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A first-principle investigation into effect of B- and BN-doped C_{60} in lowering dehydrogenation of MXH_4 (where M = Na, Li and X = Al, B)

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Abstract. The present paper reports the effect of B- and BN-doped C_{60} as catalysts for lowering the dehydrogenation energy in MXH_4 clusters (M = Na and Li, X = Al and B) using density functional calculations. MXH_4 interacts strongly with B-doped C_{60} and weakly with BN-doped C_{60} in comparison with pure C_{60} with binding energy 0.56–0.80 and 0.05–0.34 eV, respectively. The hydrogen release energy (E_{HRE}) of MXH_4 decreases sharply in the range of 38–49% when adsorbed on B-doped C_{60}; however, with BN-doped C_{60} the decrease in the E_{HRE} varies in the range of 6–20% as compared with pure MXH_4 clusters. The hydrogen release energy of second hydrogen atom in MXH_4 decreases sharply in the range of 1.7–41% for BN-doped C_{60} and decreases in the range of 0.2–11.3% for B-doped C_{60} as compared with pure MXH_4 clusters. The results can be explained on the basis of charge transfer within MXH_4 cluster and with the doped C_{60}.

Keywords. Density functional theory; complex metal hydride; C_{60} clusters.

1. Introduction

In the current scenario, harmful effects of pollution have highlighted the need for gradual transformations away from fossil fuel base, towards renewable, sustainable clean source of energy such as hydrogen [1]. Hydrogen has the highest energy density by mass and is therefore a potential future fuel option for on-board usage [2]. Among various scientific and technological challenges, search for hydrogen storage material that satisfies the commercial targets of gravimetric density and safety remains central for hydrogen economy [3,4].

Hydrogen storage in the solid state has advantages of safety and higher gravimetric density [5]. Among various solid-state storage options, the complex metal hydrides of lighter elements (Li, B, Na, Mg and Al) have high volumetric and gravimetric densities [6]. The usage of complex metal hydrides has been hindered due to their poor kinetics and higher temperature for hydrogen desorption [7].

In the last two decades, the use of various catalysts has been reported for improving dehydrogenation and re-hydrogenation behaviour of complex metal hydrides at ambient conditions [8–10]. When Ti, Sc and Ce as catalysts are introduced in $NaAlH_4$, the hydrogen desorption temperature is lowered with improved kinetics [11,12]. However, the low selectivity, poor durability and formation of undesirable bio-products have limited their success [7,12]. Therefore, the focus has shifted to other metal-free high-performance catalyst of nanocarbon [13].

Mixture of $NaAlH_4$ with carbon nanocomposite has affected the hydrogen desorption and re-hydrogenation favourably [14,15]. C_{60} when mixed with $NaAlH_4$ and $LiBH_4$ lowers the desorption temperature and improves the dehydrogenation kinetics [16–19]. C_{60}–$LiBH_4$ composite not only lowers the hydrogen desorption temperature but also provides conditions for re-hydrogenation at relatively low temperature of 350°C [15]. However, the role of fullerenes as catalyst in lowering the dehydrogenation is yet to be fully understood.

The paper describes the carbon nanostructures as catalysts for lowering dehydrogenation from complex metal hydrides. In the present paper, we have presented results on the effect of B- and BN-doped C_{60} as catalysts for lowering the dehydrogenation energy in MXH_4 clusters (M = Na and Li, X = Al and B) using density functional calculations. The hydrogen release energy of MXH_4 decreases sharply in the range of 38–49% for B-doped C_{60} and decreases in the range of 6–20% for BN-doped C_{60}. The hydrogen release energy of second hydrogen atom in MXH_4 decreases sharply in the

range of 1.7–41% for BN-doped C_{60} and decreases in the range of 0.2–11.3% for B-doped C_{60} as compared with pure MXH_4 clusters.

2. Theoretical methods

Density functional theory (DFT), as implemented in the Spanish Initiative for Electronic Simulation with thousands of atoms (SIESTA) computational code based on numerical atomic orbital density functional approach [20–22], has been used to investigate the catalytic effect of B- and BN-doped fullerenes on energetics of MXH_4. The exchange–correlation interactions were treated using generalized gradient approximation (GGA), implementing the exchange of Becke and the correlation function of Lee, Yang and Parr as (BLYP) exchange–correlation functional [23,24]. The core electrons were represented by non-local norm-conserving Troullier–Martins (TM) pseudo-potentials factorized in the Kleinman–Bylander form [24].

C_{60}–MXH_4 complexes were optimized within a cubic simulation cell of 20 Å. The valence states were described using DZP (double-zeta + polarization) basis sets with energy cut-off of 200 Ry. The structures were obtained by minimization of the total energy using Hellmann–Feynman forces, including Pulay-like corrections. Structural optimizations were performed using conjugate gradient algorithm until the residual forces in the optimization were smaller than 0.01 eV Å^{-1}.

The test calculations have been performed for C_{60} and $NaAlH_4$ cluster. In C_{60}, the calculated bond lengths of C–C and C=C are 1.46 and 1.42 Å, respectively, and HOMO–LUMO gap is 1.64 eV, which corroborate well with already reported values [25–28]. For the $NaAlH_4$ cluster, Na–Al and Al–H bond lengths calculated are, respectively, 2.55 and 1.61–1.68 Å, which show quite good agreement with already reported values [29].

The effect of doped C_{60} on MXH_4 has been measured in terms of energy required to remove one H atom, calculated as hydrogen release energy E_{HRE} using

$$E_{HRE} = [E(C_{60}(D)MXH_3) + E(H)] - E(C_{60}(D)MXH_4),$$
(1)

where E denotes total energy of the complexes mentioned in the brackets and hydrogen atom. The energy needed to remove one H atom from $NaAlH_4$ cluster is 3.95 eV, which is in agreement with the reported value [29].

The structural stabilities of MXH_4 on $C_{60-n}B_n$ and C_{60-2n} $(BN)_n$, i.e., doped C_{60} as $C_{60}(D)$, are calculated as binding energy, using

$$E_{Bin} = E[C_{60}(D)MXH_4] - E[C_{60}(D) + E(MXH_4)],$$
(2)

where $E[C_{60}(D)MXH_4]$, $E[C_{60}(D)]$ and $E(MXH_4)$ are the total energies of $C_{60}(D)MXH_4$, $C_{60}(D)$ and MXH_4, respectively.

3. Results and discussion

3.1 *Complex hydrides MXH_4 (M = Li, Na and X = Al, B)*

To investigate the effect of doped fullerenes on MXH_4 clusters, we first optimized structures of MXH_4 clusters using computational details described in Section 2 to obtain the ground state structures. The ground state structures of MXH_4 clusters are shown in figure 1. H atoms are bonded tetrahedrally in $NaAlH_4$, $NaBH_4$, $LiAlH_4$ and $LiBH_4$ in agreement with the reported results [30,31].

The structural properties of MXH_4 clusters are tabulated in supplementary table A. The hydrogen release energy of MXH_4 cluster has been calculated using equation (1) by removing one H atom from MXH_4 cluster:
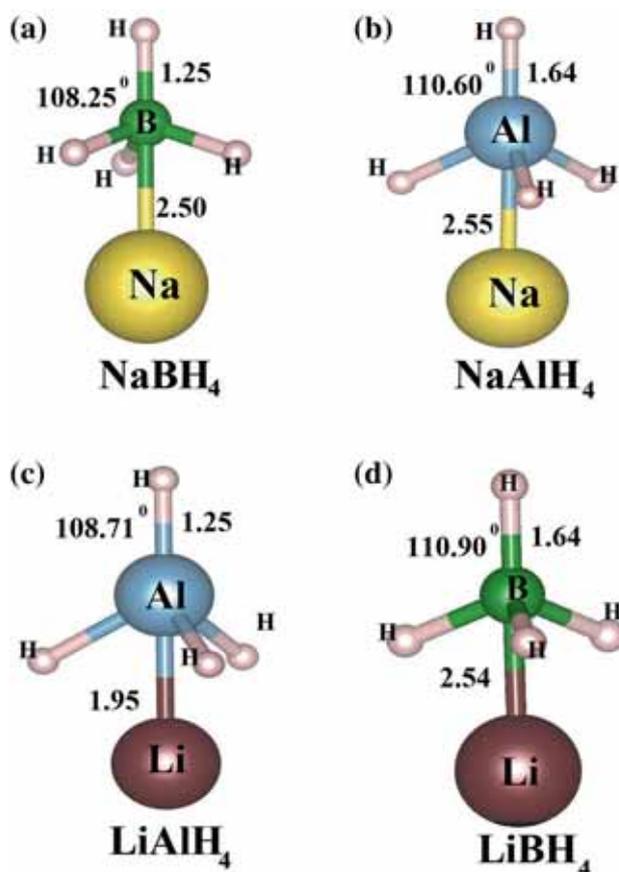

Figure 1. Optimized ground state structures of $NaBH_4$, $NaAlH_4$, $LiBH_4$ and $LiAlH_4$ clusters. The bond lengths are mentioned in Angstrom.
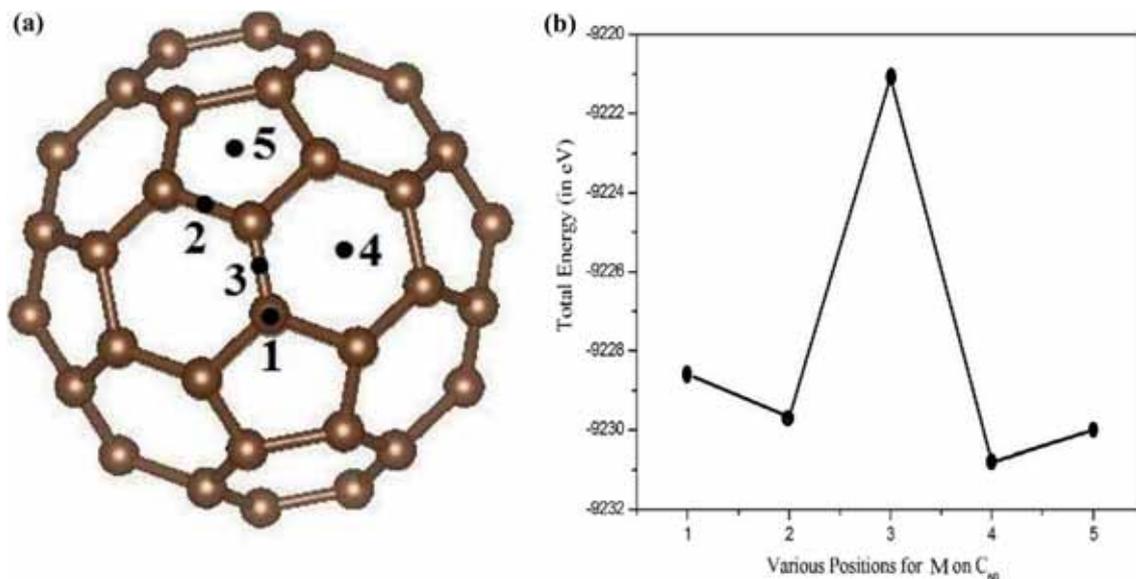
Figure 2. (**a**) Various exohedral positions of alkali atom M on fullerene surface. (**b**) Total energy of M as a function of position.

$$MXH_4 \longrightarrow MXH_3 + H. \qquad (3)$$

The structural properties of MXH_4 clusters are altered significantly on removal of H atom as shown in supplementary table A. X–H bond length decreases whereas values of M–X bond length show increase except in $NaBH_4$, on removal of H atom. MXH_4 clusters show ionic interaction between M^+ and XH_4^-, and covalent interaction between X and H. MXH_4 clusters have been described as consisting of ionic interaction between M^+ and XH_4^-, and covalent interaction between X and H. Mulliken charge analysis of MXH_4 clusters shows finite charge transfer from metal cation M^+ to anions XH_4^-, showing ionic character. In $NaAlH_4$, +0.51e charge is transferred from Na to AlH_4, resulting in ionic interaction. Hydrogen is covalently bonded to central atom (Al) in complex anions, indicated by a small amount of charge transfer to hydrogen atom as observed in the case of $NaAlH_4$ cluster; Al has an onsite charge of 2.98e. The same has been verified by plotting electronic density in different Al–H planes. The results are in good agreement with reported theoretical and experimental results [32,33].

3.2 *Interaction of MXH₄ with $C_{60-2n}(BN)_n$ and $C_{60-n}B_n$ complexes*

To model the interactions between B- and BN-doped C_{60} with MXH_4, we started by determining the minimum energy position of alkali atoms M = Na and Li on C_{60} surface. The calculations have been performed by investigating all possible configurations for determining the minimum energy position of alkali atoms M = Na and Li on C_{60} surface. The M was placed at different positions such as above the carbon atom (1), above hexagon–pentagon bond (2), above the hexagon–hexagon bond (3), above the centre of hexagon ring
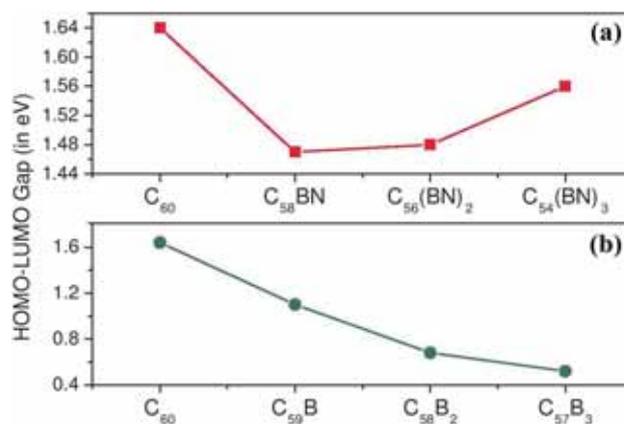

Figure 3. HOMO–LUMO gaps of $C_{60-2n}(BN)_n$ and $C_{60-n}B_n$ complexes for $n = 0$–3.

(4) and above the centre of pentagon ring (5) as shown in figure 2a. Their relative total energy of M at various positions has been plotted as a function of their position as shown in figure 2b. M above the centre of hexagon ring, i.e., at position (4), is found to be the most stable as compared with 1, 2, 3 and 5 positions by 2.21, 1.13, 9.73 and 0.8 eV, respectively. The results are in agreement with the reported results [11].

We have modelled our problem by replacing M by MXH_4 cluster in the minimum-energy structures of $C_{60}M$ and relaxing the structures till the desired convergence. To investigate the interaction of doped C_{60} with MXH_4, the C_{60} is replaced by B- and BN-doped C_{60} as $C_{60}(D)$. We have made all the possible configurations possible and the most stable configuration is preferred in all the complexes under consideration. As in the case of $C_{57}B_3$ we have considered a configuration
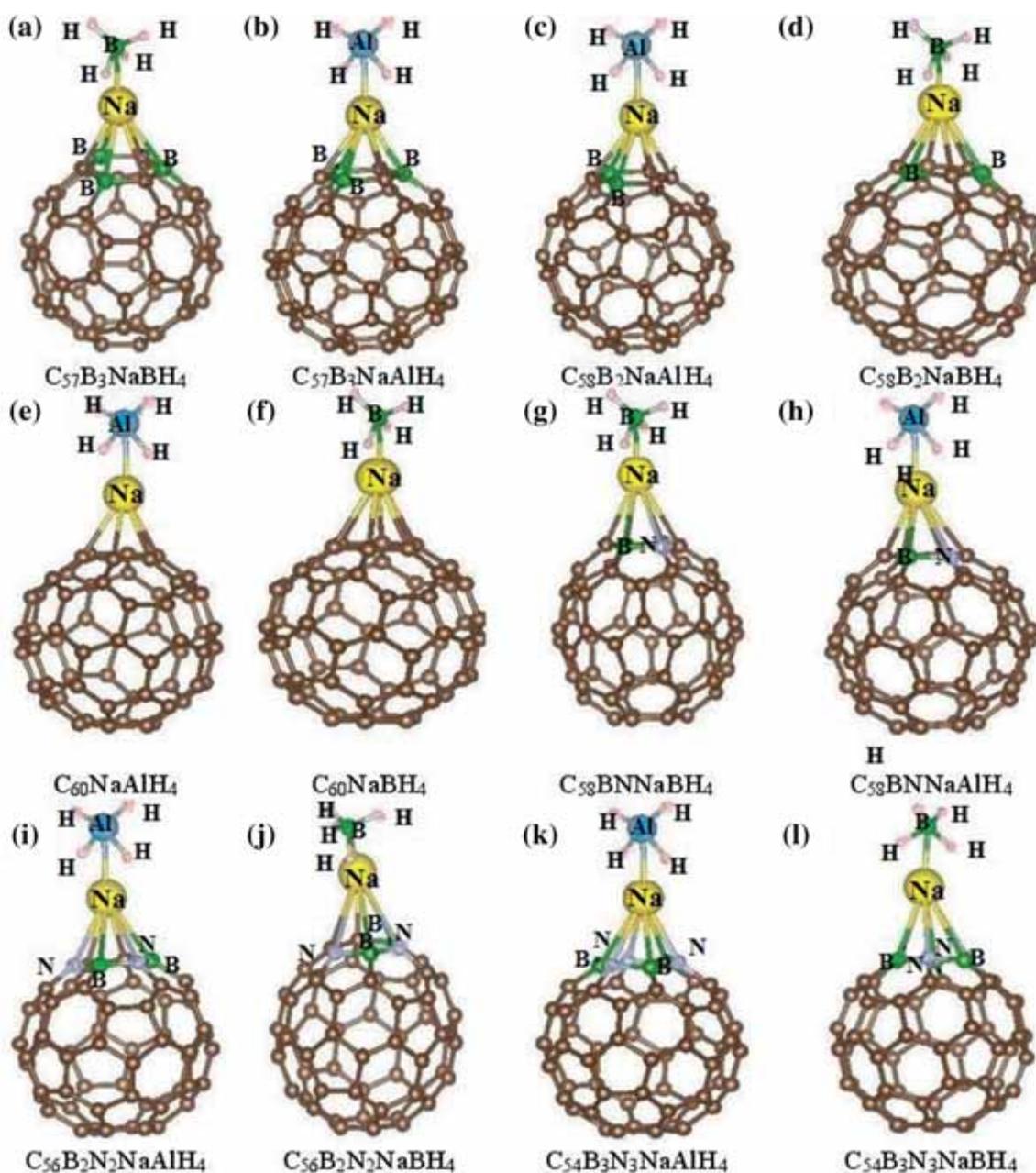
Figure 4. Optimized ground state structures of (**a**) C57B3NaBH4, (**b**) C57B3NaAlH4, (**c**) C58B2NaAlH4, (**d**) C58B2NaBH4, (**e**) C60NaAlH4, (**f**) C60NaBH4, (**g**) C58BNNaBH4, (**h**) C58BNNaAlH4, (**i**) C58B2N2NaAlH4, (**j**) C58B2N2NaBH4, (**k**) C54B3N3NaAlH4 and (**l**) C54B3N3NaBH4.

in which B is substituted at 1,3,5 or 2,4,6 positions in the hexagon and another configuration in B is substituted at 1,2,3 or 4,5,6, that is, along the same side. The former is more stable, having less energy (–8989.66 or –8989.60 eV in the hexagon on alternate positions 2,4,6 or 1,3,5, respectively) and the latter has energy of –8989.40 or 8989.42 eV, i.e., along same sides 1,2,3 or 4,5,6. Hence, position (2,4,6) is considered for further investigation in case of $C_{57}B_3$. In $C_{58}B_2$, three configurations of B doping at (1,4), (1,3) and (1,2) with energies –9068.46, –9067.74 and –9067.17 eV have been evaluated

and the one with the least energy (–9068.46 eV at (1,4)) is taken for further investigation. All such stable isomers have been considered with respect to their minimum energy on the basis of DFT calculations.

The chemical reactivity of C_{60} is enhanced when doped with B and BN. The HOMO–LUMO gap of C_{60} decreases from 1.64 to 1.12 eV, when doped with single B, therefore enhancing its chemical reactivity. When doped with single BN, the HOMO–LUMO gap decreases from 1.64 to 1.45 eV in $C_{58}BN$ as shown in figure 3. The lowest energy structure

Table 1. Binding energies in (eV) of $C_{60-n}B_n MXH_4$ and $C_{60-2n}(BN)_n MXH_4$.

Doped fullerene	$NaAlH_4$	$NaAlH_3$	$NaBH_4$	$NaBH_3$	$LiAlH_4$	$LiAlH_3$	$LiBH_4$	$LiBH_3$
C_{60}	0.76	1.34	0.48	0.95	0.78	1.50	0.47	1.03
$C_{59}B$	0.80	2.72	0.56	2.28	0.77	2.91	0.64	2.51
$C_{58}B_2$	0.08	1.89	0.18	1.46	0.15	2.06	0.07	1.66
$C_{57}B_3$	0.76	2.50	0.58	2.33	0.87	2.67	0.48	2.31
$C_{58}BN$	0.29	1.05	0.05	0.72	0.34	1.15	0.05	0.89
$C_{56}(BN)_2$	0.28	0.85	0.17	0.60	0.37	0.93	0.12	0.72
$C_{54}(BN)_3$	0.33	0.68	0.10	0.34	0.37	0.69	0.03	0.35

of $C_{60}(D)MXH_4$ complexes are shown in figure 4 and the structural properties in terms of bond length are tabulated in supplementary tables B and C as provided in the supporting information section. The tables show that the M–X bond length increases in $C_{60}(D)MXH_4$ complexes as compared with isolated $NaAlH_4$, $LiAlH_4$ and $LiBH_4$ clusters, whereas it decreases for $NaBH_4$. The increase in the M–X bond length may be understood in terms of interaction between M and doped fullerene surface. M–X* indicates bond length after removal of one hydrogen atom, which shows further increase in $C_{60}(D)MXH_4$ complexes. It may be highlighted that the bond distance between M^+ and XH_4^- unit increases and M moves towards fullerene surface.

The binding energy of $C_{60}(D)MXH_4$ complexes calculated using equation (2) has been tabulated in table 1. The binding energy of complexes shows an oscillatory behaviour with increase in number of B dopants. The binding energy increases on single B doping, decreases for 2B and increases sharply for 3B doping. The binding energy of MXH_4 in $C_{60-2n}(BN)_n C_{60}$ decreases sharply for $n = 1$ with respect to C_{60}, indicating weaker interaction of BN-doped C_{60}. The results may be explained on the basis of charge transfer between the C_{60} cluster and doped C_{60} substrate. The binding energy of $C_{60}(D)MXH_3$ is higher than that of $C_{60}(D)MXH_4$. This can be explained by stronger M and $C_{60}(D)$ interactions. The same can be understood in terms of formation of MXH_4, in which XH_4 is formed due to charge transfer from alkali (M) atom. Therefore, when one H is removed from MXH_4, the distance between M and XH_3 increases and M moves closer to $C_{60}(D)$ to bind strongly as compared with MXH_4.

The Mulliken charge analysis has been performed on MXH_4 clusters and resultant complex structures. The results can be explained on the basis of change in the ability of M to donate charge to XH_4^-. In all MXH_4 clusters, the Mulliken charge of order 0.51–0.31e is transferred from M to XH_4^- unit. The ionic interaction due to charge transfer between M^+ and XH_4^- leads to the stability. When MXH_4 interacts with the 6m ring of the C_{60}, there is a charge transfer of 0.31–0.39e from C_{60} to MXH_4. This results in weaker electropositive behaviour at M site, making the ionic interactions between M and XH_4^- weaker. The bond distance between M^+ and XH_4^- unit increases and M moves towards fullerene surface. In B-doped C_{60}, the Mulliken charge transfer from surface cage
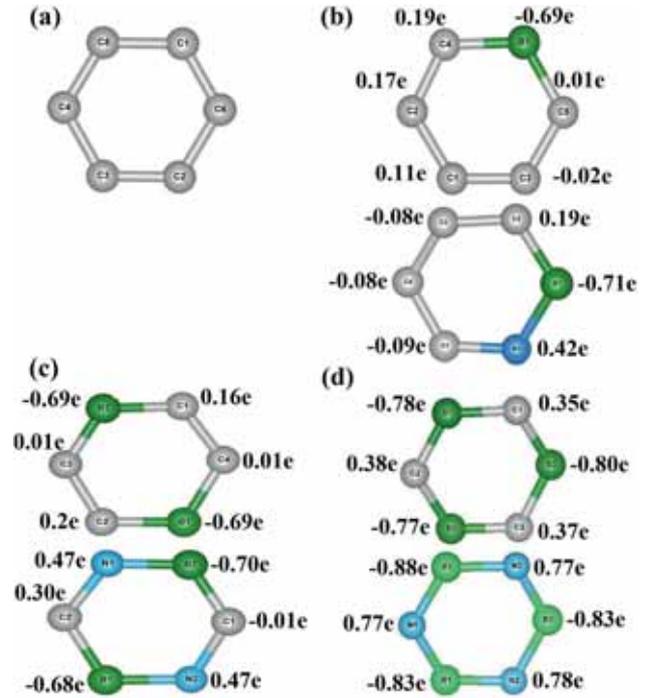
Figure 5. On-site net Mulliken charge on C, B and N atoms in the six-member ring of $C_{60-n}B_n$ and $C_{60-2n}(BN)_n$ complexes for $n = 0-3$.

to MXH_4 unit decreases from 0.23 to 0.34e for M = Na and 0.28 to 0.44e for M = Li. In BN-doped C_{60}, net charge at M is 0.16–0.36e for M = Na and Li. The smaller charge transfer in BN-doped cage can be cited for weaker binding energy.

In $NaXH_4$ cluster, Na donates 0.49–0.61e to XH_4 unit, resulting in ionic interactions. On interaction with the fullerene surface, the net charge at Na decreases significantly from 0.11 to 0.30e in $C_{60-n}B_n NaAlH_4$ and 0.49 to 0.61e in $C_{60-n}B_n NaBH_4$. When $NaXH_4$ cluster interacts with $C_{60-2n}(BN)_{2n}$ the Na donates 0.19–0.40e to XH_4. In $LiXH_4$ cluster, Li donates 0.33–0.49e to XH_4 unit. When it interacts with the fullerene surface, the net charge at Li decreases marginally to 0.28–0.44e in $C_{60-n}B_n LiXH_4$. When $LiXH_4$ interacts with $C_{60-2n}(BN)_{2n}$, the net charge at Li is 0.16–0.36e. This decrease in the net charge at alkali atom leads
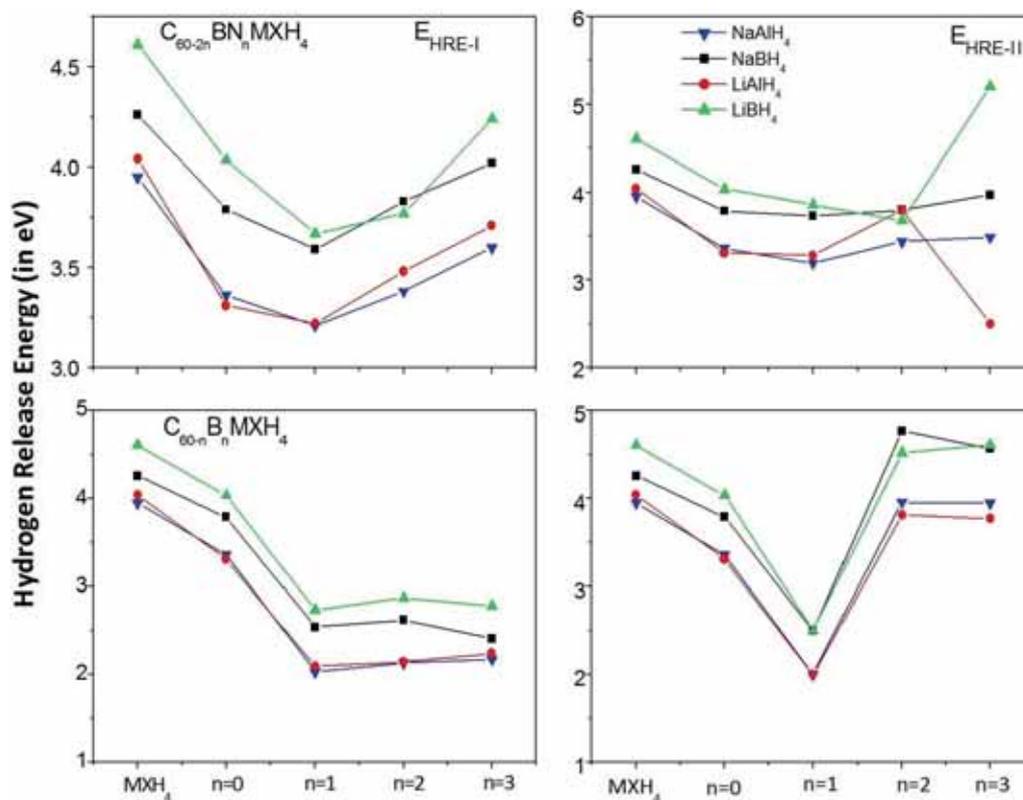
Figure 6. Hydrogen release energies of $C_{60}(D)MXH_4$ where D is B_n or $(BN)_n$. The starting point denotes the hydrogen release energy of MXH_4 units, whereas down triangles, up triangles, square and circle represent that for $NaAlH_4$, $LiBH_4$, $NaBH_4$ and $LiAlH_4$, respectively. E_{HRE-I} and E_{HRE-II} are the first- and second-order hydrogen release energy, respectively, of $C_{60}(D)MXH_4^-$ complexes.

to weakening of ionic interactions between M and XH_4 and results in weaker covalent interactions between X and H.

The Mulliken charge analysis shows net charge at boron atom, nitrogen atom and nearest neighbour carbon atoms in C_{60} as shown in figure 5. In B-doped C_{60} structures, B acts as an electron acceptor and N acts as an electron donor C. Since B carries negative charge while N carries positive charge and the compensating positive charge is carried by the adjacent C atoms, therefore B–N pair in C_{60} provides electron-rich and positive hole carriers. Thus, doping in C_{60} creates preferential sites for nucleophilic and electrophilic attack for catalytic applications [34,35].

The change in the energetics of the MXH_4 clusters has been measured in terms of dehydrogenation in $C_{60}(D)MXH_4$ complexes using equation (1) and is shown in figure 6. The hydrogen energy shows significant decrease of 38–49% in $C_{60-n}B_nMXH_4$ for $n = 1-3$ in comparison with pure C_{60}, which shows decrease in E_{HRE} up to 18% only. The alnate clusters ($NaAlH_4$ and $LiAlH_4$) show larger decrease in hydrogen release energy than boro-hydride clusters ($NaBH_4$ and $LiBH_4$). The hydrogen release energy decreases by 6–20% in $C_{60-2n}(BN)_nMXH_4$ for $n = 1-3$. For $n = 2$ and $n = 3$, the hydrogen release energy shows gradual increases with respect to $n = 1$ as shown in figure 6a and described by E_{HRE-I}.

BN-doped C_{60} is found to be less effective as a catalyst for dehydrogenation from MXH_4 as compared with B-doped C_{60}. However, BN doping is not effective in lowering the dehydrogenation energy of MXH_4 with respect to pure C_{60}. The hydrogen release energy of second hydrogen from MXH_4 has also been calculated and shown in figure 6b and described by E_{HRE-II} in the graph. The hydrogen release energy of second hydrogen atom in MXH_4 decreases sharply in the range of 1.7–41% for BN-doped C_{60} and decreases in the range of 0.2–11.3% for B-doped C_{60} as compared with pure MXH_4 clusters. B-doped C_{60} is found to be less effective as a catalyst for second dehydrogenation from MXH_4 as compared with BN-doped C_{60}.

The sharp decrease in hydrogen release energy in B- and BN-doped C_{60} may be explained on the basis of stronger interaction due to electron-deficient site in 6m ring of C_{60} surface, which is consistent with relatively higher binding energy value. The interactions of MXH_4 clusters with the doped fullerenes affect the ability of Na and Li to interact with XH_4^- anion, resulting in weaker ionic interactions between M and X and weakening of X–H bond.

At this point, we would like to mention that when the bulk material is characterized mainly by ionic and covalent interactions, its small clusters have been found to describe

many properties of the bulk accurately [36]. Therefore, the behaviour of NaAlH$_4$ and NaBH$_4$ can be described by considering their clusters. This is consistent with our results of the smaller cluster of complex hydrides, which are consistent with the dehydrogenation pattern of the experimental results on NaAlH$_4$ and NaBH$_4$ with C$_{60}$ system [16,17].

4. Conclusion

In this work, we have investigated the effect of B- and BN-doped C$_{60}$ in lowering the dehydrogenation energy of metal hydride clusters NaAlH$_4$, NaBH$_4$, LiAlH$_4$ and LiBH$_4$ (MXH$_4$) using DFT calculations. MXH$_4$ clusters interact strongly with B- and BN-doped C$_{60}$ due to electron-deficient behaviour and higher chemical reactivity of B- and BN-doped C$_{60}$. M–X bond length increases in C$_{60}$(D)MXH$_4$ complexes compared with isolated NaAlH$_4$, LiAlH$_4$ and LiBH$_4$ clusters, whereas it decreases for NaBH$_4$. This implies that bond distance between M$^+$ and XH$_4^-$ unit increases and results in weakening of various ions involved.

Our results have shown that doped C$_{60}$ is more effective in lowering the hydrogen release energy of MXH$_4$ clusters. The hydrogen release energy of MXH$_4$ decreases sharply in the range of 38–49% for B-doped C$_{60}$ and decreases in the range of 6–20% for BN-doped C$_{60}$ with respect to pure MXH$_4$ clusters. The hydrogen release energy of second hydrogen atom in MXH$_4$ decreases sharply in the range of 1.7–41% for BN-doped C$_{60}$ and decreases in the range of 0.2–11.3% for B-doped C$_{60}$ as compared with pure MXH$_4$ clusters. The results can be interpreted on the basis of altered net charge at M$^+$ and XH$_4^-$ due to interaction with doped C$_{60}$.

In conclusion, each of the MXH$_4$ clusters investigated can get stabilized with doped C$_{60}$, and doped C$_{60}$ has a potential to improve hydrogen release energy of complex metal hydrides. The present results can be further improved by replacing single unit of MXH$_4$ by its nanoparticles and increasing the number of units of MXH$_4$ clusters on the C$_{60}$ cage. The results provide valued insights on experimental work for exploring the catalytic potential of doped C$_{60}$ for complex metal hydrides.

Acknowledgements

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