

Final Report of the Project No.AOARD -08-4017

1. Title of Project: “**Investigation of Hydrogen storage in Single Walled Carbon Nanotubes for fuel cells**”.
2. Name of the Principal Investigator: **Dr. K. Iyakutti**
3. Name of the Project Fellow: V.J.Surya
4. Date of commencement: 01-04-2008
5. Report of work done

Our work involves identifying light weight adsorbates other than metal atoms that are used to functionalize CNT to enhance its storage capacity. So we have employed light weight, hydrogen rich metal and non-metal hydrides. The total energy calculations are carried out using density functional theory implemented in VASP. Ultra soft pseudopotentials are used.

(i) Study of hydrogen storage in single walled carbon nanotube functionalized with NH₃

Ammonia or Azane exists in gaseous form. It has a lone electron pair and so we can say it is electron rich. Thus our study enables to understand the hydrogen storage capability of a electron rich and neutral molecule, NH₃. The simulation cell of dimensions 24 Å × 24 Å × 4.98 Å with two unit cells of SWCNT (5, 5) is considered. The radius of the (5, 5) CNT is 3.44 Å. The investigation is done for two different coverages namely half and full coverages. Half coverage has five NH₃ molecules on the surface of SWCNT and is denoted as C5NH₃. Full coverage case contains ten NH₃ molecules and is expressed as C10NH₃.

The structure of C5NH₃ is relaxed. A single H₂ is attached to all NH₃ and the structure is relaxed. The system is denoted as C5(NH₃+H₂). The binding energy is 0.10 eV/H₂. Another H₂ is attached and the structure is relaxed. The binding energy per H₂ is 0.097. In a similar way we have attached third, fourth and fifth molecule on each NH₃. All the constructed systems are relaxed. All the H₂ are physisorbed and are equally perturbed when compared to the unbound H₂ (H-H=0.74 Å). The storage capacity of C5(NH₃+5H₂) is 8.18 wt% and the desorption temperature is calculated using van't Hoff equation and is 115K.

Naturally we can expect increase in storage capacity when more number of adsorbates is introduced. So we have included five more NH₃ molecules on the surface of SWCNT. The clustering of NH₃ molecules is noted. On addition of H₂ the clustering pattern changed. Initially single H₂ is attached to each NH₃ in C10NH₃. The structure is relaxed and the binding energy per H₂ is 0.1 eV. After that second, third, fourth and fifth H₂ are attached and the structures are relaxed. The binding energy is noted in C10(NH₃+4H₂) and is 0.098eV/H₂. The corresponding desorption temperature is 125K. The maximum storage capacity corresponds to C10(NH₃+5H₂) and is 13.2 wt%. Since the clustering is weak it has no effect on the storage capacity. But the bonding nature of some adsorbed H₂ is changed.

We conclude that functionalization with electron rich and neutral molecule, NH₃ enhances the storage capacity of SWCNT to a larger extent. The uniform perturbation of

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14. ABSTRACT Out of the four systems(NH3, AlH3, NiH3 and BH3) theoretically investigated, the single walled Carbon Nanotube (SWCNT) functionalized with BH3 is found to be suitable hydrogen storage medium. It has hydrogen storage capacity, 11.5 wt% and the corresponding H2 desorption temperature is 306 K. The system has to be fine tuned for a better performance.					
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H-H bond lengths in the case of half coverage is noted and it is a new feature. Also we can infer that both in half coverage and full coverage cases the binding energy lie below the range recommended for efficient hydrogen storage medium. So due to the low binding energy, H₂ desorption takes place below the room temperature.

(ii) Aluminum hydride coated single walled carbon nanotube as a hydrogen storage medium

We have taken the (5, 5) single walled carbon nanotube for our study. The AlH₃ molecule is allowed to approach the CNT from large distances, to determine the energetically preferred absorption position of AlH₃. The AlH₃ molecule is attached to the SWCNT and this system is denoted as CAIH₃. The binding energy of AlH₃ with CNT is found to be 1.46eV. This serves as the reference system (CAIH₃). Interestingly, AlH₃ group forms complex with hydrogen molecules. To find out the different reaction products between H₂ and CAIH₃, a series of energy minimization calculations with one, two, three, four, five and six H₂ molecules and optimization of the atomic positions (x, y, z) have been carried out. Hydrogen molecule is allowed to move freely from large distance with the initial bond length of 0.747Å. It moves towards CAIH₃ and interacts with the system and gets adsorbed with an increased bond length of 0.768Å. We obtained the binding energy as 0.16 eV for the first H₂. There is also a possibility to attach more number of H₂ to this system. In the second H₂ adsorption, the H-H distance is 0.749Å and it is slightly low compared to the first H₂. The binding energy is reduced to 0.09eV.

So there is a possibility to attach more number of AlH₃ to the nanotube to increase the hydrogen storage capacity. We have investigated the two cases namely C5AlH₃ and C10AlH₃.

As a result each AlH₃ can bind up to three or four hydrogen molecules. These systems are quite stable and the H₂ can be extracted from the system without disturbing the C-Al bonding or detaching the AlH₃ from the carbon nanotube. Of the two systems C5AlH₃ (half) and C10AlH₃ (full), C5AlH₃ system is qualified as a viable hydrogen storage material. The average binding energy per H₂ is in the range of 0.10 eV to 0.2 eV which is recommended for a HSM. The hydrogen storage capacity for half coverage is 8.3 wt%. This value meets the standard fixed by U.S. Department of Energy. Here again the H₂ release is below the room temperature.

(iii) Functionalization of single walled carbon nanotube with borane for hydrogen storage

We have chosen another light weight molecule BH₃. It is also hydrogen rich. But it is electron deficient. This study highlights the high adsorption capability of this electron deficient adsorbate dispersed on the surface of the CNT. The half coverage case (C5BH₃) has five BH₃ molecules and the full coverage case (C10BH₃) has ten BH₃ molecules on the full hexagons of CNT.

Initially single H₂ is attached to each BH₃ in the relaxed structure of C5BH₃. This structure is relaxed and the H₂ has been displaced close to BH₃. Similarly second, third, fourth and fifth H₂ molecules are attached to each BH₃. The systems are relaxed. The bond lengths noted after relaxation reveal that one of the H₂ is bound closely to BH₃

which has resulted in the H-H bond lengthening. This feature is noted in all the systems. If the desorption has to take place at ambient conditions, the ideal H₂ binding energy range should be 0.2 - 0.4 eV. The system C5(BH₃+4H₂) has the binding energy 0.21 eV/H₂. This lies in the energy range required for a viable HSM. The storage capacity is 6.83 wt%. It is almost equal to the target set by U.S. DOE. The corresponding desorption temperature is calculated using van't Hoff equation and it is 268K.

We intend to increase the storage capacity of the system by introducing five more BH₃ molecules. The system is denoted as C10BH₃. Similar to the half coverage case we have attached hydrogen molecules to each of the BH₃ molecules in the relaxed structure of C10BH₃ one by one, up to a maximum of five H₂. The clustering started in C10(BH₃+3H₂). Two of the BH₃ molecules have come closer at a distance of 2.13 Å between them. The binding energy per H₂ in C10(BH₃+3H₂) is 0.26eV. The desorption temperature is 328K and is well above the room temperature. The storage capacity is 8.9wt%. A single dimer is observed in C10(BH₃+4H₂) and C10(BH₃+5H₂). Some of the H₂ molecules are dissociated into H atoms. We can expect these H atoms to combine as H₂ while desorption. Remaining H₂ are molecularly physisorbed. The binding energy per H₂ in C10(BH₃+4H₂) is 0.24eV. The corresponding desorption temperature is 306K and is nearly equal to the room temperature. The storage capacity of this system is 11.5wt%.

We conclude that light weight, hydrogen rich and electron deficient, BH₃ enhances the hydrogen storage capacity of SWCNT and this system has notable binding energy which lies in the range recommended for achieving DOE target at ambient conditions. The systems C5(BH₃+4H₂) and C10(BH₃+4H₂) are capable of releasing H₂ around room temperature. So the SWCNT functionalized with BH₃ becomes as a practicable hydrogen storage medium for fuel cells.

(iv) Molecular hydrogen storage in SWCNT functionalized with Nickel hydride

In this study (5, 5) SWCNT is functionalized with Nickel hydride (NiH₂) molecules. The simulation cell contains two unit cells of (5, 5) SWCNT. The half coverage comprises five NiH₂ molecules attached to the relaxed CNT. Initially single hydrogen molecule is attached to every single NiH₂ and after relaxation the binding energy per H₂ is calculated as 0.059eV. On subsequent addition of H₂ molecules a gradual decrease in the binding energy per H₂ is noted. For C5(NiH₂+4H₂) an increase in binding energy per H₂ is noted and is 0.14eV. Some of the attached H₂ molecules are absorbed by NiH₂ molecules, which have resulted in the increase of the binding energy. The binding energy per H₂ in C5(NiH₂+5H₂) is 0.079eV. The desorption temperature for hydrogen release is calculated as 175K and 101K for C5(NiH₂+4H₂) and C5(NiH₂+5H₂). The storage capacities of C5(NiH₂+4H₂) and C5(NiH₂+5H₂) are 4.89 wt% and 6.05 wt%.

The full coverage encloses ten NiH₂ molecules in (5, 5) SWCNT and the composition is relaxed. The clustering of NiH₂ molecules is observed in contrast to the half coverage where the occurrence is absent. On further addition of H₂ molecules the clustering pattern is found to change. A gradual decrease in the binding energy per H₂ is noticed. The system C10(NiH₂+H₂) and C10(NiH₂+2H₂) have the binding energy 0.19eV/H₂ and 0.12eV/H₂, correspondingly the desorption temperatures are 246K and 157K. The binding energy for single H₂ in C10(NiH₂+4H₂) and C10(NiH₂+5H₂) are 0.082eV and 0.056eV respectively. The corresponding desorption temperatures are 104K and 72K.

Due to clustering the hydrogen atoms in NiH₂ have come out and some has combined as H₂ molecules. This feature is detected in all configurations of full coverage. We can expect these molecules obtainable for use in the fuel cells. So the clustering has enhanced the storage capacity of the system. The storage capacities of C10(NiH₂+4H₂) and C10(NiH₂+5H₂) are 6.91 wt% and 8.50 wt% . The binding energy per H₂ in all the systems indicates that all H₂ are physisorbed. Since the binding energy per H₂ gets reduced on higher coverage of H₂ molecules, the systems deliver hydrogen below the room temperature.

Summary:

Out of the four systems investigated, the single walled Carbon Nanotube functionalized with BH₃ is found to be suitable hydrogen storage medium. It has hydrogen storage capacity, 11.5 wt% and the corresponding H₂ desorption temperature is 306 K. The system has to be fine tuned for a better performance.

6. Papers published/ submitted for publication:

S. No	Title of article	Vol., page, year	Authors' names
1	Aluminum Hydride coated single walled (5,5) carbon nanotube as hydrogen storage medium	Int. Journal of Hydrogen Energy, doi:10.1016/j.ijhydene.2008.09.086 (2008)	K.Iyakutti, Y.Kawazoe, M.Rajarajeswari and V.J.Surya
2	Functionalization of single walled carbon nanotube with borane for hydrogen storage	Submitted to Physica E	V.J.Surya and K.Iyakutti, M.Rajarajeswari and Y.Kawazoe
3	Clustering of functional molecules on a single walled carbon nanotube surface and its effect on hydrogen storage	Submitted to Nanotechnology	K. Iyakutti , V. J. Surya ¹ , M .Rajarajeswari N Venkataramanan and Y. Kawazoe

7. Conferences attended

S. No	Details of the conference	Place of conference	Title of Paper presented	Date
1	Asian Conference on Nanoscience and Nanotechnology, AsiaNANO 2008	Biopolis, Singapore	Study of hydrogen storage in Aluminum hydride coated single walled carbon nanotubes, K.Iyakutti , Y. Kawazoe , M.Rajarajeswari and V.J.Surya	Nov. 3-7, 2008
2	Asian Conference on Nanoscience and Nanotechnology, AsiaNANO 2008	Biopolis, Singapore	Hydrogen Storage in BH_3 and NH_3 functionalized (5,5) SWCNT	Nov. 3-7, 2008
3	DAE 53 rd Solid State Physics Symposium (2008)	BARC, Mumbai	Hydrogen storage in (5, 5) Single Walled Carbon Nanotube functionalized with Nickel hydride	To be held Dec.16 – 20, 2008

Work in Progress with the follow on project:

1. Study of the effect of finite length of SWCNT hydrogen storage using metal hydrides
2. Molecular dynamics calculations for all the systems investigated are to be completed.
3. The SWCNT (5, 5) is functionalized with lithium hydride, LiH and its storage capacity is being investigated.
4. To study the effect of curvature of the tube on the hydrogen storage, we are investigating large diameter tubes (10,0) and (10,10).
5. Searching for other materials which will be capable of releasing H_2 at ambient conditions.

Hydrogen Storage in BH_3 and NH_3
functionalized (5,5) SWCNT

Hydrogen storage in CNTs:

- The high surface to volume ratio , light weight and extensive gas adsorption properties made CNTs to be considered as the promising candidates for hydrogen storage.
- The experimental results by Dillon et al formed the basis for the hydrogen storage in CNTs. Since then a lot of works have been devoted to explore the hydrogen storage capacity of CNTs.
- The interaction between H_2 and bare CNT is weak and so it can't remain attached even at ambient conditions. So functionalization/ doping of CNTs with various atoms, molecules and metal complexes enhances the storage capacity when compared to bare CNTs.

- The functionalization of CNT with transition metal atoms has increased the storage capacity to a higher extent than the value predicted by U.S. Department of energy. But transition metal have heavy mass.
- To achieve high gravimetric and volumetric densities it is important to find light weight atoms/complexes which enhances the storage capacity of SWCNT.
- We have chosen BH_3 and NH_3 molecules for functionalization and they have molecular masses, 13.8 gmol^{-1} and 17.03 gmol^{-1} respectively
- Both being light weight molecules and hydrogen rich can adsorb hydrogen to certain extent and our study highlights this fact.



- Borane or Boron trihydride has molecular structure analogue to AlH_3 .
- It exists in gaseous form.
- It is the parent compound of all boranes.
- Generally boranes are electron deficient and highly reactive.



- Ammonia or Azane exists in gaseous form.
- It has trigonal pyramidal shape.
- It has lone pair of electrons.

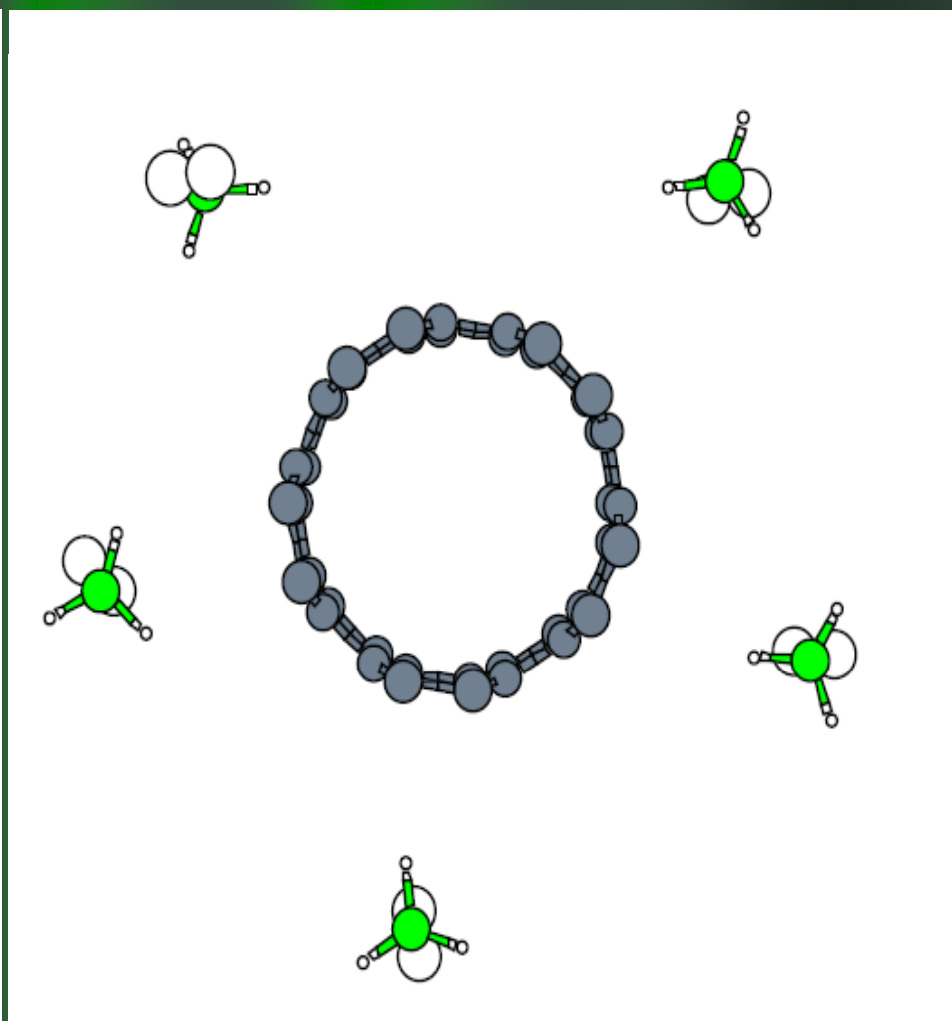
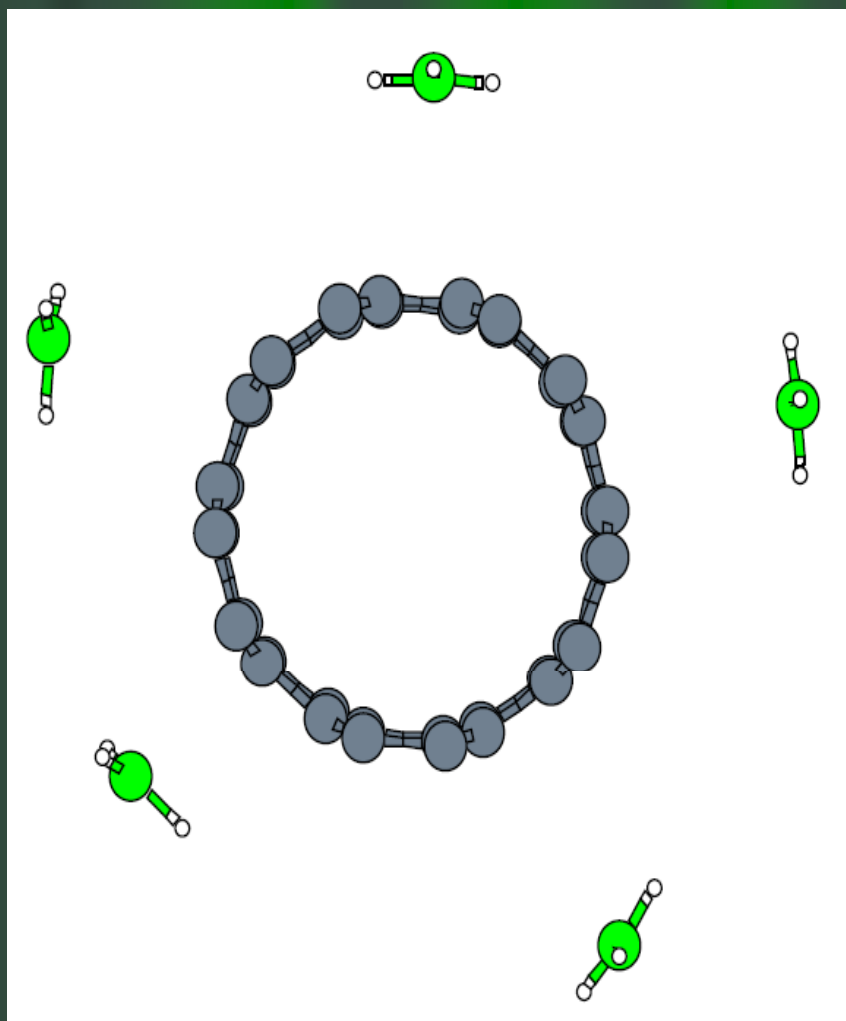
Methodology and modelling

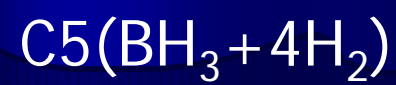
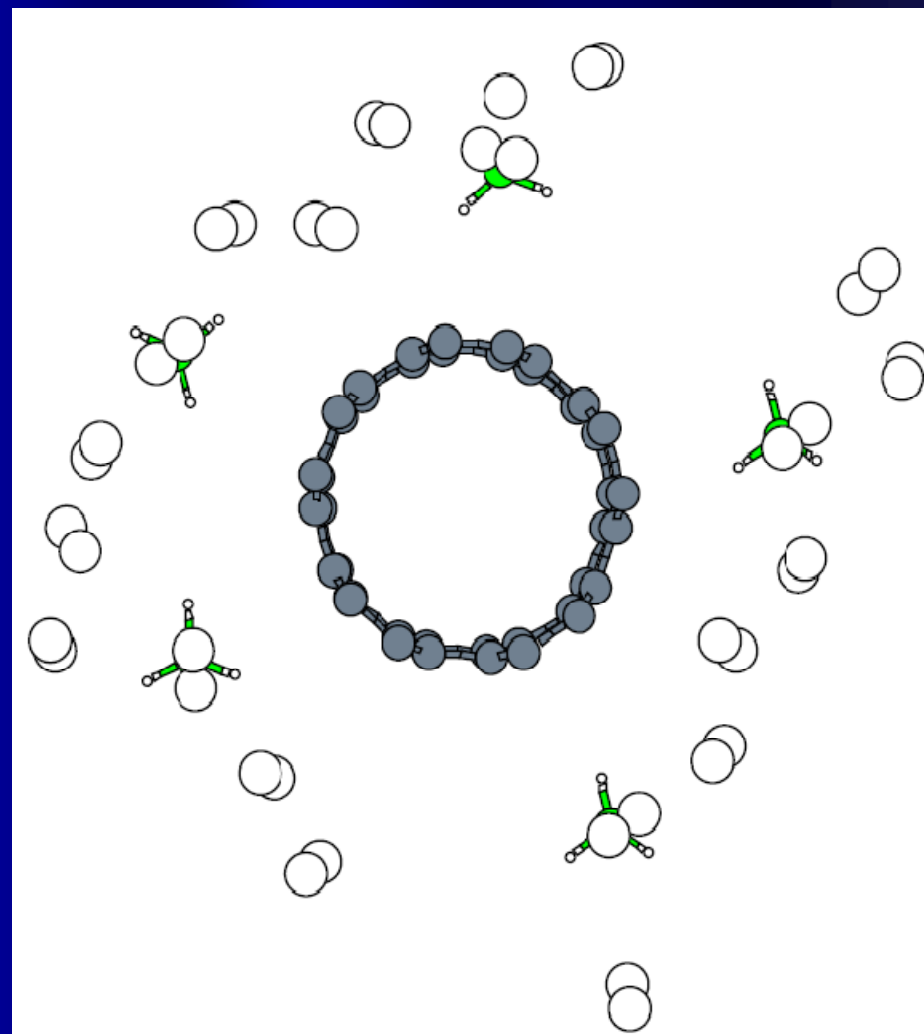
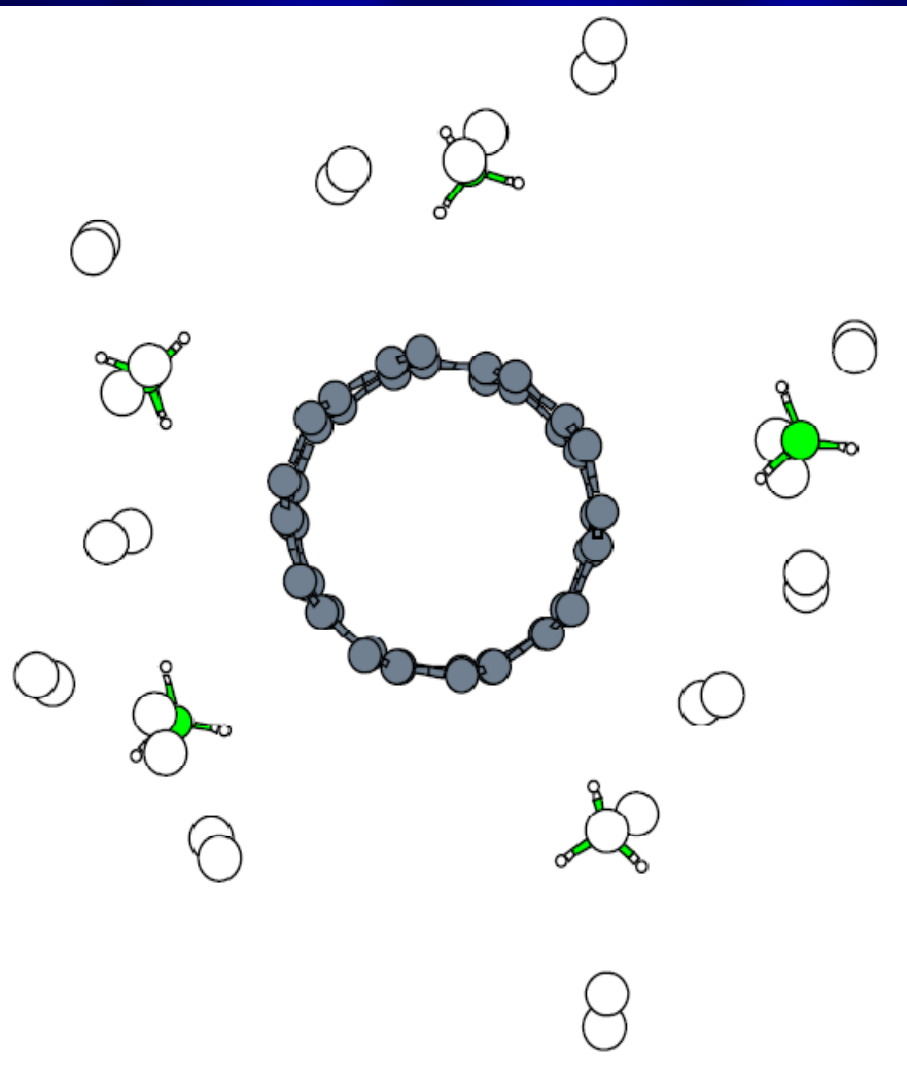
- The total energy calculations are carried out using density functional theory implemented in VASP code.
- Two unit cells of SWCNT (5,5) in the simulation cell of dimension $24 \times 24 \times 4.98 \text{Å}^3$ is taken.
- Ultra soft pseudopotentials are used with
 - C: $2s^2 2p^2$
 - B: $2s^2 2p^1$
 - N: $2s^2 2p^3$
 - H: $1s$as valence states.
- The coordinates of SWCNT (5,5) are generated. BH_3 and NH_3 molecules are attached to the relaxed geometry of CNT, resulting in the formation of CBH_3 and CNH_3 systems.
- The investigation is done for half coverage which has 5 molecules and full coverage which has 10 molecules of BH_3 and NH_3 .

C5BH₃

The hydrogen molecules are attached to the relaxed structure of C5BH₃. The structures are optimized. The binding energy per H₂ and the storage capacities are calculated.

System	Binding energy per H ₂ (eV)	Storage capacity , wt%
C5(BH ₃ +H ₂)	0.65	1.8
C5(BH ₃ +2H ₂)	0.35	3.53
C5(BH ₃ +3H ₂)	0.26	5.21
C5(BH ₃ +4H ₂)	0.21	6.83
C5(BH ₃ +5H ₂)	0.18	8.4

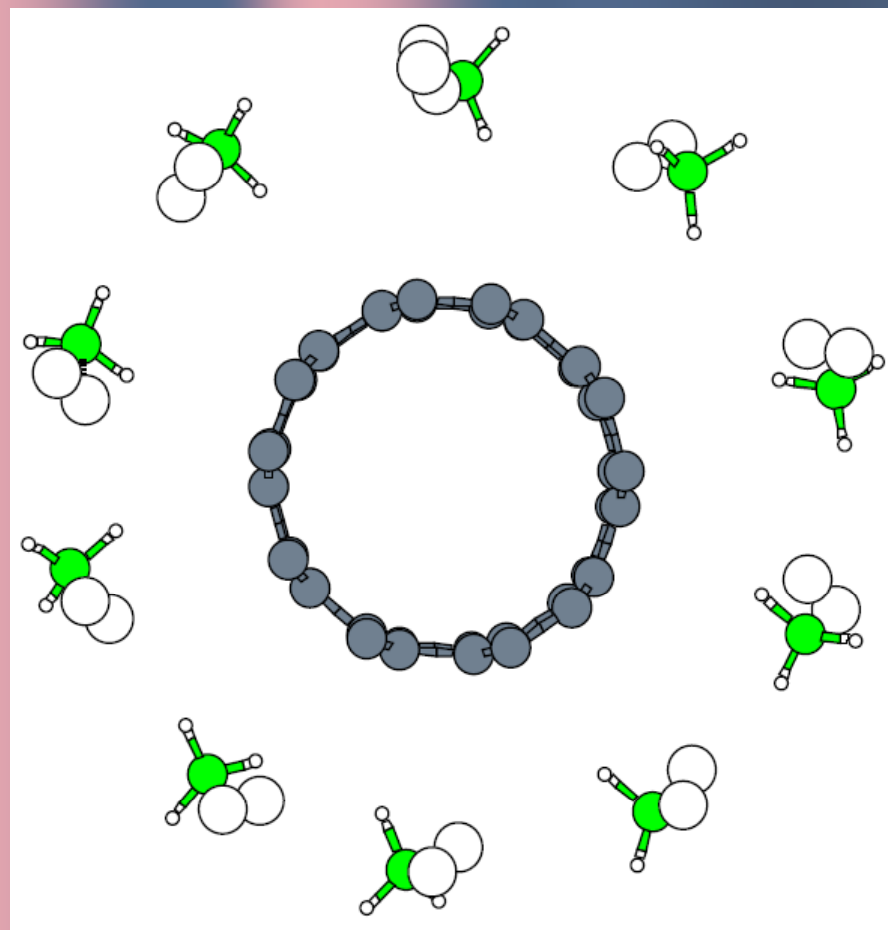
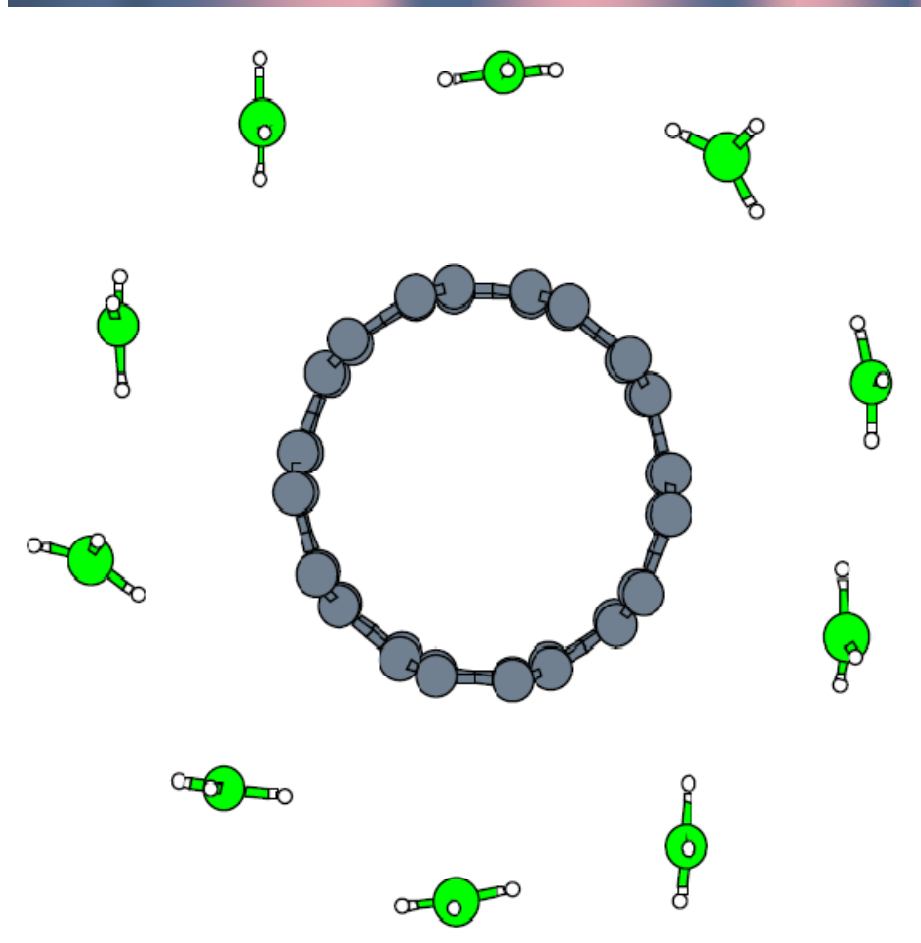


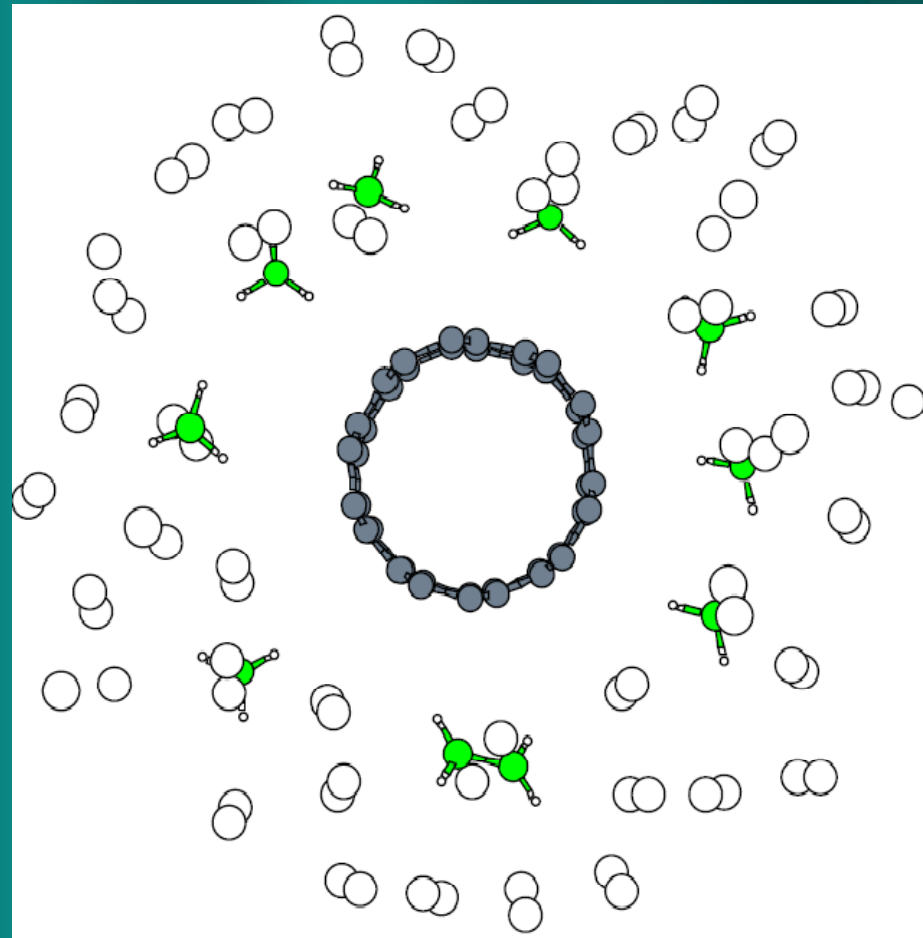
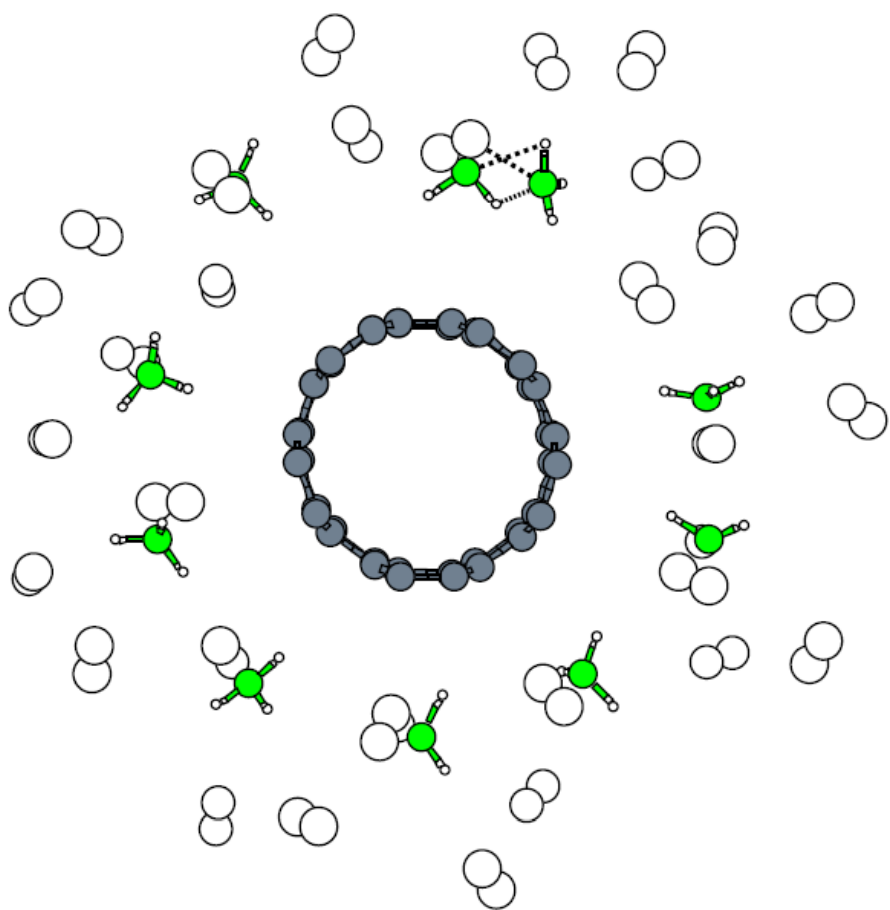


C10BH₃

As in the case of half coverage five hydrogen molecules are added one by one to each BH₃ in the relaxed structure of C10BH₃. The binding energy for single H₂ and storage capacity of all relaxed systems are calculated.

System	Binding energy per H ₂ , eV	Storage capacity, wt%
C10(BH ₃ +H ₂)	0.67	3.15
C10(BH ₃ +2H ₂)	0.36	6.12
C10(BH ₃ +3H ₂)	0.26	8.90
C10(BH ₃ +4H ₂)	0.24	11.5
C10(BH ₃ +5H ₂)	0.18	14

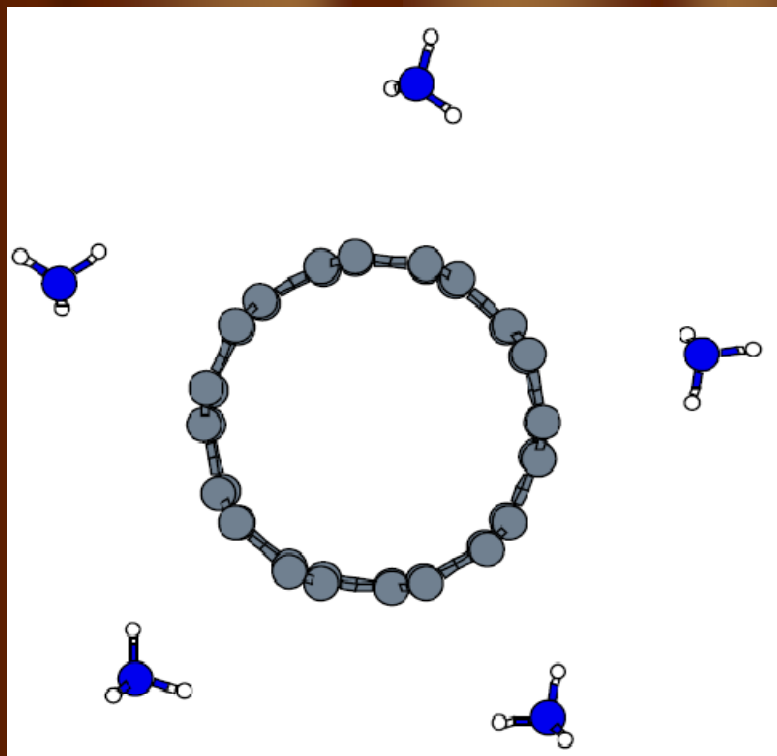




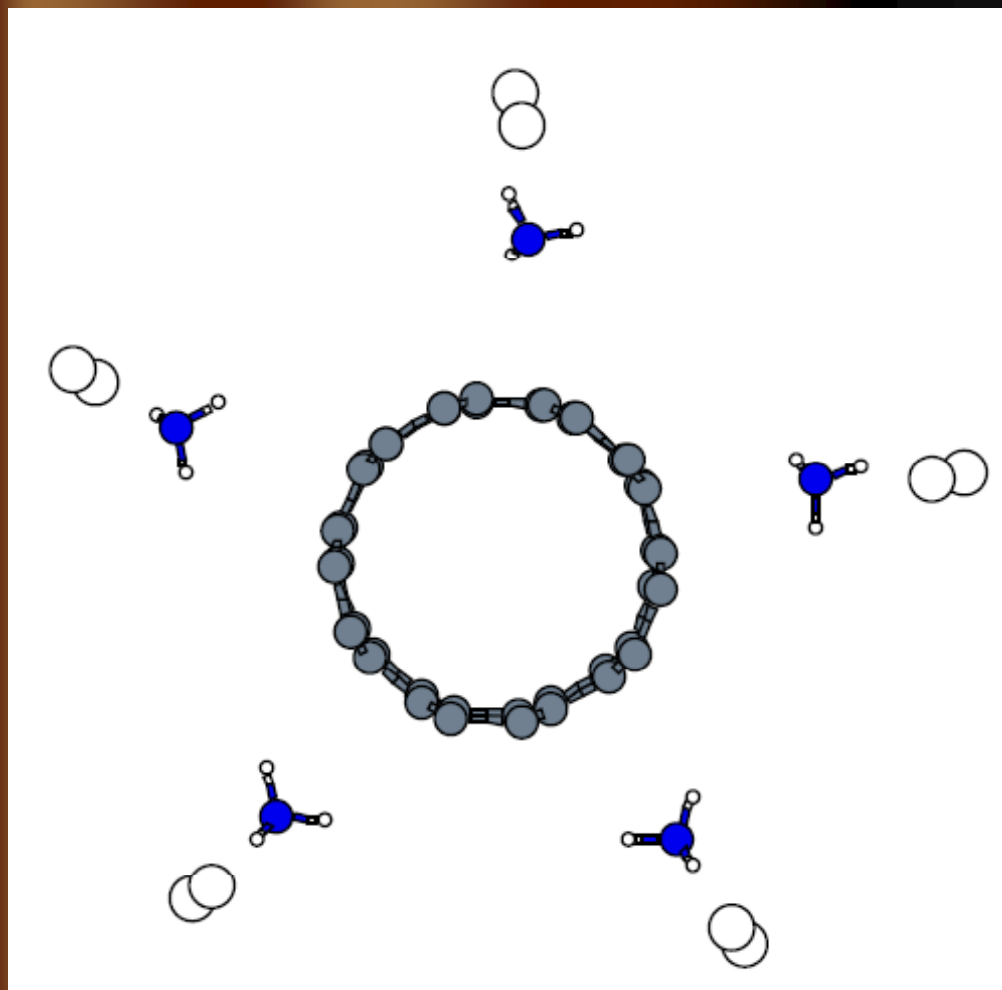
C5NH₃

As in C5BH₃, five hydrogen molecules are attached to each NH₃ in C5NH₃. The binding energy per H₂ and storage capacity of all optimized systems are calculated.

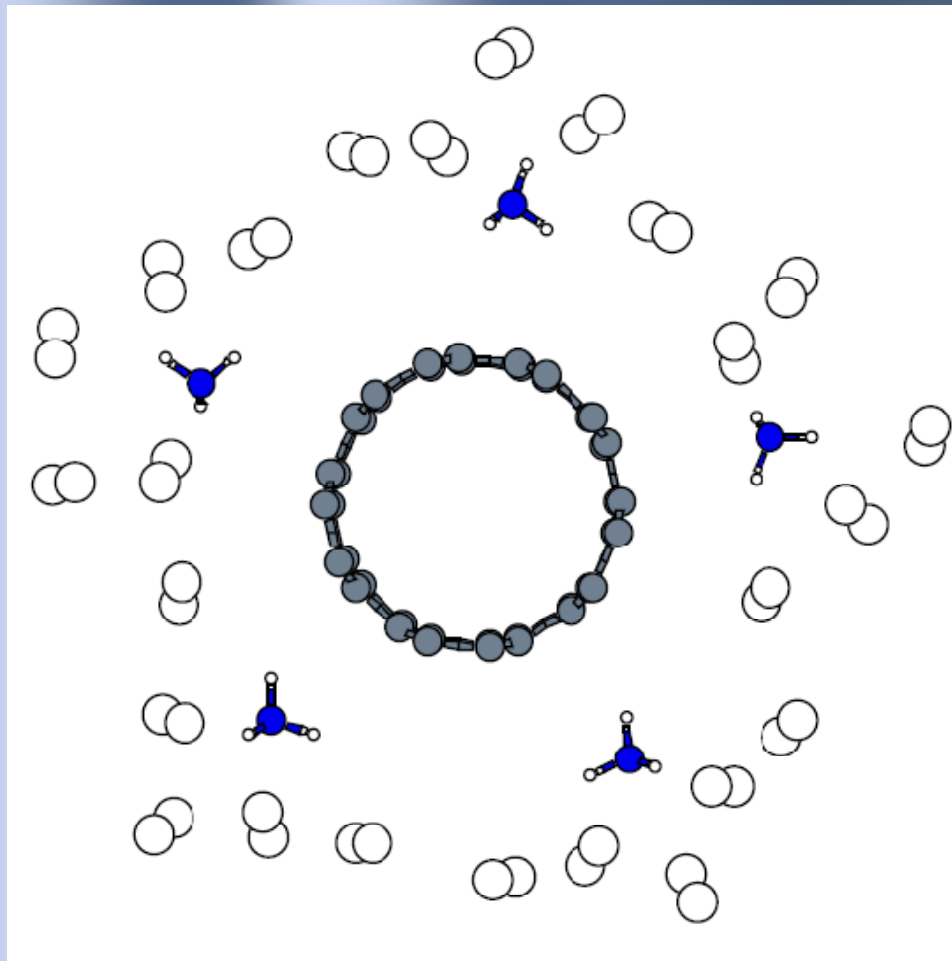
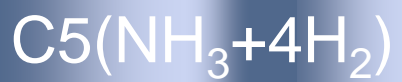
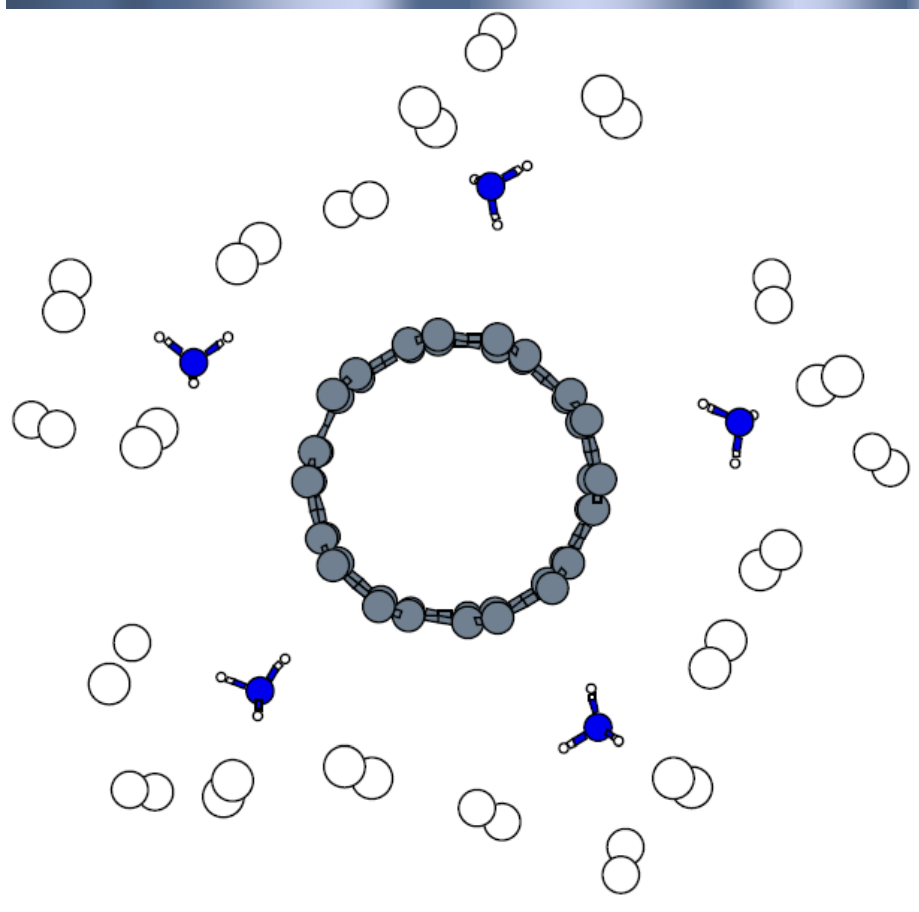
System	Binding energy per H ₂ , eV	Storage capacity, wt%
C5(NH ₃ +H ₂)	0.10	1.75
C5(NH ₃ +2H ₂)	0.097	3.44
C5(NH ₃ +3H ₂)	0.095	5.07
C5(NH ₃ +4H ₂)	0.092	6.65
C5(NH ₃ +5H ₂)	0.091	8.18



C_5NH_3



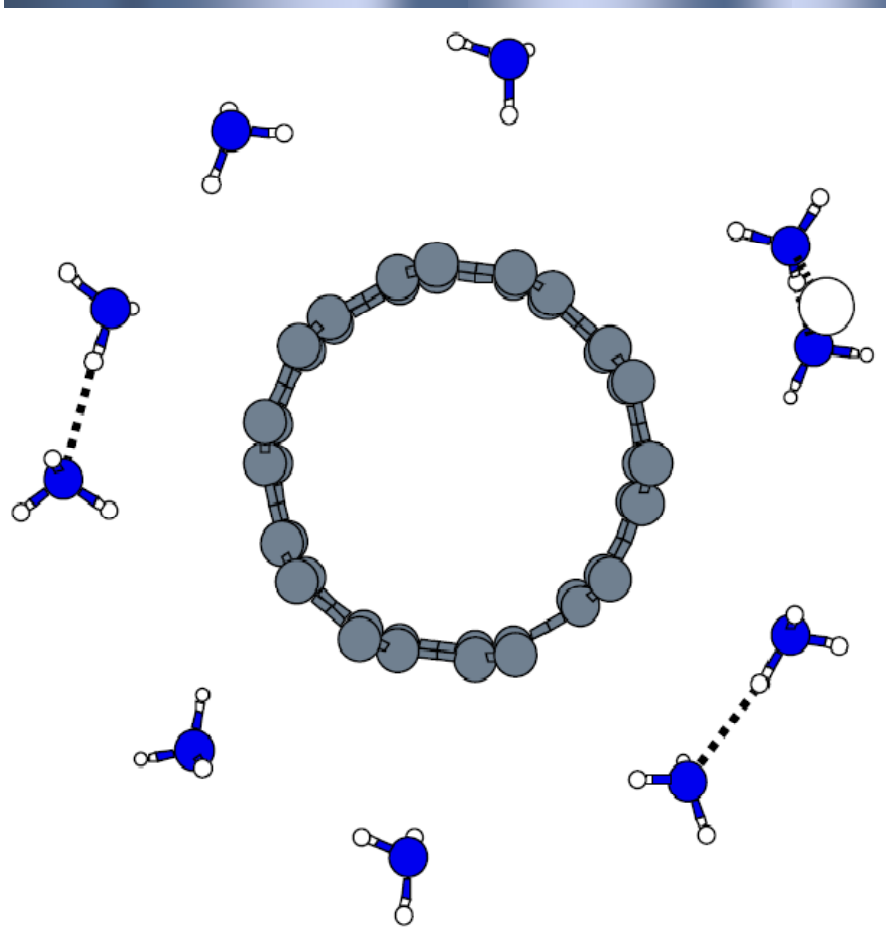
$C_5(NH_3+H_2)$



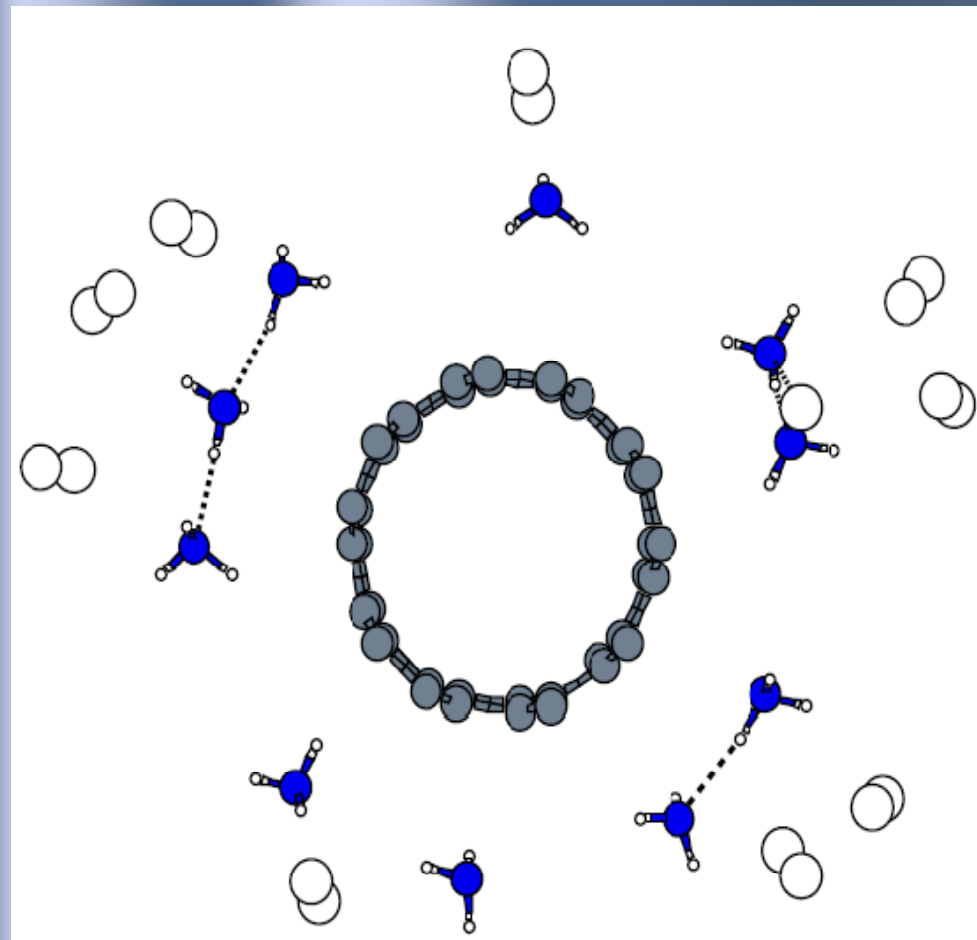
C10NH₃

On addition of another H₂ to C10(NH₃+H₂), we observed decrease in the binding energy and it is low. The binding energy per H₂ and storage capacities of all the systems are calculated.

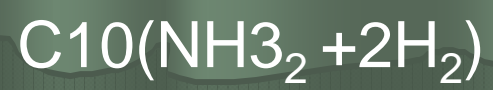
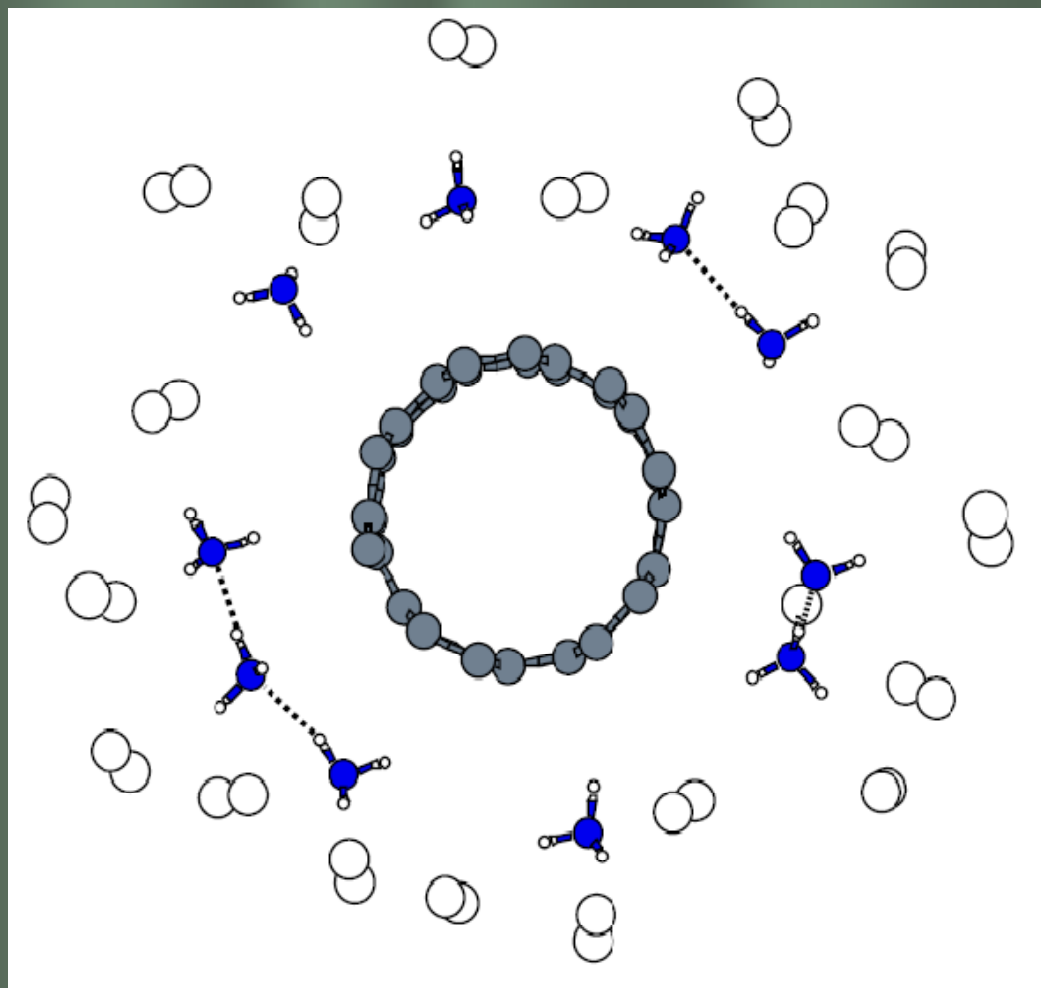
System	Binding energy per H ₂ , eV	Storage capacity, wt%
C10(NH ₃ +H ₂)	0.10	3
C10(NH ₃ +2H ₂)	0.099	5.83
C10(NH ₃ +3H ₂)	0.097	8.50
C10(NH ₃ +4H ₂)	0.098	11.1
C10(NH ₃ +5H ₂)	0.092	13.2



C₁₀NH₃



C₁₀(NH₃+H₂)



- The ideal H_2 binding energy range to achieve DOE target is 0.2-0.4eV and so desorption takes place at ambient conditions.
- Our study reveals that $C_5NH_3+nH_2$ has less binding energy when compared to that of $C_5BH_3+nH_2$ ($n=1,2,3,4\&5$).

CBH₃

C5BH₃

- On addition of hydrogen molecules one of the B-H bond length has increased from 1.18Å to 1.20Å. Since BH₃ is electron deficient there is a significant charge transfer between BH₃ and H₂ molecules.
- Moreover in each system one hydrogen molecule is closely bound to BH₃ at a distance of 1.32Å. The bond length has extended from 0.74Å to 0.85Å.
- Remaining H₂ molecules are less perturbed and their bond length has increased to 0.749Å.

C10BH₃

- Here too in full coverage one of the adsorbed H₂ molecules is more perturbed and the bond length is 0.85Å .
- Single BH₃ dimer is observed in C10(BH₃+4H₂) and C10(BH₃+5H₂). The formation of the dimer doesn't seem to enhance the binding energy per H₂ molecule.

CNH₃

C5NH₃

- All the hydrogen molecules perturbed equally. The H-H bond distance has increased uniformly to 0.75Å.
- A gradual decrease in the binding energy per H₂ is noted when compared to C5BH₃+nH₂ (n=1,2,3,4&5) systems.

C10NH₃

- As in C5NH₃ the hydrogen molecules are almost equally perturbed.
- Here clustering between NH₃ molecules is noted. Since the clustering weak it doesn't increase the binding energy of single H₂.

Salient Features: CBH_3

- The system $\text{C5}(\text{BH}_3+4\text{H}_2)$ has the binding energy per H_2 as 0.21eV . The corresponding desorption temperature is calculated using van't hof equation and it is 268K .
- The system $\text{C10}(\text{BH}_3+4\text{H}_2)$ has a notable binding energy of 0.24eV . The desorption temperature is 306K and it is equal to room temperature. The storage capacity exceeds the DOE target and is $11.5\text{wt}\%$.

Salient features : CNH_3

- The binding energy per H_2 in $\text{C5}(\text{NH}_3+5\text{H}_2)$ is 0.092eV . The desorption temperature is 116K . It is far below the room temperature.
- In $\text{C10}(\text{NH}_3+2\text{H}_2)$ the binding energy for single H_2 is 0.099eV and the desorption temperature is estimated as 126K .

Conclusion

- On comparing both the systems, CBH_3 qualifies as an viable HSM with high hydrogen storage capacity and desorption of hydrogen takes place at room temperature.
- The functionalization with electron deficient light weight molecules like BH_3 enhances the hydrogen storage capacity to a larger extent.
- The functionalization with electron rich molecule like NH_3 enhances the storage capacity but the binding energy per H_2 gets decreased and so they can't release H_2 at room temperature.

Acknowledgement

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