Writing-Original Draft, Sridhar Sahu: Supervision, Review & Editing, Project administration, Funding acquisition.

Funding Information:
Engineering Research Board (SERB), Govt. of India under Extramural Research grant (No. EMR/2014/00014)

Competing Interests:
We hereby declare that we have no competing interest.

Conflict of interest:
We hereby declare that we have no conflicts of interest.

Availability of data and material:
All data generated or analysed during this study are included in this published article and its supplementary information files.

Code availability:
Not applicable.

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Figures
Figure 1

Optimized geometry of Lithium doped Boranes at M06/6-311++G(d,p) level of theory. Stability of the hydrogenated clusters is an important aspect to focus on while studying.

Figure 2

Optimized geometry of Hydrogen trapped lithium doped boranes at M06/6-311++G(d,p) level of theory.
Figure 3

Variation of HOMO-LUMO gap with number of H2 molecules per cluster of hydrogen trapped lithium decorated borane clusters.
Figure 4

Variation of average adsorption energy with number of adsorbed H2 molecules per cluster.
Figure 5

Hirshfeld charges of B, Li and H of BnHnLi6, n=5-7 clusters at M06/6-311++G(d,p) level of theory.

Figure 6

Density of States (DOS) for BnHnLi6, n=5-7 clusters at M06/6-311++G(d,p) level of theory.
Partial density of states (PDOS) of host as well as hydrogen trapped complexes. A Fermi energy is set to zero and indicated by red dashed line.

Figure 7

Potential energy trajectories of hydrogen loaded lithium doped boranes at 0K, 77K, 100K, 200K, 300K, 373K and 473K temperatures.

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