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HYDROGEN STORAGE IN FUNCTIONALIZED BORAZINE: A DENSITY FUNCTIONAL THEORY APPROACH

Dnyaneshwar Kalyan [a]
& Ravinder Konda[b]
[a]*Dept. of Physics,*
Sri Datt Art commerce and Science College,
Hadgaon, Nanded-431712.
&
[b]*Dept. of Physics,*
Late Babasaheb Deshmukh Gorthekar College,
Umri, Nanded-431807.

ABSTRACT

Storage of alkali and transition functionalized $B_3N_3H_6$ for hydrogen storage has been studied using Density Functional Theory method. We found that $B_3N_3H_6Li$, $B_3N_3H_6Ti$ can interact with maximum two and five hydrogen molecules respectively with respective gravimetric hydrogen uptake capacity of 4.40 and 7.28 wt % respectively. The uptake capacity has been calculated excluding the weight of hydrogen atoms which are bonded to Boron and Nitrogen. The hydrogen adsorption energies, different structural parameters are obtained for these complexes. The hydrogen adsorption energies obtained are in the range of physisorption and chemisorptions which is essential for a material to be ideal for hydrogen storage.

Corresponding author: Ravinder konda (E-mail- rkonda98@gmail.com)

RESEARCH PAPER

1. Introduction

Present energy sources like fossil fuels not only cause air pollution and destruct our precious ozone layer but are also limited in their supply. We have to find another energy source which should be unlimited in its supply and should be environment friendly. Considering the increasing air pollution and exploitation of fossil energy resources, the implementation of new energy concept is essential for the future industrialized society[1-2]. Hydrogen has been proposed as an ideal energy carrier and clean fuel for the future. It is also expected to be used as an alternative for fossil fuel. As scientist look for alternative energy source, fuel cells operate in a basic environment have garnered much attention. Hydrogen is the most abundant element in the universe and has the special characteristics like colorless at normal temperature and pressure, lower in density, lower melting and boiling points, high diffusion coefficient and high specific heat capacity etc. It has the highest energy content than any common fuel by weight (about three times more than the gasoline), but the lowest energy content by volume (about four times less than the gasoline). At temperatures below −262 °C hydrogen exists as a solid with a density of 70.6 kg/m^3. Hydrogen has all the good qualities for using it to generate electricity when it is used in a fuel cell. However storing the hydrogen on broad vehicles is the major problem.

There are different techniques available to store hydrogen each with its own advantages and disadvantages. For hydrogen economy to be a reality the problem of hydrogen storage needs to be solved. Hydrogen storage research is important for mobile and stationary applications. For mobile hydrogen storage, the material based storage system must meet the needs of hydrogen fuel cell vehicles in terms of volume, weight, percent hydrogen, cost, fast adsorption and desorption kinetics. Materials based stationary hydrogen applications must be more cost effective and energy efficient than pressurized gaseous hydrogen storage or uniquely meet particular requirements of specific stationary applications.

Finding a suitable material with high hydrogen uptake capacity and faster H_2 adsorption desorption kinetics will help us to use fuel cells in automobile sector and will convert our transportation system from one dominated by oil to one dominated by hydrogen. The important benefit of a hydrogen storage economy is that fuel cells are non- polluting and no carbon emissions are produced. When electricity is generated using fuel cell, the only byproduct it gives as a water and some heat is also produced which can be used for other applications. If every vehicle on a road is powered by fuel cell, then there will be no air pollution, which is the requirement for the clean and green environment. One of the difficulties in hydrogen economy to be a reality is finding a suitable material for hydrogen storage with high uptake capacity and faster adsorption and desorption kinetics at ambient conditions. Different groups at national and international levels are involved for the development of a material for hydrogen storage. Tremendous efforts have been made for the development of material that can hold sufficient hydrogen in terms gravimetric and volumetric densities and kinetic properties. It includes carbon nanotubes, metal organic and inorganic frame work, chemical hydrides, polymers nanocomposites etc. [3-20]. Most of the studies are focused on organometallic structures. As compared to the small organometallic complexes, metal decorated inorganic (inorganometallic) complexes have received less attention as a hydrogen storage material. In this work we are going to study the H_2 uptake

capacity of inorganometallic (IOM) complexes using quantum chemical methods and verify whether it satisfies the targets set by U.S. DOE.

2. Computational details

We optimized the geometries of TM doped borazine using Density Functional Theory with PBEPBE method, alongwith 6-311G(d, p) level basis set. All calculations were performed using the Gaussian suite of programs [21,22,23].The averaged adsorption energy without zero point energy correction (ΔE) is calculated as

$$\Delta E = \{E[B_3N_3H_6]+(n*E[H_2])-E[B_3N_3H_6\ (nH_2)]\}/n$$

Here E[X] is the total energy of X without zero point energy correction and IOM is $B_3N_3H_6$
The averaged adsorption energy with zero point energy correction (ΔE_{ZPE}) is calculated as

$$\Delta E_{ZPE} = \{E_{ZPE}[B_3N_3H_6]+(n*E_{ZPE}[H_2])-E_{ZPE}[B_3N_3H_6(nH_2)]\}/n,$$

where $E_{ZPE}[X]$ is the total energy of X with zero point energy correction.
The averaged adsorption energy with Gibbs free energy correction (ΔE_G) is calculated as

$$\Delta E_G = \{E_G[B_3N_3H_6]+ (n*E_G[H_2])-E_G[B_3N_3H_6\ (nH_2)]\}/n$$

where $E_G[X]$ stands for the total energy of X with Gibbs free energy correction.
Various interaction energies for H_2 adsorbed complexes are obtained using many-body analysis technique.

3. Results and discussion

Figure 1 shows optimized structures of $B_3N_3H_6M$(M=Li, Ti) complexes at PBEPBE/6-311G (d, p) level of theory. Two and five H_2 molecules are adsorbed on Li and Ti metal atoms. The H_2 uptake capacity of the $B_3N_3H_6Li$, $B_3N_3H_6Ti$ complexes is found to be 4.40, 7.28, wt % respectively.

Table 1 shows structural parameters for TM doped borazine before and after adsorption of H_2 molecules. As can be seen from Table 1, the Ring-M atom bond length $B_3N_3H_6Li$, $B_3N_3H_6Ti$, $B_3N_3H_6Li(2H_2)$, $B_3N_3H_6Ti(5H_2)$ complexes is found to be 2.53, 2.51, 2.53, 2.72 respectively. After the adsorption of H_2 molecules on Ti the bond lenths is elogated, no change is observed in the Li doped complexes. Two H_2 molecules are adsobed on $B_3N_3H_6Li$ complex at a distance of 1.90 Å. Five hydrogen molecules are adsorbed on $B_3N_3H_6Ti$ complex in that one hydrogen molecule is disociated.The H_2 molecules are adsorbed at a ditance of 1.99, 1.87, 1.80, 1.87 and 1.74-1.88 Å respectively.

Calculated averaged H_2 adsorption energies without (ΔE), with zero point energy correction (ΔE_{ZPE}) and with Gibbs free energy correction (ΔE_G) at 298.15 K and 1 atm. pressure are presented in Table 2 for maximum H_2 adsorbed complexes. Table 2 shows the H_2 adsorption on $B_3N_3H_6Li$ complexes is energetically unfavourable at ambient conditions whereas it is favourable on $B_3N_3H_6Ti$ complexes. It can also be seen from Table 2 that the zero point energy correction for adsorption energy is significant and not negligible. The H_2 adsorption energies for Li doped borazine are lower than that for the Ti doped borazine systems indicating weak interaction of H_2 molecules with the former than the latter.

Since adsorption of two H_2 molecules on $B_3N_3H_6Li$ complexes is energetically unfavorable at ambient conditions. Also, we have calculated H_2 adsorption energies at different temperatures to know the suitable temperature range over which H_2 adsorption is energetically favorable. For obtaining H_2 adsorption energies at different temperatures, the pressure is kept constant as 1 atm. Figure 3 shows temperature dependent H_2 adsorption energies respectively for $B_3N_3H_6Li(2H_2)$ and $B_3N_3H_6Ti(5H_2)$ complexes. Figure 3 shows that H_2 adsorption on $B_3N_3H_6Ti$ complexes is energetically favourable at all the temperatures considered here at PBEPBE/6-311G (d, p) level of theory. H_2 adsorption on $B_3N_3H_6Li$ is possible below 125 K .

The stability of H_2 adsorbed complexes is confirmed by the gap between Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO). The HOMO-LUMO gap with successive adsorption of H_2 molecules for all the four complexes is shown in Figure 3. It can be seen that the HOMO-LUMO gap for the $B_3N_3H_6Li(2H_2)$ and $B_3N_3H_6Ti(5H_2)$ complexes maximum is found to be 1.90 and 2.50eV respectively. It is observed that the substitution of boran and nitrogen can enhance the stability the complexes. Also HOMO-LUMO gap for the H_2 adsorbed complexes is higher than that for the respective isolated organometallic complexes indicating more kinetic stability of former than the latter.

Conclusions

Density functional theory with PBEPBE functionals and 6-311G (d, p) basis set have been used to study the effect of boron and nitrogen substitution on H_2 uptake capacity of Li and Ti decorated benzene. Boron substitution enhances the H_2 uptake capacity of benzene Electronic structure calculations show that two and five H_2 molecules get adsorbed on $B_3N_3H_6Li$ and $B_3N_3H_6Ti$ complex respectively. The H_2 uptake capacity predicted here for the boron and nitrogen substituted TM doped benzene complexes is satisfying the target set by US DOE-2025.

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REFERENCES

[1] L. Schlapbach, A. Züttel, *Nature*, 2001, **414**, 353**.**
[2] M. Dornheim, pirajAin, 2011, **978**, 953.
[3] S. Orimo, Y. Nakamori, JR. Eliseo, A. Zu¨ ttel and CM. Jensen, *Chem Rev*, 2007, **107**, 4111.
[4] C.W. Hamilton, RT. Baker, A. Staubitz, I. Manners and N. Be, *Chem Soc Rev*, 2009, **38**, 279.
[5] V.V. Struzhkin, B. Militzer, WL. Mao, HK. Mao and RJ.Hemley, *Chem Rev*, 2007, **107**, 4133.
[6] A.W.C. van den Berg, CO. Area´n, *Chem Commun*, 2008, **6**, 668.
[7] J. Weber, M. Antonietti, A. Thomas, *Macromolecules*, 2008, **41**, 2880.
[8] N.L. Rosi, J. Eckert, M. Eddaoudi, DT. Vodak, J. Kim, M. O'Keeffe,et al, *Science*, 2003, **300**, 1127.
[9] J.L.C. Rowsell, OM. Yaghi, Angew, *Chem Int Ed*, 2005, **44**, 4670.
[10] M. Fichtner, *Adv Eng Mater*, 2005, **7**, 443.
[11] R.A. Andrievski, *Phys Usp*, 2007, **50**, 691.
[12] C.M. Brown, Y Liu, DA Neumann, *Pramana - J. Phys.*, 2008, **71**, 755.
[13] M. Suri, M Dornfeld, E Ganz, *J. Chem. Phys.*, 2009, **131**, 174703.
[14] D.A. Gomez, AF Combariza, G Sastre, *Phys. Chem. Chem. Phys.*, 2009, **11**, 9250.
[15] T. Sagara, J. Klassen, J. Ortony, E. Ganz, *J. Chem. Phys.*, 2005, **123**, 014701.
[16] A.B. Phillips, B.S. Shivaram, *Nanotechnology*, 2009, **20**, 204020.
[17] L. Kong, V.R. Cooper, N. Nijem, K. Li, J. Li, Y.J. Chabal, DC Langreth, *Phy. Rev. B.*, 2009, **79**, 081407.
[18] Y.J. Choi, J.W. Lee, J.H. Choi, J.K. Kang, *Appl. Phys. Lett.*, 2008, **92**, 173102.
[19] H.L. Park, S.C. Yi, Y.C. Chung, *Int. J. Hydrogen Energy*, 2010, **35**, 3583.
[20] H. Gao, X.B. Wu, J.T. Li, G.T. Wu, J.Y. Lin, K. Wu, D.S. Xu, *Appl. Phys. Lett.*, 2003, **83**, 3389.
[21] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G,E. Scuseria, M.A. Robb and J.R. Cheeseman, et al. *Gaussian 03. Revision E.01. Wallingford CT: Gaussian, Inc*, 2004.
[22] H.L. Park, S.C. Yi and Y.C. Chun, *Int J Hydrog Energy*, 2010, **35**, 3583–3587.
[23] D.R. Lide. CRC Handbook of Chemistry and Physics, 75th Ed. New York, 1994.

Table 1: Structural parameter $B_3N_3H_6M(nH_2)$ (n= 0, 1, 2)(M=Li, Ti) complexes obtained at PBEPBE/6-311G(d,p) level with subsequent addition of H_2 molecules. Bond lengths are in Å

Complex	RING-TM (avg)	TM-1H_2	TM-2H_2	TM-3H_2	TM-4H_2	TM-5H_2
$B_3N_3H_6Li$	2.53	------	------	------	------	------
$B_3N_3H_6Li(2H_2)$	2.53	1.90	1.90	------	------	------
$B_3N_3H_6Ti$	2.21	------	------	------	------	------
$B_3N_3H_6Ti(5H_2)$	2.72	1.99	1.87	1.80	1.87	1.88-1.74*

*** Indicates dissociation of hydrogen molecule**

Table 2. Calculated averaged H_2 adsorption energy without (ΔE), with zero point energy correction (ΔE_{ZPE}) and with Gibbs free energy correction (ΔE_G) in eV at 298.15K for $B_3N_3H_6M(nH_2)$ (n = 0, 1, 2, 3, 4 and 5)(M=Li, Ti) complexes obtained at PBEPBE/6-311G(d, p) level of theory.

Complex	ΔE	ΔE_G	ΔE_{ZPE}
$B_3N_3H_6Li(2H_2)$	0.19	-0.20	0.08
$B_3N_3H_6Ti(5H_2)$	0.73	0.26	0.56

Caption to Figures

Figure 1. Optimized structures of $B_3N_3H_6Li(2H_2)$ and $B_3N_3H_6Ti(5H_2)$ at PBEPBE/6-311G(d, p) level of theory.

Figure 2. Temperature dependent Gibbs free energy corrected adsorption energies for $B_3N_3H_6Li(2H_2)$ and $B_3N_3H_6Ti(5H_2)$ complexes at PBEPBE/6-311G(d, p) level of theory.

Figure 3-. HOMO-LUMO gap with successive addition of H_2 molecules on $B_3N_3H_6Li$ and $B_3N_3H_6Ti$ complexes at PBEPBE/6-311G(d, p) level of theory.

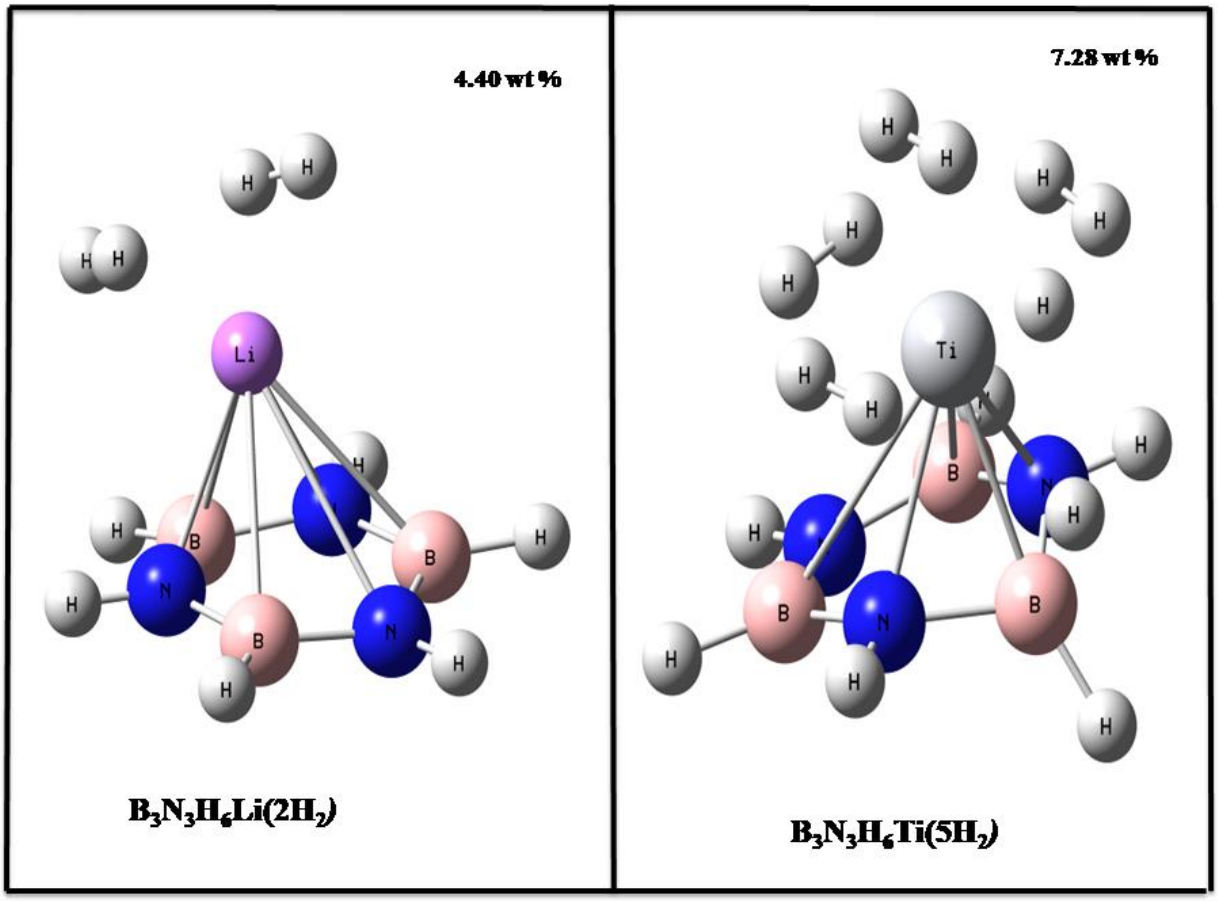

Figure 1

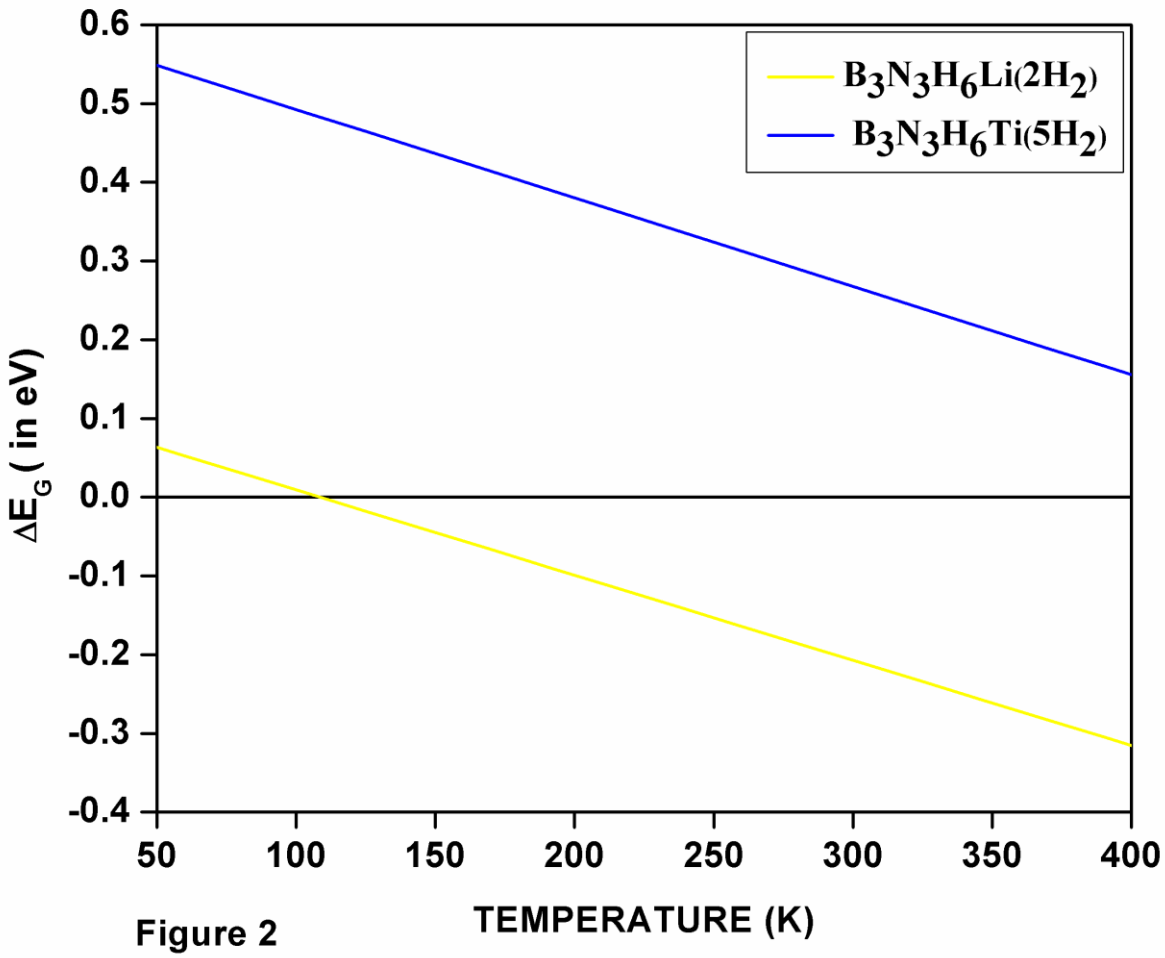
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
-0.4
ΔE_G (in eV)
50
100
150
200
250
300
350
400
TEMPERATURE (K)
B3N3H6Li(2H2)
B3N3H6Ti(5H2)

Figure 2

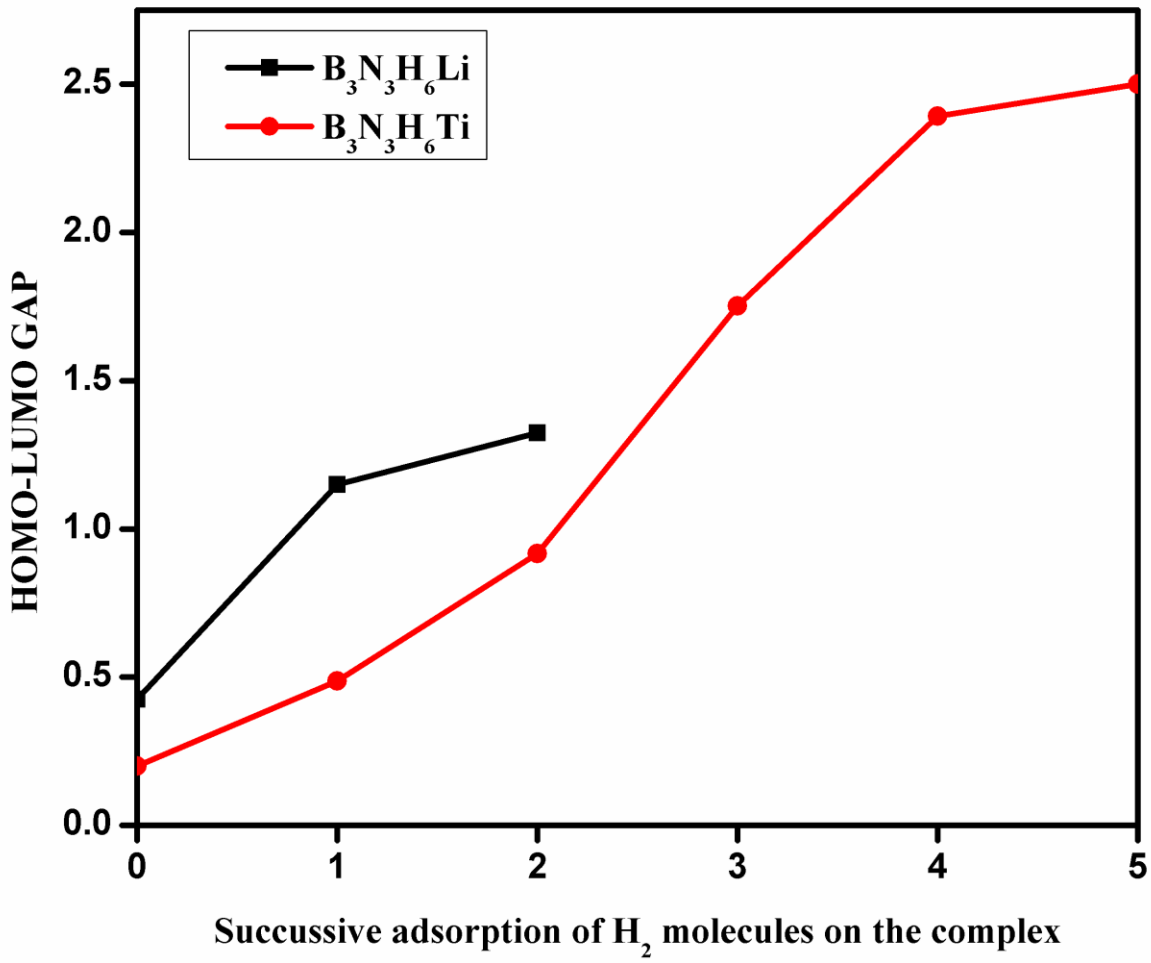
B3N3H6Li
B3N3H6Ti
HOMO-LUMO GAP
2.5
2.0
1.5
1.0
0.5
0.0
0
1
2
3
4
5
Successive adsorption of H2 molecules on the complex

Figure 3