



Effect of dopants and defect in graphene nanoribbons on dehydrogenation of MXH_4 , where $M = Na, Li$ and $X = Al, B$

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ABSTRACT

The present paper reports the effect of Graphene Nanoribbons (GNRs) for improving the dehydrogenation of MXH_4 , where $M = Na, Li$ and $X = Al, B$ through density functional calculations. The rectangular Armchair GNRs and ZigZag GNRs with width up to 7.57 Å & 10 Å and length of 15 Å & 10 Å respectively were considered for the investigation. The effect of dopant and defect was introduced by doping with different dopants (B, N, Al, Cl and F) and introducing vacancy defect respectively. The MXH_4 interacts with the surface atoms of GNRs with binding energy from 0.31–0.89 eV with AGNR and from 0.26 eV to –1.42 eV with ZGNR respectively. Charge transfer of 0.12–0.26 e take place from GNR surface to MXH_4 molecule resulting in significant decrease in hydrogen release energy (E_{HRE}). Doped and defective AGNR lowers E_{HRE} of MXH_4 sharply by 19–56% whereas ZGNR decreases E_{HRE} by 18–70% respectively. The results agree qualitatively with the available experimental result and outline the importance of nano carbon as a catalyst for improving the performance of light complex metal hydride systems.

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1. Introduction

Complex metal hydrides have attracted a lot of scientific interest as a material for hydrogen storage due to their chemical stability and high hydrogen gravimetric density [1]. On account of higher chemical stability, reaction kinetics of complex metal hydrides requires high hydrogen desorption temperature, which is the central for their possible usage in realizing hydrogen economy [2]. The various methods such as introducing appropriate catalyst, reducing the size of the metal hydrides and confining the metal hydrides nanoparticles in nanoporous materials, have been used to improve the kinetics and thermodynamics of hydrogen adsorption and desorption [1,2]. However, none of these methods so far have been able to meet the commercial targets for reversible hydrogen storage at ambient conditions.

In last two decades, there has been a focus in finding a suitable catalyst for improving the reaction kinetics and hydrogen release energy of complex metal hydrides [3–5]. Transition metal based catalysts such as $TiCl_3$ when admixed with $NaAlH_4$, results in lowering of desorption temperature with reversible adsorption and desorption [5]. The disadvantages associated with transition metal catalysts such as their high cost, poor durability and formation of

undesirable side products have limited their potential as an effective catalysts and have necessitated the need for finding metal free catalysts [6]. Carbon nanostructures due to high chemical reactivity, large surface area and their curvature results in large delocalized stacking interactions with surface molecules have emerged as a potential catalyst for improving the performance of hydrides [3]. So far, fullerenes, carbon nanotubes (CNTs), graphene and activated carbon have been studied for improving the kinetics/energetics of complex metal hydrides [3–5,7–12]. C_{60} when admixed with $NaAlH_4$ lowers the desorption temperature from 400 °C to a range 180–230 °C rehydrating $NaAlH_4$ to 4.3 wt% over 8 h with 2.1×10^7 Pa H_2 pressure [5]. Fullerenes with small diameter and high surface curvature and CNTs have been found to be more effective in improving the energetics of complex metal hydrides [13–16].

In recent past, graphene and activated carbon have also been explored for improving the kinetics/energetics of complex metal hydrides [1–3]. The helical graphitic nanofibres (HGNF) when admixed with $LiMg(AlH_4)_3$ and $LiAlH_4$ improves their desorption kinetics by lowering activation energy for first decomposition step to 66 kJ/mol and 68 kJ/mol respectively. The dehydrogenation temperature decreases from 159 °C to 128 °C for $LiMg(AlH_4)_3$ and 105 °C to 70 °C for $LiAlH_4$ respectively in comparison to planar graphitic nanofibres (PGNF) [17]. $NaAlH_4$ when admixed with 2 wt% HGNF and PGNF, dehydrogenation temperature decreases

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from 170 °C to 143.6 °C and 152.6 °C respectively [18,19]. First principle calculations have predicted lowering of hydrogen release energy (E_{HRE}) of $LiBH_4$ from 2.62 eV to 1.75 eV when supported by graphite fragments [11]. Graphyne when admixed with $LiAlH_4$, $LiBH_4$ and $NaAlH_4$ lowers E_{HRE} from 3.89 eV, 4.64 eV and 3.70 eV to 1.84 eV, 2.49 eV and 3.30 eV, respectively. Similar behavior has been observed using graphdiyne which decreases E_{HRE} by 1.48 eV, 2.18 eV and 1.28 eV respectively [20]. In addition presence of defects and impurities in graphene have also shown improvement in H_2 removal energy [21]. However the exact understanding of the mechanism of effect of pristine and doped graphitic carbon is still incomplete.

Earlier, we have studied the effect of fullerenes and CNTs in lowering dehydrogenation from $NaAlH_4$ [13–16,22,23]. In this work, we have extended our investigation to study the effect on complex metal hydride clusters when supported on the ultra thin graphene nanoribbons GNRs surface. The effect of dopants (B, N, Al, Cl and F) and vacancy defect has also been investigated systematically. Our results show that doped and defective armchair graphene nanoribbons (AGNR) and zigzag graphene nanoribbons (ZGNR) are more effective in lowering E_{HRE} of MXH_4 in comparison to pristine GNR.

2. Theoretical methods

The calculations are performed using Density functional theory (DFT) within the pseudo potential plane wave method as implemented in SIESTA computational code, which have been used to investigate the catalytic effect of AGNRs and ZGNRs on energetics of MXH_4 [24–26]. The exchange–correlation interactions were treated using generalized gradient approximation (GGA) which implemented BLYP exchange–correlation Functional. The core electrons were represented by non-local norm-conserving Troullier–Martins (TM) pseudo potentials factorized in the Kleinman–Bylander form [27]. The valence electronic configuration taken for Li, Na, Al, H, B, C, N, F and Cl atoms are $2s^1$, $3s^1$, $3p^1$, $1s^1$, $2p^1$, $2p^2$, $2p^3$, $2p^5$ and $3p^5$ respectively. The pseudopotential radii employed in our calculations for s and p orbitals are all 2.26 au for Li, 2.94 au for Na, 1.89 au for Al, 1.49 au for H, 1.00 au for B, 1.52 au for C, 1.54 au for N, 1.41 au for F and 1.66 au for Cl respectively. The valence states were described using DZP (double-zeta + polarization) basis sets with energy cutoff of 200 Ry [28]. The quality of the pseudopotentials used for the calculations of GNRs is supported by the test calculations on the various systems described ahead. All complexes were optimized within the cubic simulation cell of 20 Å. The structures obtained were relaxed 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 are smaller than 0.01 eV/Å.

3. Results and Discussion

To study the catalytic effect of pristine GNR, interaction of MXH_4 supported on GNR surface were studied using computational details described in Section 3. GNR with zigzag and armchair configurations were considered for investigation. The effect of dopants and vacancy defect in GNR, on interaction with MXH_4 and change in dehydrogenation energy have also been investigated.

3.1. Pristine GNRs

Firstly, we have obtained the ground state structures of pristine GNRs with both zigzag and armchair edges. Calculations have been performed using unit cell with 64 C atoms with hydrogenation ($C_{64}H_8$) and 66 C with hydrogenation ($C_{66}H_{12}$) for AGNR & ZGNR

respectively. We considered zig-zag and armchair GNRs up to width of 10 Å and length up to 15 Å respectively. The calculated C–C bond length on edges and away from edges have been found to be 1.24 Å and 1.42 Å respectively which is in good agreement with the reported results [29]. The choice of the GNR has been considered on the basis of layer dependent electronic properties and higher reactivity of surface adsorbed molecules on GNRs in comparison graphene [23,30–33].

The minimum energy position for alkali M atom on the GNR surface was determined by placing M on the top of C atom (T), on C–C bond (B) and on center of the hexagon (H) as shown in Fig. 1 at variable distance from the edge sites. Total energy calculation predict the center of GNR as more stable configuration in comparison to positions nearer to the edges by 0.2–0.3 eV. Further, M at the center of hexagon ring (H position) to be more stable than at T and B position by 0.23 eV and 0.20 eV respectively. The predicted behavior is in agreement with reported results [30]. The interaction of MXH_4 with GNR surface was modeled by replacing M at minimum energy position with MXH_4 and relaxing the surface structure.

To study the effect of functionalized GNR with MXH_4 , we have introduced dopants (B, N, F, Al and Cl) and vacancy defect in GNRs. The choice of dopants was determined on the basis of their electron deficient behavior (B), electron rich behavior (N), higher electronegativity (F), higher chemical reactivity (Al) and higher affinity to react with the cluster (Cl). To determine the most stable position of dopant and defect, we have considered different positions such as S1, S2, S3 and S4 on ZGNRs as shown in Fig. 2. S2 is found to be the most favorable position as compare to other positions by 0.11–0.2 eV. Similarly, minimum energy position of dopants and defect on AGNRs were determined. The minimum energy configuration of MXH_4 at minimum energy position supported on pristine, doped and defective AGNR and ZGNR are shown in Fig. 3 and 4, respectively. The structural properties of MXH_4 cluster supported on GNRs surface and in free space are tabulated in Tables 1 and 2. $NaAlH_4$ stabilizes at 3.01 Å from ZGNR surface and at 2.97 Å from AGNR surface. The Na–Al distance of $NaAlH_4$ cluster increases from 2.55 Å in free space to 2.81 Å and 2.79 Å on ZGNR and AGNR, indicating weaker interaction and altered Al–H bonds.

Similar behavior has been observed for $LiAlH_4$ and $LiBH_4$ i.e. M–X distance decreases for both GNRs except in case of $NaBH_4$, while B–H distance changes marginally. Maximum increase in M–X distance is observed for $NaAlH_4$ cluster on interacting with pristine GNRs. The structural properties for pure and doped GNRs with $NaAlH_4$ as a representative case are tabulated in Table 2. Results indicate significant change in bond lengths as compare to pure MXH_4 clusters, C–M distance decreases which results in stronger interaction with GNRs surface. The increase in interaction may be understood from decreased C–M distance on the introduction of dopants and defects implies the increased interaction

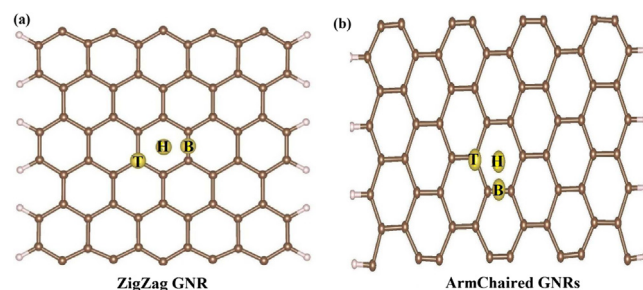


Fig. 1. Exohedral positions of alkali atom M for various ZGNRs and AGNRs, where T stands for top position of alkali atom on C atom; H is for the position over the centre of hexagon; B is over the mid position of the C–C bond.

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