$C_{60-n}X_n$ (X = B, N, Al & O) as Catalyst for Dehydrogenation in $NaMH_4$ (M = Al & B)

Meenakshi[1]* and Hitesh Sharma[2]
[1,2]Department of Physics, I.K. Gujral Punjab Technical University, Jalandhar, Punjab–144601, India
*E-mail: *mmalhotra62@gmail.com*

Abstract—*Search for appropriate hydrogen storage material is one of the key challenges which must be addressed for using hydrogen for on board fuel application. Complex metal hydrides meet the commercial targets of high gravimetric density and volumetric density but their application is limited by their poor kinetics and energetic. In the recent past, several experiments have been reported improvement in the kinetics and energetic of complex metal hydrides using of metal and non-metal catalyst. The choice of catalyst is central to improve the performance of hydrides. Recent experiments have shown that carbon-nanostructures act as an effective catalyst for improving the kinetics of complex hydrides at lower temperature. However, the role of carbon nanostructures is still debated.*

In the present work we have shown that doped fullerenes C60-nXn for n = 1 where X = B, N, Al and O can act as an effective catalyst for complex metal hydrides. The investigations were performed within in the framework of using Density functional theory calculations. The problem was modeled by investigating the interaction of $NaMH_4$ clusters with the C60-nXn.The binding energy of the doped C60 complexes increases sharply to 0.56 eV -2.36 eV. The hydrogen release energy decreases by 11% & 15% in C60$NaMH_4$ w.r.t. pure $NaMH_4$ units. The hydrogen energy decreases sharply by 40% & 49% in C60-nBn$NaMH_4$, 22% &17% in C60-nNn$NaMH_4$, 24.3% & 21% in C60-nOn $NaMH_4$, 13% & 16% in C60-nAln$NaMH_4$ for n = 1 respectively. There is significant charge redistribution from $NaMH_4$ unit to C60-nXn which results in weakening of ionic and covalent interactions thus lowering of Hydrogen release energy. The results suggest that B doped C60 can act as a good catalyst for improving the energetics of complex metal hydrides.

Keywords: *DFT, Hydrogen Storage, Metal Hydrides, Catalytic Properties, Carbon-Nanostructures*

INTRODUCTION

The increase in pollution, drastic climatic changes like global warming, and decreasing world supply of fossil fuels has focus and demand for alternate source of clean renewable energy [1]. Hydrogen is a very attractive and advantageous option in regards as it is a clean burning fuel and it possesses higher energy content per mass unit so potential future fuel for mobile industry [2, 3]. In spite of all such merits, a couple of technical challenges in hydrogen production, transportation and storage posses a problem of realization of it as hydrogen fuel base flawless economic system [4]. However, biggest challenge in the hydrogen economy is finding hydrogen storage material that must meet commercial requirements of high gravimetric, volumetric density, fast kinetics and favorable thermodynamics [5].

Among solid, liquid and compressed pressurized gas cylinders, Solid state storage meet the commercial targets of safety and DOE [6]. In Solid state storage materials particular attention has been focused recently on Complex Hydrides $NaAlH_4$ and $NaBH_4$ as these can store hydrogen at relatively low pressure and ambient temperature and M exhibits a high gravimetric density of 20 wt% [7]. The major scientific challenge for the possible usage of Complex metal hydride is their poor kinetics and strong conditions of (550–700°C temperature and 30–150 bar pressure) for dehydrogenation reaction [8]. To improve the kinetics, various solutions are being explored such as use of catalysts, confining Complex metal hydride into nano sized scaffolds [9, 10]. Bogdonovic and Schwickardi first used Ti based catalyst to improve the kinetics of $NaAlH_4$ but their usage in reaction and formation of undesirable bio-products lessen their potential as desired catalysts in dehydrogenation reaction [11].

Carbon-nanomaterials such as CNT, Carbon-nanofibres, Carbon-nanostructures and fullerenes have captured the attention of material scientists due to their high storage capacities over several order of magnitudes [12]. However their use as catalyst in lowering the dehydrogenation needs to be fully investigated theoretically like use of various possible fullerenes, CNT, Graphene sheets as the catalysts. We have investigated the catalytic effect of Carbon-nanostructures due to their tunable electronic properties and redistribution of charges results in weakening of ionic interactions of Complex metal hydrides. In present work we have extended our investigation into the effect of C_{60} with B, N, O and Al doped fullerenes for dehydrogenation $NaMH_4$ (M = Al and B). The use of doped fullerenes as catalysts considerably decreases the Hydrogen release energy of complex metal hydrides.

COMPUTATIONAL DETAILS

Density functional theory (DFT) as implemented in SIESTA computational code based on numerical atomic orbital density functional approach [13, 14, 15] is used to investigate the catalytic effect of B, N, Al and O doped fullerenes on energetics of $NaMH_4$. The exchange-correlation interactions are treated using generalized gradient approximation (GGA) which implements the exchange of Becke and the correlation function of Lee, Yang and Parr as BLYP exchange-correlation Functional [16, 17]. The core electrons are represented by non-local norm-conserving Troullier-Martins (TM) pseudo potentials factorized in the Kleinman-Bylander form [17]. $C_{60}NaMH_4$ complexes are optimized within the cubic simulation cell of 20 Å. The valence states are described using DZP (double-zeta + polarization) basis sets with energy cutoff of 200 Ry. The structures are obtained by minimization of the total energy using Hellmann-Feynman forces, including Pulay like corrections. Structural optimizations are performed using conjugate gradient algorithm until the residual forces in the optimization are smaller than 0.01 eV/ Å.

The test calculations have been performed for C_{60} and $NaMH_4$.In C_{60}, the calculated C-C, C = C bond lengths of 1.46 Å and 1.42 Å are in agreement with the experimental values [18, 19]. The calculated values of HOMO-LUMO gap and electron affinity are 1.64 eV and 2.54 eV respectively, which are in good agreement with the reported values in the literature [20, 21]. For $NaAlH_4$, Al-H bond lengths of 1.61 Å -1.68 Å are in agreement with the reported value [22]. The energy needed to remove one H atom from $NaAlH_4$ cluster is 3.95 eV, which is in agreement with the reported value of 3.80 eV [22].

RESULT AND DISCUSSION

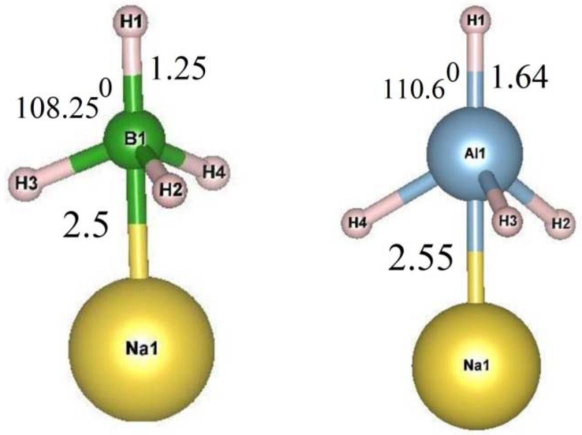
Complex Hydrides $NaMH_4$ (M = Al, B)

We first obtained the ground state structures of $NaMH_4$ units using computational details described in the Section 2. The obtained ground state structures are shown in the Fig. 1. The optimized $NaMH_4$ structure shows ionic interaction between Na^+ and MH^-_4 whereas H interacts covalently with M in MH_4. The structural parameters of Na and MH_4 are tabulated in Table 1. The H is bonded tetrahedrally in $NaAlH_4$ and $NaBH_4$. Bond angles are in agreement with the reported values of angle H–B–H in range of 107.2^0 -111.7^0 and angle H–Al–H in range of 107.2^0-114.7^0 [23, 24].

To calculate the hydrogen release energy of $NaMH_4$ unit one H atom was removed from $NaMH_4$ and structure was allowed to relax again to lowest energy configuration. The hydrogen release energy of $NaMH_4$ has been calculated for the decomposition reaction as:

$$NaMH_4 \longrightarrow NaMH_3 + H \tag{1}$$

The M-H bond length decreases marginally in all $NaMH_4$ units on removal of H from $NaMH_4$. The structural parameters on hydrogen removal are shown in Table 1. Table shows that Na-M bond length increases on removal of H atom from all hydride units indicating weaker ionic interaction between M and Na.



$NaBH_4$ $NaAlH_4$

Fig. 1: Ground State Structures of $NaBH_4$ and $NaAlH_4$. The Bond Lengths are in Å.

Table 1: Na-M, M-H Bond Lengths (in Å) of Ground States of $NaMH_4$ and $NaMH_3$

Complex Hydride	Bond Lengths		Complex Hydride	Bond Lengths	
	Na-M (in Å)	M-H (in Å)		Na-M (in Å)	M-H (in Å)
$NaAlH_4$	2.55[2.60][22,23]	1.64[1.65][22,23]	$NaAlH_3$	2.79	1.63
$NaBH_4$	2.5[2.90][24,25]	1.25[1.10-1.34][24,25]	$NaBH_3$	2.43	1.22

Electronic Properties of $C_{60-n}X_n$

The electronic structure of C_{60} exhibits 5 fold degeneracy in HOMO energy levels [18] with energy gap of 1.64eV between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The introduction of dopant in C_{60} modifies electronic charge distribution and shifts the Fermi level resulting in change in its electronic properties. The catalytic applications of C_{60} can be due to its extra stability because of I_h symmetry and ability to tune its electronic properties due to substitutional, endohedral and exohedral doping[19]. Among various doping methods, the substitutional doping with similar sized elements have been found more effective to tune electronic and structural properties of C_{60} [18,19]. Therefore doped C_{60} based nanostructures can be used for dehydrogenation in $NaMH_4$ units described in earlier section.

B-doped C_{60}

When C_{60} is doped with single B atom it becomes deficient by one electron and leads to distortion in icosahedral (I_h) symmetry of C_{60} molecule [26]. B doping changes the electronic distribution which decreases the HOMO-LUMO gap to 1.12 eV w.r.t. C_{60} molecule as shown in Fig. 2. The five fold degeneracy is lifted as B atom provides one hole to HOMO level with h_u

symmetry which leads to decrease in HOMO-LUMO gap. In all structures B acts as electron acceptor w.r.t C. The Mulliken charge analysis shows net charge in Q/e ($e = 1.6 \times 10^{-19}$ C) of −0.72e electrons on the boron atom and +0.14 e, +0.14 e and +0.16 e on nearest neighbor carbon atoms in C_{60}. Since B carries negative charge and the compensating positive charge is carried by the adjacent C atoms, this becomes preferential site for nucleophilic and electrophilic attack respectively.

N-doped C_{60}

N-doped fullerenes show enhanced chemical properties and exhibit variable electronic properties, which make them potential candidates for applications as catalyst [27]. N doped behave as electron carriers as N atom is having one extra electron. As a result of N doping, icosahedral (I_h) symmetry of C_{60} molecule is disturbed. The distortion in symmetry leads to a sharp decrease in HOMO-LUMO gap as shown in Fig. 2. N donates 0.431e charge to surrounding C atoms.

Al-doped C_{60}

Al behaves as a electron donor. Al doping changes the reactivity of C_{60} [28]. Al doping leads to change in electronic properties and distortion in symmetry of C_{60} molecule, as shown in sharp decrease in HOMO-LUMO gap as shown in Fig. 2 and significant charge transfer of 0.611e charge from C to Al.

O-doped C_{60}

The surface modification of O doped C_{60} contributes to change in polarity and surface structure of C_{60}. It provides two electrons and includes oxidation and reduction to create binding sites for further combinations with complex metal hydride groups atoms [29]. The HOMO-LUMO gap of $C_{59}O$ decreases as shown in Fig. 2 and a significant charge transfer of 0.162 e from O to C.

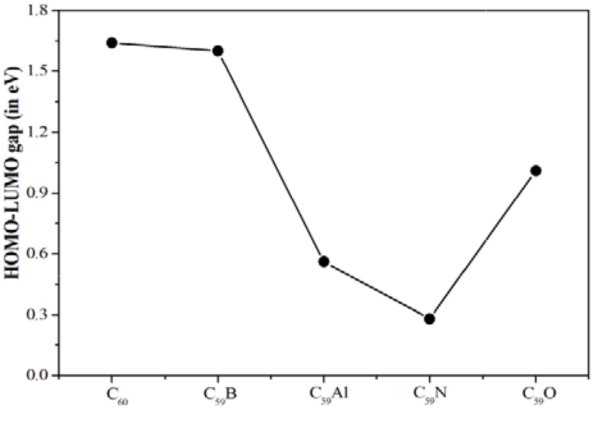


Fig. 2: HOMO-LUMO Gap of Various Doped Fullerenes

Interaction of $NaMH_4$ with $C_{60-n}X_n$ ($C_{59}X$ for n = 1, where X = B, N, Al & O)

To model the interaction between $NaMH_4$ with doped C_{60}, we started by placing alkali atoms M exohedrally at different positions on the surface of fullerenes and relaxing structures till the desired accuracy was achieved. Among all the configurations considered, Na was found to be more stable above the center of 6-member (6m) ring in C_{60} which is in agreement with the reported results [30]. The minimum energy structure of $C_{60}M$ was taken as the initial starting structure for further investigation. We modeled our problem by placing single $NaMH_4$ unit in place of M on C_{60} and relaxing the structure. The effect of doping on the interaction by considering of introducing the various dopants into the C_{60} cage. The lowest energy structures of $C_{59}XNaMH_4$ complexes are shown in Fig. 3 and the structural properties in terms of bond length are tabulated in Table 2. It is clear from the table that, the Na-M bond length increases in $C_{59}XNaMH_4$ complexes w.r.t. their values in Table 1 for isolated $NaAlH_4$, where as it decreases in $NaBH_4$ except for $C_{59}Al$. From Table 2 it is clear that on removal of one H atom distance of C-Na decreases while distance of Na-M increases which shows a weaker interaction in Na and M atom and may results in decrease in the hydrogen release energy from complex metal hydrides. To investigate the structural stability of $C_{59}XNaMH_4$ complexes, the binding energy have been calculated using the equation:

$$E_{bin}=E(C_{59}X\ NaMH_4)-[E(C_{59}X)+E(NaMH_4)] \quad (2)$$

where E ($C_{59}X\ NaMH_4$), E($C_{59}X$) & E($NaMH_4$) are the total energies $C_{59}XNaMH_4$,$C_{59}X$ and $NaMH_4$ respectively. The binding energy of $C_{59}XNaMH_3$ and $C_{59}XNaMH_4$ complexes are shown in Fig. 4 respectively.

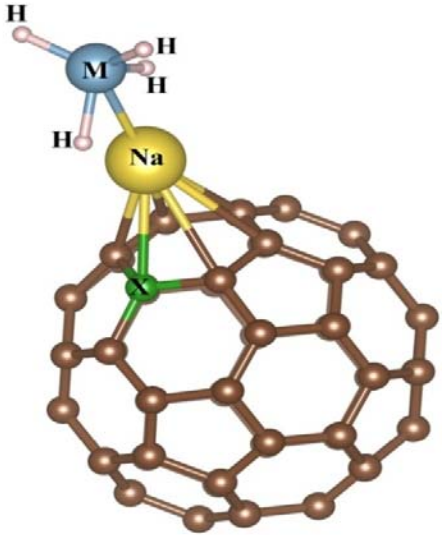


Fig. 3

Shows Optimized Ground State Structures of C59XNaMH4 (X = B, N, Al and O) & (M = Al and B) Complexes. The Elements of $NaMH_4$ have been Shown with their Symbols

Table 2: Bond Lengths (in Å) of Various Doped Carbon Fullerenes $C_{59}XNaMH_4$ Here C-Na* and M-Na* are the Bond Lengths after the Removal of H Atom from $C_{59}XNaMH_4$ Complexes

Complex	Metal Hydride	B or C–Na	Na-M	X–H	C-Na*	M-Na*
C_{60}	$NaAlH_4$	2.90	2.81	1.64	2.56	3.63
C_{59} B		2.30	2.83	1.64	2.55	3.67
C_{59} Al		2.93	3.39	1.65	2.89	3.15
C_{59} N		2.94	2.79	1.64	2.58	3.65
C_{59} O		3.62	2.82	1.64	3.32	3.36
C_{60}	$NaBH_4$	3.04	2.43	1.26	2.56	3.3
C_{59} B		2.76	2.42	1.25	2.53	3.61
C_{59} Al		3.13	2.58	1.26	2.83	2.65
C_{59} N		3.04	2.24	1.25	2.69	2.60
C_{59} O		3.74	2.26	1.25	3.32	2.69

The binding energy of the doped C_{60} complexes increases sharply to the range from 0.56 eV to 2.36 eV. The binding energy of $C_{59}XNaMH_4$ complexes increases sharply after the removal of single H atom that is it is less than $C_{59}XNaMH_3$ complexes which results stronger binding after removal of one H atom of these complexes. The graph shows that binding energy of all $C_{59}XNaMH_4$ complexes except in N doping where (M = Na) sharply increases. The stability of the complex may be explained on the basis the basis charge transfer between the $NaMH_4$ unit and doped C_{60} substrate as stated above. In all structures B acts as electron acceptor w.r.t C. The Mulliken charge analysis shows net charge in Q/e ($e = 1.6 \times 10^{-19}$ C) of −0.72 e electrons on the boron atom and +0.14e, +0.14e and +0.16 e on nearest neighbor carbon atoms in C_{60}. N donates 0.431e to surrounding C atoms. There is significant charge transfer of 0.611e from C to A, 0.162 e O to C atoms. N and O behave as an electron donor group where as B and Al behaves as an electron acceptor group.

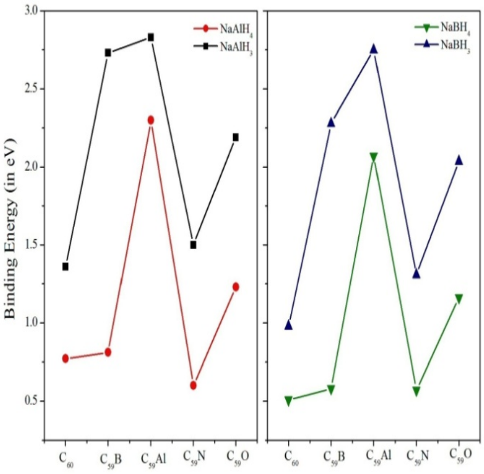


Fig. 4

Binding Energies of various Doped fullerenes. Here squares & circles are for $NaAlH_3$ &$NaAlH_4$ and up & down triangles are for $NaBH_3$& $NaBH_4$ respectively

Dehydrogenation from $C_{59}X$ $NaMH_4$ Complexes

The dehydrogenation from $C_{59}XNaMH_4$ complexes have been calculated in terms of hydrogen release energy by removing one hydrogen atom from $NaMH_4$ unit. The structures of the complexes were further relaxed after removal of one hydrogen atom from complex metal hydride unit. The structural properties of the complexes changes after the removal of hydrogen as shown above in Table 2. The bond distance between carbon atom of cages and M decreases, M-X bond distance increases and X-H bonds show very small change. The hydrogen release energy have been calculated using:

$$E_{hre} = [E\ (C_{59}XNaMH_3) + E\ (H)] – E\ (C_{59}X\ NaMH_4) \quad (3)$$

where E denotes total energy of the complexes and molecules mentioned above.

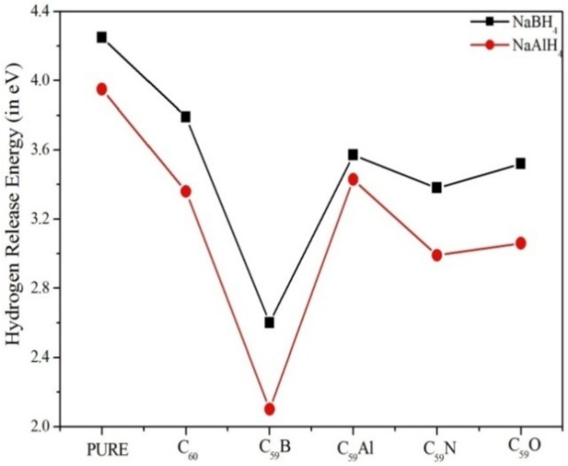


Fig. 5

Hydrogen release energies of $C_{59}XNaMH_4$ complexes. The starting point in the graph denotes the hydrogen release energy of $NaMH_4$ units where circle and square represents $NaAlH_4$ and $NaBH_4$ respectively.

The Hydrogen release energy decreases by 11% and 15% in $C_{60}NaAlH_4$ and $C_{60}NaBH_4$ respectively. For $NaAlH_4$, the hydrogen energy decreases by 40%, 22%, 24.3% & 13% in $C_{59}B$, $C_{59}N$, $C_{59}O$, $C_{59}Al$ respectively.

For $NaBH_4$, the hydrogen energy decreases by 49%, 17%, 21% and 16% in $C_{59}B$, $C_{59}N$, $C_{59}O$, $C_{59}Al$ respectively. The hydrogen release energy of $NaMH_4$ decreases when it interacts with the doped and pure $C_{60.}$ The doped C_{60} shows larger decrease in the Hydrogen release energy as compared to pure C_{60} as shown in Fig. 5. Doping of C_{60} leads to sharp decrease in H-Release energy and decrease is maximum in B doping and all others are also showing decrease in H-Release energy trend from pure complex metal hydrides. These results may be explained on the basis of alter charge transfer between fullerene surface and $NaMH_4$ unit, which leads to weakening of their interaction between Na and MH_4. The changes in the net charge at site results in change in the ionic interactions and decrease the hydrogen release energy. The effect of dopant on the electronic properties of fullerenes is one of the strong factor which could be exploited for altering electro-static interactions with the complex metal hydrides. Thus, doped fullerenes results in decrease of Hydrogen Release energy of complex metal hydrides.

SUMMARY AND CONCLUSION

In the present work we have shown that doped C_{60} can act as an effective catalyst for dehydrogenation in complex metal hydrides. The investigations were performed using density functional theory calculations. The salient features of the present study are summarized as:

- The reactivity of the C_{60} is found to increase on introduction of B, Al, N and O dopants. The HOMO-LUMO gap of C_{60} decreases from 1.64 eV to 1.27 eV, 0.45 eV, 0.29 eV, 1.1 eV on B, Al, N and O doping respectively.
- The $NaMH_4$ interact with $C_{59}X$ complexes with binding energy varying from 0.6 eV-1.23 eV for $NaAlH_4$ and 0.51eV-2.1eV for $NaBH_4$ respectively.
- The Hydrogen release energy decreases by 11% and 15% in $C_{60}NaAlH_4$ and $C_{60}NaBH_4$ respectively. For $NaAlH_4$, the hydrogen energy decreases by 40%, 22%, 24.3% and 13% in $C_{59}B$, $C_{59}N$, $C_{59}O$, $C_{59}Al$ respectively. For $NaBH_4$, the hydrogen energy decreases by 49%, 17%, 21% and 16% in $C_{59}B$, $C_{59}N$, $C_{59}O$, $C_{59}Al$ respectively.

The results suggest that B doped C_{60} an act as an effective catalyst for improving the energetics of complex metal hydrides. The results may be explained on the basis of change in the charge transfer between Na and MH_4 with doped C_{60}. The present results may provide valued insights for experimental work for exploring the catalytic potential of doped C_{60} for complex metal hydrides. The use of doped fullerenes as catalysts considerably shows significant decrease in hydrogen release energy of complex metal hydrides.

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