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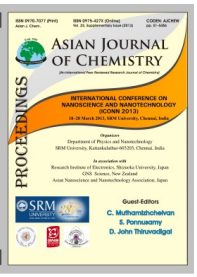

Role of Single Walled Carbon Nanotube in Nanophase MgH_2 Hydrogen Storage System†

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While the hydrogen storage property of bulk MgH_2 is remarkable, the nanophase MgH_2 is not completely understood. Wu *et al*. experimentally investigated the hydrogen storage properties of MgH_2/single walled carbon nanotube composite systems and found that, while all the carbon additives acted as effective composite phase, Single-walled carbon nanotubes exhibited the most prominent catalytic function to enhance the hydrogen storage properties of MgH_2. We wish to confirm this role of single walled carbon nanotube in MgH_2/single walled carbon nanotube using first principles calculation. We functionalized single walled carbon nanotube with MgH_2 and hydrogenated. It is found that one can get a hydrogen storage capacity of 5.0-6.4 wt % with the hydrogen binding energy around 0.3 eV, in this carbon nanotube-8MgH_2 complex. Our study confirms that the carbon nanotubes neither act as catalysts nor as a component of the composite phase.

Key Words: Nanophase, MgH_2/Single walled carbon nanotube composite, Hydrogen storage, Catalytic function.

INTRODUCTION

Safe, efficient and compact hydrogen storage medium is the key factor in the hydrogen fuel technology. The target set by the U.S. department of energy (DOE) for an automobile on-board storage system is that the hydrogen storage capacity should be higher than 4.5 wt. %. Further, the medium should be capable of releasing hydrogen at ambient conditions. Among various hydrogen storage materials, magnesium hydride (MgH_2) has been studied as a potential hydrogen storage medium. It possesses high hydrogen capacity (7.66 wt. %) and high reversibility. Also it is a low cost material. Through first principles study, we have investigated the hydrogen storage properties of bulk and nano MgH_2. In the bulk MgH_2, the storage capacity is found to be 7.7 wt. %[1]. In the nano MgH_2, we have considered different phases like (CNT-MgH_2) composite and MgH_2 nanoparticle. The remarkable hydrogen storage properties for nanocrystalline MgH_2 synthesized by the hydrogenolysis of Grignard reagents is investigated by Setijadi *et al*.[2]. There have been few reports regarding the roll of carbon nanotubes on hydrogen storage behaviours of MgH_2. Wu *et al.*[3] experimentally investigated the hydrogen storage properties of MgH_2/single walled carbon nanotube composite systems that were prepared by mechanical milling of Mg with various carbon additives. It was found that, while all the carbon additives acted as effective composite phase, single walled nanotubes exhibited the most prominent catalytic function to enhance the hydrogen storage capacity. We wish to confirm this role of single walled carbon nanotube in MgH_2/single walled carbon nanotube using first principles calculation.

COMPUTATION METHOD

The density functional theory based total energy calculations are performed using the plane wave code VASP[4]. Ultra soft pseudopotentials are employed with suitable valence state configurations C: $2s^2\ 2p^2$, Mg: $3s^2\ 3p^6$ and H: $1s$. For MgH_2/single walled carbon nanotube complex, the calculations are carried out for two unit cells of single walled carbon nanotube in the simulation cell of dimensions 30 Å × 30 Å × 4.98 Å. The dimensions are large enough to enclose the adsorbates and H_2 molecules on single walled carbon nanotube surface. The Brillouin zone is sampled by 1 × 1 × 8 mesh points within Monkhorst and Pack special k-point scheme[5]. The cutoff energy for the plane wave basis set is 286.56 eV. It has been reported that local density approximation gives reasonable adsorption energy compared to MP2 calculations[6]. In our calculations

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electron exchange and correlation are included using local density approximation with the PW91 functional. The ionic relaxation is done using conjugate gradient algorithm. The convergence is obtained when the energy change per atom is less than 0.1×10^{-5} eV and the forces are less than 0.5×10^{-3} eV/Å. The Gaussian smearing is carried out throughout the calculations. For the MgH_2 nanoparticle system, we have removed the carbon nanotube in MgH_2/single walled carbon nanotube complex and considered a simulation cell dimension of 30 Å × 30 Å × 24 Å in order to terminate the z direction propagation.

In our investigation, (10, 10) single walled carbon nanotube is functionalized with MgH_2 [CNT-MgH_2 composite (Fig. 1)]. The two unit cells contain eight full hexagons. There are eight MgH_2 on the hexagon sites. After relaxation, dimerization of MgH_2 molecules is observed and it does not affect the H_2 adsorption of the system, contradicted by Sun *et al.*[7]. The hydrogen molecules are attached with the bond length, 0.74 Å to the MgH_2 molecules.

RESULTS AND DISCUSSION

In present investigation of single walled carbon nanotube functionalized with MgH_2 (Fig. 1) and hydrogenated (Fig. 2), we found that one can get a hydrogen storage capacity of 5.0 - 6.4 wt % with the hydrogen binding energy around 0.3 eV. In this CNT-8MgH_2 complex we removed the catalytic CNT and the nanoparticle system (8MgH_2) is hydrogenated (Fig. 3). The resulting system is 8MgH_2 in which each MgH_2 molecule can take six H_2. As a result, this system has very large hydrogen storage capacity and the H_2 binding energy is in the range 0.1 to 0.15 eV.

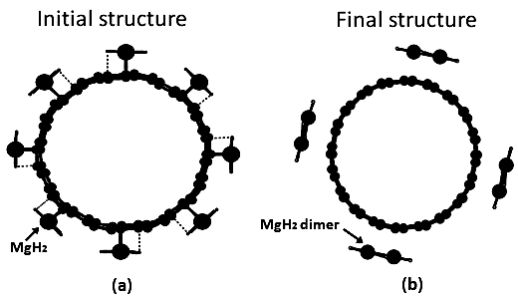

Fig. 1. CNT-8MgH_2 complex (a) Initial structure (b) Final structure

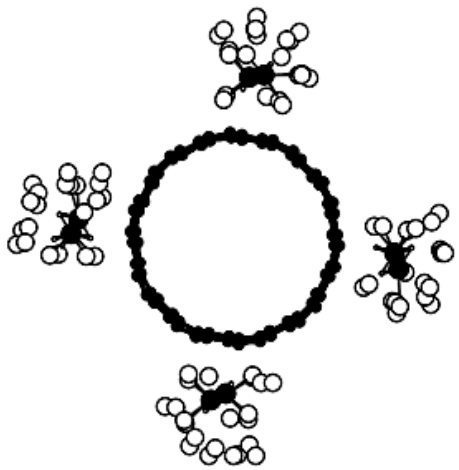

Fig. 2 Hydrogenated CNT-8MgH_2 complex

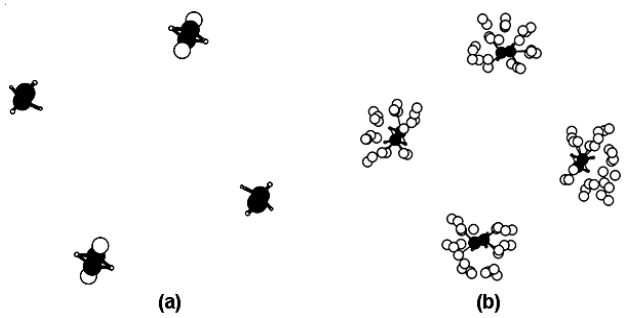

Fig. 3. (a) CNT removed CNT-8MgH_2 complex (8MgH_2), (b) corresponding hydrogenated system

In the 8 MgH_2 hollow section, if one MgH_2 molecule is added at the centre then one gets a 9 MgH_2 system (Fig. 4a). As before, to each of the 8 MgH_2 molecule at the periphery can attach 6 H_2 molecules, whereas to the MgH_2 molecule at the center one can attach more than 12 H_2 molecules (Fig. 4b) leading to high hydrogen storage capacity. The H_2 binding energy is in the range 0.1 to 0.2 eV. Table-1 summarizes the binding energy per molecule (in eV) and gravimetric storage capacity (wt. %) for hydrogenated systems of 8 MgH_2 and 9 MgH_2. Table-1 confirms that the storage capacity increases with the hydrogen attachment in 9 MgH_2 system and even though the central MgH_2 in 9 MgH_2 system can uptake 12H_2 molecules, the gravimetric storage capacity remains same (31.5 wt. %) for six hydrogen attached 8 MgH_2 and 9 MgH_2 systems ($Mg8H_6H$ and Mg_9H_6H). Our value of hydrogen storage capacity 6.4 wt % for the MgH_2 -single walled carbon nanotube complex is very close to the experimental value 6.7 wt % of Wu *et al.*[3] For the MgH_2 nano particle system we get an unusually large value compared to that of the value reported by Setijadi *et al.*[2].

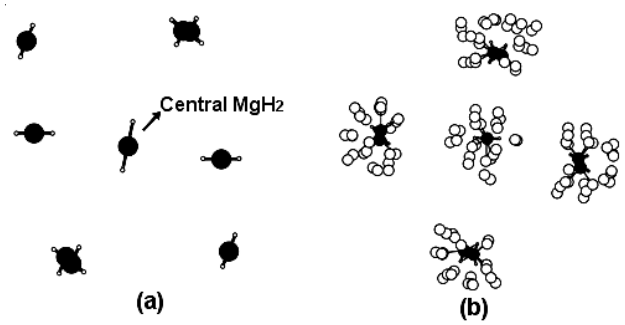

Fig. 4. (a) One MgH_2 attached at center of 8MgH_2 system (b) respective hydrogenated system

TABLE-1
SUMMARY OF BINDING ENERGY PER MOLECULE (IN eV) AND GRAVIMETRIC STORAGE CAPACITY (WT. %) FOR EACH HYDROGENATED SYSTEM (MgH_2-NANOPARTICLES)

System	E_B per molecule (eV)	Storage capacity (wt. %)
Mg8H6H[a]	0.15	31.5
Mg9HH[b]	0.15	29.0
Mg9H2H[c]	0.16	29.9
Mg9H4H[d]	0.20	30.7
Mg9H6H[e]	0.12	31.5

[a]Six H, attached 8MgH, system; [b]Single H, attached 9MgH, system; [c]Two H, attached 9MgH, system; [d]Four H, attached 9MgH, system; [e]Six H_2 attached 9MgH_2 system

Conclusion

When the single walled carbon nanotube is removed the MgH_2 system does not collapse and the hydrogen storage capacity has not decreased. Thus, it is concluded that the CNTs neither act as catalysts nor as a component of the composite phase. However practically, during desorption of H_2 from MgH_2 system, the presence of CNT may add to the stability of the MgH_2 system. In that case, single walled carbon nanotubes role as part of the effective single walled carbon nanotube/ MgH_2 composite phase is more appropriate, like all the carbon additives, than as a catalyst.

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