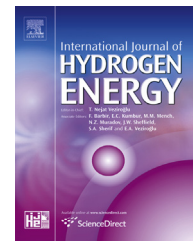




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# Boron substituted and un-substituted aromatic complexes as hydrogen storage media

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## ABSTRACT

Interaction of H<sub>2</sub> molecules with functionalized boron substituted and un-substituted naphthalene has been studied. Computational results reveal that gravimetric hydrogen uptake capacities of C<sub>10</sub>H<sub>8</sub>Ti<sub>4</sub>, C<sub>6</sub>B<sub>4</sub>H<sub>8</sub>Ti<sub>4</sub>, C<sub>10</sub>H<sub>8</sub>Li<sub>4</sub>, and C<sub>6</sub>B<sub>4</sub>H<sub>8</sub>Li<sub>4</sub> complexes are 9.16, 8.23, 7.20 and 9.64 wt % respectively from the electronic structure method. The possible H<sub>2</sub> desorption temperatures are 369.79 K and 420.80 K for C<sub>10</sub>H<sub>8</sub>Ti<sub>4</sub>(16H<sub>2</sub>) and C<sub>6</sub>B<sub>4</sub>H<sub>8</sub>Ti<sub>4</sub>(14H<sub>2</sub>) complexes respectively. The 4s orbitals of Ti atoms play an important role in hydrogen adsorption process. The C<sub>6</sub>B<sub>4</sub>H<sub>8</sub>Li<sub>4</sub> complex interacts very weakly with hydrogen molecules at ambient conditions. ADMP molecular dynamics simulations performed at room temperature reveal that only nine hydrogen molecules can be adsorbed on both C<sub>10</sub>H<sub>8</sub>Ti<sub>4</sub> and C<sub>6</sub>B<sub>4</sub>H<sub>8</sub>Ti<sub>4</sub> complexes. The results obtained using ADMP molecular dynamics simulations at room temperature have shown that C<sub>6</sub>B<sub>4</sub>H<sub>8</sub>Li<sub>4</sub> complex does not bind a single hydrogen molecule during simulation. The transition metal containing complexes have positive characteristics over alkali metal containing complexes as a possible hydrogen storage material.

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## Introduction

Clean, highest energy to mass ratio, renewable and eco-friendly nature are the advantages of hydrogen as a fuel over hydrocarbon fuels [1]. Being full of positive aspects as a future's fuel [2,3], the disadvantages of hydrogen are in its production and the requirement of larger volume for storage [4]. These two obstacles have explored wide area of research and become a challenge for global research community. More than a decade has already been passed but still the problem of hydrogen storage is having serious attention. This issue is

directly concerned with every human being. The traditional ways of storing hydrogen viz. pressure tanks and cryogenic storage are self-energy consuming and cannot be used at least in mobile or light vehicular applications with proper safety. There are many more materials like chemical hydrides and metal hydrides available in which hydrogen is present in atomic form [5–10]. An extraction of hydrogen from these complexes or materials is again an energy consuming process prior to its use in hydrogen powered fuel cells. These issues have urged to find a promising material which can store hydrogen with higher gravimetric and volumetric capacity [11]. The material should also have favorable

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thermodynamics at near ambient conditions for hydrogen adsorption/desorption process. The search of such ideal material is very important otherwise hydrogen economy will become a hypothetical thing.

Till now several experimental and computational studies on long range of various materials have been performed. Functionalized organic as well as inorganic materials have been studied extensively [12–19]. Previous theoretical reports have shown that boron substitution may tune up different properties related to the hydrogen storage [20]. Mono and di-boron substituted benzene ring functionalized with alkali as well as alkaline earth metals have been studied theoretically for hydrogen storage purpose [21]. Multi-functionalized naphthalene complexes have been tested for hydrogen storage [22].

In this work, boron substituted functionalized naphthalene viz.  $C_6B_4H_8Ti_4$ ,  $C_6B_4H_8Li_4$  and un-substituted viz.  $C_{10}H_8Li_4$ ,  $C_{10}H_8Ti_4$  have been chosen from the hydrogen storage point of view. The variation in structural parameters before and after hydrogen adsorption has been reported. Different properties like hydrogen uptake capacity, hydrogen adsorption energies, desorption temperature, temperature/pressure dependence of adsorption energies etc. of multi-functionalized boron substituted naphthalene have been studied. The nature of bonding has been explored. The ADMP molecular dynamics simulations have also been performed to see the variation in different bond lengths during the real time dynamics. The results of hydrogen uptake capacities from ADMP simulations and electronic structure method are compared.

## Computational details

All the geometries are optimized using the 1997 hybrid functional of Perdew, Burke and Ernzerhof (PBE) [23] in combination with split valence 6-31G(d,p) basis set. The molecular dynamics (MD) simulations have been carried out using atom centered density matrix propagation (ADMP) [24]. The time step ( $\Delta t$ ) of ADMP–MD was set at 0.2 fs. The temperature was maintained using the velocity scaling method during the MD simulations. All the calculations are performed using the Gaussian 09 suite of programs [25].

The averaged adsorption energy without zero point energy correction ( $\Delta E$ ) is calculated as

$$\Delta E = \{E[\text{BSOM}] + (n \times E[H_2]) - E[\text{BSOM}(nH_2)]\}/n \quad (1)$$

where  $E[X]$  is the total energy of X without zero point energy correction and BSOM (Boron Substituted Organometallic Complex) is either  $C_6B_4H_8Li_2$  or  $C_6B_4H_8Ti_2$ . The averaged adsorption energy with zero point energy correction ( $\Delta E_{ZPE}$ ) is calculated as

$$\Delta E_{ZPE} = \{E_{ZPE}[\text{BSOM}] + (n \times E_{ZPE}[H_2]) - E_{ZPE}[\text{BSOM}(nH_2)]\}/n \quad (2)$$

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

$$\Delta E_G = \{E_G[\text{BSOM}] + (n \times E_G[H_2]) - E_G[\text{BSOM}(nH_2)]\}/n \quad (3)$$

where  $E_G[X]$  stands for the total energy of X with Gibbs free energy correction.

## Results and discussion

In this work, we have optimized the geometries of  $C_{10}H_8Ti_4$ ,  $C_6B_4H_8Ti_4$  and  $C_6B_4H_8Li_4$  complexes using PBEPBE method and 6-31G(d,p) basis set. The bond lengths of naphthalene obtained using this particular combination of method and basis set are in excellent agreement with experimental determinations. However at present no experimental results are available for the complexes which we have studied here for the sake of comparison. The optimized geometries have been shown in Fig. 1. We have doped total four metal atoms (either Ti or Li): two on top of a ring and two from the bottom. It is found from the optimized geometries that the average distance between metal atom and C/B atoms of a ring in  $C_{10}H_8Ti_4$  and  $C_6B_4H_8Ti_4$  complex is 2.19 Å and 2.18 Å respectively which increases to 2.58 Å in  $C_{10}H_8Ti_4(16H_2)$  and 2.41 Å in  $C_6B_4H_8Ti_4(14H_2)$  complexes. The Ti–Ti distance on either top or bottom of a ring is 2.40 Å in  $C_{10}H_8Ti_4$  complex whereas it is increased by 0.30 Å in  $C_6B_4H_8Ti_4$  as compared to the  $C_{10}H_8Ti_4$  complex. This Ti–Ti distance further increases to 2.75 Å (top and bottom both side) in  $C_6B_4H_8Ti_4(14H_2)$  complex whereas in  $C_{10}H_8Ti_4(16H_2)$  complex Ti–Ti distance is not equal on top (3.12 Å) and bottom (3.38 Å) side of a ring.

In lithium containing complexes viz.  $C_{10}H_8Li_4$  and  $C_6B_4H_8Li_4$  the average distance of Li atom from host atoms in a ring is 2.34 Å and it decreases to 2.19 Å upon boron substitution i.e. in  $C_6B_4H_8Li_4$  complex. There is no considerable change found between host atom and Li distance upon maximum hydrogen adsorption on  $C_{10}H_8Li_4$  and  $C_6B_4H_8Li_4$  complexes. The Li–Li distance on both side of a ring is 3.13 Å and 2.95 Å in  $C_{10}H_8Li_4$  and  $C_6B_4H_8Li_4$  complexes respectively and it increases to 3.21 Å in  $C_{10}H_8Li_4(6H_2)$  and decreases to 2.91 Å in  $C_6B_4H_8Li_4(8H_2)$  complex.

We found that  $C_{10}H_8Ti_4$  and  $C_6B_4H_8Ti_4$  complexes can interact with 16 and 14 hydrogen molecules respectively. In  $C_{10}H_8Ti_4(16H_2)$  complex three hydrogen molecules are adsorbed in dissociated form whereas in  $C_6B_4H_8Ti_4(14H_2)$  complex 4 hydrogen molecules are dissociated. The Ti–H<sub>2</sub> distances (only molecular H<sub>2</sub>) in  $C_{10}H_8Ti_4(16H_2)$  and  $C_6B_4H_8Ti_4(14H_2)$  complexes range from 1.85 to 1.93 Å and 1.85–2.07 Å respectively. The H–H bond lengths in both the complexes are also changed than that of isolated H<sub>2</sub> molecule. The H–H bond lengths in  $C_{10}H_8Ti_4(16H_2)$  and  $C_6B_4H_8Ti_4(14H_2)$  complexes are found to be elongated than that of isolated free H<sub>2</sub> molecule (0.74 Å). It indicates that there is Kubas interaction between metal atom and H<sub>2</sub> molecules [26]. Fig. 2 shows optimized structures of H<sub>2</sub> adsorbed complexes.

As far as  $C_{10}H_8Li_4(6H_2)$  and  $C_6B_4H_8Li_4(8H_2)$  complexes are concern, adsorption of all hydrogen molecules is in molecular form unlike Ti doped complexes studied here. In both  $C_{10}H_8Li_4(6H_2)$  and  $C_6B_4H_8Li_4(8H_2)$  complexes Li–H<sub>2</sub> distances are above 2 Å which results in lower adsorption energies. In these two complexes the H–H distances of adsorbed H<sub>2</sub> molecules hardly changes by 0.02 Å than that of isolated H<sub>2</sub> molecule.

The gravimetric uptake capacities of  $C_{10}H_8Ti_4$ ,  $C_6B_4H_8Ti_4$ ,  $C_{10}H_8Li_4$  and  $C_6B_4H_8Li_4$  are 9.16, 8.23, 7.20 and 9.64 wt %

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