Computational Insights on Functional Materials for Clean Energy Storage

Modeling, Structure and Thermodynamics

TANVEER HUSSAIN
The exponential increase in the demands of world’s energy and the devastating effects of current fossil fuels based sources has forced us to reduce our dependence on the current sources as well as finding cleaner, cheaper and renewable alternates. Being abundant, efficient and renewable, hydrogen can be opted as the best possible replacement of the diminishing and harmful fossil fuels. But the transformation towards the hydrogen-based economy is hindered by the unavailability of suitable storage medium for hydrogen. First principles calculations based on density functional theory has been employed in this thesis to investigate the structures modelling and thermodynamics of various efficient materials capable of storing hydrogen under chemisorption and physisorption mechanisms.

Thanks to their high storage capacity, abundance and low cost, metal hydride (MgH$_2$) has been considered as promising choice for hydrogen storage. However, the biggest drawback is their strong binding with the absorbed hydrogen under chemisorption, which make them inappropriate for operation at ambient conditions. Different strategies have been applied to improve the thermodynamics including doping with light and transitions metals in different phases of MgH$_2$ in bulk form. Application of mechanical strain along with Al, Si and Ti doping on MgH$_2$ (001) and (100) surfaces has also been found very useful in lowering the dehydrogenation energies that ultimately improve adsorption/desorption temperatures.

Secondly, in this thesis, two-dimensional materials with high surface area have been studied for the adsorption of hydrogen in molecular form (H$_2$) under physisorption. The main disadvantage of this kind of storage is that the adsorption of H$_2$ with these nanostructures likes graphane, silicene, silicane, BN-sheets, BC$_3$ sheets are low and demand operation at cryogenic conditions. To enhance the H$_2$ binding and attain high storage capacity the above-mentioned nanostructures have been functionalized with light metals (alkali, alkaline) and polylithiated species (OLi$_2$, CLi$_3$, CLi$_4$). The stabilities of the designed functional materials for H$_2$ storage have been verified by means of molecular dynamics simulations.

Keywords: Density functional theory, Molecular dynamics, Hydrogen storage, Chemisorption, Physisorption, Functionalization

Tanveer Hussain, Uppsala University, Department of Physics and Astronomy, Box 516, SE-751 20 Uppsala, Sweden.

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To my beloved parents
Cover illustration:

Hydrogen storage in polylithiated (CLi$_3$) functionalized boron-carbide sheet. Black, red, green and cyan balls represent C, B, Li and H atoms.
This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

I  Structural, electronic and thermodynamic properties of Al- and Si-doped α-, γ- and β-MgH$_2$: Density functional and hybrid density functional calculations
   Tuhina Adit Maark, Tanveer Hussain and Rajeev Ahuja

II Transition metals doped MgH$_2$ for hydrogen storage: A hybrid density functional calculation
   Tanveer Hussain, Tuhina Adit Maark, Biswarup Pathak and Rajeev Ahuja *(Under review in AIP Advances)*

III Strain and doping effects on the energetics of hydrogen desorption from the MgH$_2$ (001) surface
   Tanveer Hussain, Abir De Sarkar, Tuhina Adit Maark, Weiwei Sun and Rajeev Ahuja
   *Europhysics Letters, 101, 27006 (2013)*

IV The effects of strain and doping on the release of hydrogen from the MgH$_2$(110) surface
   Weiwei Sun, Tanveer Hussain, Abir De Sarkar, Tuhina Adit Maark, Wei Luo and Rajeev Ahuja
   *(Submitted)*

V Ab initio study of lithium-doped graphane for hydrogen Storage
   Tanveer Hussain, Biswarup Pathak, Tuhina Adit Maark, Carlos Moyses Araujo, Ralph H. Scheicher and Rajeev Ahuja
   *Europhysics Letters, 96, 27013 (2011)*
VI Calcium doped graphane as a hydrogen storage material
Tanveer Hussain, Biswarup Pathak, Muhammad Ramzan, Tuhina Adit Maark and Rajeev Ahuja

VII Strain induced lithium-functionalized graphane as a high capacity hydrogen storage material
Tanveer Hussain, Abir De Sarkar and Rajeev Ahuja

VIII Metal Functionalized Silicene for Efficient Hydrogen Storage
Tanveer Hussain, Sudip Chakraborty and Rajeev Ahuja
(In Press ChemPhysChem)

IX Functionalization of hydrogenated silicene with alkali and Alkaline earth metals for efficient hydrogen storage
Tanveer Hussain, Thanayut Kaewmaraya, Sudip Chakraborty and Rajeev Ahuja
(In Press Physical Chemistry Chemical Physics)

X Polylithiated (OLi$_2$) functionalized graphane as a potential hydrogen storage material
Tanveer Hussain, Tuhina Adit Maark, Abir De Sarkar and Rajeev Ahuja

XI Functionalization of hydrogenated graphene by polylithiated species for efficient hydrogen storage
Tanveer Hussain, Abir De Sarkar and Rajeev Ahuja
(Under Review in International Journal of Hydrogen Energy)

XII Hexagonal Boron Nitride Sheet Decorated by Polylithiated Species for Efficient and Reversible Hydrogen Storage
Tanveer Hussain, Abir De Sarkar, Tae Won Kang and Rajeev Ahuja
Hydrogen storage in polylithiated BC$_3$ monolayer sheet
Yunguo Li, Tanveer Hussain, Abir De Sarkar and Rajeev Ahuja
Solid State Communications, 170, 39 (2013)

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My contributions

My contributions to the papers in the present thesis are illustrated in the following. For those papers where I am the first author I have taken the main responsibility in performing calculations, analyzing the data and writing the manuscript.

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The following papers are also co-authored by me but not included in this thesis.

- **Functionalization of graphane with alkali and alkaline earth metals: An insulator to metallic transition**
  Tanveer Hussain, Biswarup Pathak, Tuhina Adit Maark, Muhammad Ramzan, and Rajeev Ahuja

- **Functionalized Boranes for Hydrogen Storage**
  Biswarup Pathak, Kalpataru Pradhan, Tanveer Hussain, Rajeev Ahuja and Purusottam Jena

- **High pressure phase determination and electronic properties of Lithiumamidoborane**
  Muhammad Ramzan, Tanveer Hussain and Rajeev Ahuja

- **Hydrogen diffusion in bulk and nanoclusters of MgH₂ and the role of catalysts on the basis of ab initio molecular dynamics**
  Muhammad Ramzan, Tanveer Hussain and Rajeev Ahuja

- **Enriching Physisorption of H₂S and NH₃ Gases on a Graphane Sheet by doping with Li adatoms**
  Tanveer Hussain, Puspamitra Panigrahi and Rajeev Ahuja
  *(Under Review in Dalton Transactions)*

- **Vacancy Induced Jahn Teller Distortion of MnMgO in 3D bulk, 2D slab and 1D wire structures, a DFT study**
  Puspamitra Panigrahi, Tanveer Hussain, C. Moyses and Rajeev Ahuja
  *(In manuscript)*

- **Hole Induced Stabilization of Ferromagnetism at MnMgO Surface: A First-principles Prediction**
  Puspamitra Panigrahi, Tanveer Hussain, C. Moyses and Rajeev Ahuja
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1 Introduction

The advanced and accurate knowledge of materials especially at atomic and molecular level are essential for performing various desired technological functions bringing about revolution in modern day life. Progress in computational materials science with the development of variety of computational methodologies has opened up a number of new horizons regarding exploration of material properties having utmost technological importance. A wide range of material properties can be predicted with great precision before executing the experimental investigation, which could avoid expensive, tedious and time-consuming exercise. While predicting/describing a certain phenomenon, designing a novel material or investigating its characteristic properties at atomic level, computational material science has been proved to be of significant importance. The trend in designing functional materials with reduced (nanometer) size consisting of few hundreds of atoms only and to improve the accuracy, it has become inevitable to go beyond the previously used Newtonian mechanics, which lacks accuracy and unable to deal with small systems down to nanometers scale. Thanks to the development of efficient and state-of-the-art techniques like first principles calculations, and the availability of increased computer simulation power, the designing of new materials and the improvement in the properties of the existing ones has become possible. The density functional theory based first principles calculations has been found promising while investigating the novel functional nanostructures (doped/defected graphene, graphane, BN-sheets, silicene etc.) for vivid industrial and technological applications including hydrogen production, hydrogen storage and gas sensing.

The ever growing need of energy which, is expected to be more than double in next few decades have triggered the extensive use of current fossil fuels sources (oil, coal, gas) resulting in their depletion at tremendous rate. This situation reflects the unsustainability of current sources coupled with the CO, CO₂ and other greenhouse gases associated with them, which are a great source of pollution and hence a threat to the environment. So, it is high time to find a clean, economical, renewable and efficient solution that could reduce our dependence on diminishing fossil fuels by replacing them with suitable alternate. Hydrogen (H₂) can be considered as the most promising alternate and energy carrier owing to its abundance and clean reaction with oxygen releasing only water as by product [1-4]. Along with environmental friendliness and the highest energy density per mass than any other element
of the periodic table, renewability has also made H₂ an interesting choice for future energy solution. However, the gaseous nature of H₂ and its nonexistence in free state in nature (it is found in combined form in water etc.) are the biggest obstacles towards the realization of so-called hydrogen economy. Contrary to high energy content by mass, H₂ possesses only 0.09kg/m³ by volume due to its gaseous nature, which makes it extremely difficult to be stored in large amount in small volume [5]. Thus, in order to use H₂ as energy carrier in place of current harmful energy sources, and to overcome the technological barrier for its use in mobile applications, the issue of the storage will have to be solved in an efficient way. The main topic of the current thesis is to investigate the appropriate and efficient ways to store the hydrogen for the transition towards hydrogen economy.

Conventionally the H₂ storage issue can be tackled by the following approaches

(i) Storage under pressure (ii) Storage by liquefaction. But both of these methods involve lots of drawbacks and are inappropriate. In the first method the H₂ gas undergoes pressure of several hundred (~ 700) bar to reach to a density of 42kg/m³ contrary to 0.09kg/m³ at ordinary pressure. For storage of 5kg, a tank of 125 liters is needed. Though there is a surge to find suitable composite which could store reasonably large amount of H₂ at relatively lower pressure but still the safety issues caused by very high pressure and the lack of cost effectiveness make it inappropriate solution for H₂ storage. On the other hand liquidation of H₂ demands a cryogenic temperature of few kelvin at ambient pressure. In order to attain a H₂ storage capacity of 70kg/m³, the temperature should be as low as -253 °C [6]. However to attain such a low temperature in order to keep H₂ in liquid form, by avoiding vaporization, and then to use the liquid H₂ for mobile or other applications, a large amount of energy is needed. Thus the complications involved and the economics do not suggest the liquefaction as promising storage solution. Apart from the above mentioned unviable options involving certain drawbacks, the materials based solid-state storage seems to be an interesting and workable strategy. The choice of the suitable storage material depends on the fulfillment of certain condition like (i) high storage capacity (ii) operation at ambient condition (iii) economic viability (iv) environmental friendliness (v) reversibility and (vi) safety.

Materials fulfilling the criteria stated above can serve the purpose of long standing H₂ storage problem. The H₂ can either be stored in the lattice of a suitable host material in atomic form (Chemisorption) or to the surface of a material in molecular form (Physisorption). The mechanism of chemisorption deals with the dissociation of H₂ molecules into H atoms and then the formation of new hydrides by the absorption of these H atoms in the lattice of the host materials [7,8]. This strategy could be advantageous in absorbing large amount of atomic hydrogen but the large weight of metal-hydride system denies high gravimetric and volumetric densities. Another issue is that
strong ionic or covalent bonds are formed between the hydrogen atoms and the host material, which require lots of energy to be supplied in order to release hydrogen. This situation hinders the reversibility and operation at ambient conditions (as the hydrogen can only be absorbed/released at relatively higher temperature) whereas cost effectiveness is another problem [9]. However the issues related with H₂ storage governed by chemisorption can be solved in different ways. It has been very well known and studied that using suitable catalyst can enhance the adsorption/desorption of H₂ in metal hydrides. It has also been seen that the thermodynamics can be improved by nanostructuring of these systems and with the application of mechanical strain on metal hydride surfaces [10-14]. Some of the prominent materials, which store hydrogen by chemisorption, are LiAlH₄, NaAlH₄ KAIH₄, LiNH₂, Li₂NH, LiBH₄ and MgH₂ etc. [15-20].

The other strategy governing solid-state hydrogen storage in materials in molecular form without dissociation is called physisorption, which enable the H₂ molecules to be adsorbed by the host material’s surface via weak forces commonly know as van der Waal’s forces. Unlike chemisorption, in this mechanism no chemical bonds exist between H₂ molecules and the host material, which improves the thermodynamics and allows absorption/desorption quite rapidly. Apart from that high storage capacity can also be achieved if the host material possesses large surface area, as the H₂ storage capacity varies directly with the material’s surface area [21,22]. Some of the prominent materials with high surface area like carbon based materials, metal organic framework, graphene; boron nitride sheet etc. storing hydrogen employing physisorption mechanism could be of great importance [23-27]. But the weak van der Waal’s interaction between H₂ molecules and the host materials usually around 10kJ/mol. is too small to retain the H₂ molecules adsorbed with the material at ambient conditions. Therefore the adsorption energies of H₂ physisorbed with the metals need to be enhanced in order to achieve high capacity of H₂ for practical applications.

The outline of the current thesis is as follows: In chapter 2 the fundamental and general concepts of the theoretical methods (Density functional theory, molecular dynamics simulations etc.) used in thesis have been described briefly. The following sections comprise of a detailed insight on the hydrogen storage methodologies, conventional storage methods and their drawbacks and solid-state storage techniques. The phenomenon of Chemisorption has been presented with emphasizes on MgH₂ in chapter 3. The Physisorption approach for hydrogen storage with the intensive studies on metal, and polylithiated species functionalized on two-dimensional nanostructures (graphane, boron-nitride sheet, boron carbide sheet, silicene etc.) have also been reported in chapter 4. Finally, we have presented the conclusion and outlook in chapter 5.
2 Theoretical Methods and Approximations

This section contains the basic theoretical methodology and the approximations used in all the works constitute this thesis. The detailed description of density functional theory has been presented, which is the basic technique in all the works presented in this thesis.

2.1 Density functional theory:
2.1.1 Many body problem:
In order to study the materials in solid-state physics, which generally have large number of atoms (~10^{23}) the solution of many body problems become inevitable. While studying such systems, where large number of atoms (many electrons and nuclei) interacts with each other, their properties can be determined by solving the Schrodinger equation

\[ H \Psi(r, R) = E \Psi(r, R) \]  

(2.1)

The Hamiltonian is

\[ H = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_i \frac{\hbar^2}{2M_i} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} + \frac{1}{2} \sum_{i \neq j} \frac{Z_i Z_j e^2}{|R_i - R_j|} \]

\[ -\sum_{i,j} Z_i Z_j e^2 \sqrt{|r_i - R_i|}, \]  

(2.2)

Here in the equation 2.2 the terms \(\hbar = \hbar/2\pi\) represents reduced Plank's constant, \(m_e, r_i, e\) are the mass, position and charge of the \(i^{th}\) electron respectively. Where \(M_i, R_i\) and \(Z_i\) represents the mass, position and the charge of the \(i^{th}\) nuclei respectively. The first two terms give the kinetic energies of electron and the nuclei whereas the remaining terms represent the electron-electron, nuclei-nuclei and electron-nuclei interactions respectively. In order to study any system we need to solve Eq. (2.1) with the Hamiltonian given in Eq. (2.2), which is almost impossible except for the simplest of hydrogen atom. For any other system consisting of large number of electrons and nuclei, it is inevitable to employ some approximations, even for helium. One of the most extensively used approximation method in almost all the methodologies is Born-Oppenheimer approximation [28]. Under this approximation we can consider the wave functions of both electron and the nuclei separately. As the motion of electron is much higher than that of nuclei due
its larger mass, so the nuclei can be considered as stationary. Hence, the kinetic energy term of the nuclei can be neglected due to its frozen equilibrium state. This leads to the fact that the nuclei can be treated as external potential $V_{\text{ext}}$ applied to the fast moving electrons. By considering the wave functions of electron $\Psi_e(r, R)$ and the nuclei $\Psi_n(R)$ separately we will have the

$$\Psi(r, R) = \Psi_e(r, R)\Psi_n(R)$$ \hspace{0.5cm} (2.3)

And the Schrodinger equation for only electrons will take the form

$$H_e\Psi_e(r, R) = E_e\Psi_e(r, R)$$ \hspace{0.5cm} (2.4)

After the applications of Born-Oppenheimer approximation, the Hamiltonian will be

$$H = -\sum_i\frac{h^2}{2m_e}\nabla_i^2 + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|r_i - r_j|} - \sum_{i, l} \frac{Z_le^2}{|r_i - R_l|}$$ \hspace{0.5cm} (2.5)

Though treatment of the systems look much simplified now, but still in case of large number of electrons, computational cost would be very high and unaffordable. The electron-electron interaction represented by third term of Eq. (2.5) needs further approximation, as it cannot be tackled with this approximation only. In order to deal with this problem other approximation like Density Functional Theory (DFT) has been employed, which will be described in the following paragraphs

2.1.2 The Hohenberg-Kohn theorems:

To solve the Schrodinger equation in order to analyze the ground state properties of any systems, one of the most popular and promising techniques currently employed is the density functional theory (DFT). By means of different approximations, this methodology has found its application ranging from atoms, molecules to complex systems in Physics, Chemistry, and Material Science. It is based on the two theorems by Hohenberg and Kohn[29, 30].

Theorem 1:

It states that in case of a system of interacting particles (electrons) in an external potential $V_{\text{ext}}(r)$, there exists one-to-one correspondence between the potential and the ground-state density $\rho(r)$ of the interacting particles. This ground-state density thus determines uniquely the ground-state properties of the system.

$$\langle \Psi|A|\Psi \rangle = A[\rho(r)]$$ \hspace{0.5cm} (2.6)
Theorem 2:
It states that the universal total energy function $E_{HK}$ can be defined for a system of interacting particles under the application of external potential $V_{ext}(r)$ as given below

$$E[\rho(r)] = E_{HK}[\rho(r)] + \int V_{ext}(r)\rho(r)dr$$  \hspace{1cm} (2.7)

In Eq. (2.7) the term $E_{HK}[\rho(r)]$ represents the total internal energies of all the interacting particles constituting system. The true ground-state density of the system $\rho_0(r)$ will result into true ground-state energy ($E_0$), which will be the global minimum of the functional mentioned in the theorem stated above.

A brief discussion of both of these theorems without proving them follows. The first theorem is understood by considering the fact the charge density of a system of interacting particles with ground state in an external potential can generate all the observable of the system. Thus the properties of the system can be obtained with the charge density rather than wave function. The second theorem talks about the universal energy functional of the system of interacting particles. The exact ground state energy of the system is actually the global minimum of this functional. It should also be kept in mind that the actual ground state charge density of the system caused the energy functional to reach the minimum energy configuration.

By considering the H-K theorem, Kohn-Sham proposed that the system of interacting particles could be replaced by the non-interacting particles with the same exact ground state density for both. The total ground state energy proposed by Kohn-Sham can be written as

$$E[\rho(r)] = T_0[\rho(r)] + \frac{1}{2} \iint \frac{\rho(r)\rho(r')drdr'}{|r-r'|} + \int V_{ext}(r)\rho(r)dr +$$

$$E_{xc}[\rho(r)dr] + E_{ll}$$ \hspace{1cm} (2.8)

In equation (2.8) the first three terms correspond to the kinetic energy of non-interacting particles (electrons), the electron-electron interaction energy (Hartree energy) and the potential energy (external) due to the nuclei respectively. The fourth term is the exchange-correlation functional. The last term represents the interaction between the nuclei. The Eq. (2.8) can further be minimized and reduced to the following

$$\left[-\frac{1}{2} \nabla^2 + V_{eff}(r)\right] \psi_i(r) = E_i\psi_i(r)$$ \hspace{1cm} (2.9)

Where $\psi_i(r)$ represents the K-S orbitals instead of wave function and

$$V_{eff} = V_{Hartree} + V_{ext} + V_{xc}$$ \hspace{1cm} (2.10)
So, the energy of many body-problem can be evaluated exactly provided the exchange-correlation potential in Eq. (2.10) is known.

2.2 Exchange-correlation functionals:
The only unknown in Eq. (2.10) is the exchange-correlation functional term, which needs to be approximated in order to use Kohn-Sham equation for practical purposes.
Two extensively used approximations for this purpose are the Local Density Approximation (LDA) and the Generalized gradient approximation (GGA).

2.2.1 Local Density Approximation:
In this approximation the (homogenous) interacting electron gas has been used to approximate the exchange-correlation functional [31,32]. The exchange-correlation energy can be approximated as

$$E_{xc}^{LDA} = \int \rho(r) E_{xc}^{hom}(\rho(r)) dr$$  \hspace{1cm} (2.11)

Being simple and accurate, it has been used extensively and forms integral part of almost all the modern DFT codes. It works surprisingly well in systems where the charge density varies slowly. Though in some of the cases it proved to be very useful even in systems where charge density varies rapidly, but still the underestimation of lattice parameters, band gaps and the overestimations of cohesive and binding energies are some of its limitations [33].

2.2.2 Generalized Gradient Approximation:
In systems having rapidly varying or inhomogeneous electron density the exchange-correlation energy can be approximated in better way by considering both the density and the gradient of density. This approach of considering the gradient of density is called generalized gradient approximation (GGA) expressed as

$$E_{xc}^{GGA} = \int \rho(r) E_{xc}^{GGA}(\rho(r), \nabla \rho(r)) dr$$  \hspace{1cm} (2.12)

GGA approximation has been found useful to improve the accuracy while calculating certain physical quantities especially atomization energies, total energies and lattice parameters etc. The most commonly used GGA-functional are given by Becke, Perdew, Wang, Enzerhof etc. [34-37].

2.3 Projector Augmented Wave (PAW) Method:
Here we will describe briefly the PAW method. This is one of the most effective, accurate and efficient approaches including the features of ultra-soft pseudopotentials and augmented plane-wave while performing DFT in the electronic structure calculations treating all electrons with frozen core [38-
The different behavior of the electronic wave function in space is because of its variable distance from the nucleus (close or far from nucleus) in the bonding region. Due to the rapid oscillation of the wave function close to the nucleus and the uniform variation outside the atomic centered sphere, it could be separated into inside and outside the sphere. For rapid variations of the wave function inside the sphere the partial wave expansion and for uniform variation outside the atomic sphere plane waves or some other suitable methods can be considered for the description of electrons. But the derivatives of both the functions inside as well as outside the atomic centered sphere should be matched at the boundary of the sphere.

A linear transformation $T$, which is basis of the PAW methods, will transform the all electron wave function $\psi$ to a pseudo wave function $\tilde{\psi}$

$$|\psi\rangle = T|\tilde{\psi}\rangle.$$  \hspace{1cm} (2.13)

The all electron wave function and the pseudo wave function can further be expanded into the all electron partial (2.14) and pseudo partial waves (2.15) as following

$$|\psi\rangle = \sum_i c_i |\phi_i\rangle$$ \hspace{1cm} (2.14)

$$|\tilde{\psi}\rangle = \sum_i c_i |\tilde{\phi}_i\rangle$$ \hspace{1cm} (2.15)

In order to get the all electron partial wave $\phi_i$ one needs to solve the radial Schrodinger equation for the case of isolated atom. It would also be worth mentioning that the both the partial waves, the all electron partial wave and the pseudo partial wave will be same outside the augmented sphere that is

$$\phi_i = \tilde{\phi}_i$$

Here we define a projection function $\Pi_i$ that is orthonormal to the function $|\tilde{\phi}_i\rangle$ and satisfies the following relation

$$\langle \Pi_i | \tilde{\phi}_i \rangle = \delta_{ij}$$ \hspace{1cm} (2.16)

Hence the transformation operator $T$ defined in (2.13) will take the form

$$T = 1 + \sum_i \langle |\phi_i\rangle - |\tilde{\phi}_i\rangle \rangle$$ \hspace{1cm} (2.17)

So the all electron wave function given in (2.14) could also be represented as
\[ |\psi\rangle = |\tilde{\psi}\rangle + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle)\langle P_i|\tilde{\psi}\rangle \]  
\hspace{1cm} (2.18)

It should be noted that all the works presented in this thesis have employed the PAW method as implemented in Vienna-ab-initio simulation package (VASP) [41].

**2.4 Force Theorem:**
The force acting on an ion while performing DFT calculations are supposed to be zero or should reach a specified criteria in order to attain the exact ground state configuration. The term geometry optimization refers to the configuration where the positions of the ions as well the shape and volume of the cell is also converged. The Hellmana-Fynman theorem [42] can be used to calculate the force \( F \) acting on an ion at a position \( R \) by

\[ F = -\frac{\partial E}{\partial R} \]  
\hspace{1cm} (2.19)

The total energy of the system can be expressed as

\[ E = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \]  
\hspace{1cm} (2.20)

In Eq. (2.20) \( \psi \) represents the wave function and it needs to be to normalized, so the Eq. (2.19) will take the form

\[ F = -\left\langle \psi \left| \frac{\partial}{\partial R} \right| \psi \right\rangle - \left\langle \Psi \left| H \right| \Psi \right\rangle - \left\langle \Psi \left| H \left( \frac{\partial \Psi}{\partial R} \right) \right| \right\rangle \]  
\hspace{1cm} (2.21)

In case of exact ground state energy of the wave function we will have

\[ F = -\left\langle \psi \left| \frac{\partial H}{\partial R} \right| \psi \right\rangle \]  
\hspace{1cm} (2.22)

**2.5 Hybrid Functionals:**
Though both the LDA and GGA has been proved very useful approximations being implemented in DFT for the solution of many problems with reasonable accuracy. But, while calculating the energy gap of materials (molecules, solids) the use of GGA and LDA will not show the true picture due to the lack of accuracy of these approximations. In order to cope with this issue various techniques has been developed which includes DFT+U, hybrid functionals, GW approximations etc. [43-47]. Especially, the hybrid functional which correspond to the combination of exact nonlocal Hartree-Fock exchange and the local exchange-correlation functional has been tested and is found to be very useful to deal with band gap problems. The different
types of hybrid functionals are distinguished by the amount of exact energy exchange mixed with the energy functional. For example the PBE0 functional will take the form as

$$E_{X}^{PBE0} = \alpha E_{X}^{HF} + (1 - \alpha) E_{X}^{PBE} E_{C}^{PBE}$$  \hspace{1cm} (2.23)

The coefficient $\alpha$ is the mixing parameter which is set as $\alpha = \frac{1}{4}$

$$E_{X}^{PBE0} = \frac{1}{4} E_{X}^{HF} + \frac{3}{4} E_{X}^{PBE} + E_{C}^{PBE}$$  \hspace{1cm} (2.24)

The other useful functional of this family proposed by Heyd-Scuseria-Ernzerhof called HSE. In this functional the division of exchange interaction has been proposed in short-range (SR) and long-range part (LR). It is represented as

$$E_{X}^{HSE} = \alpha E_{X}^{HF,SR}(\mu) + (1 - \alpha) E_{X}^{PBE,SR}(\mu) + E_{X}^{PBE,LR}(\mu) + E_{C}^{PBE}$$  \hspace{1cm} (2.25)

In this thesis while studying the structural, electronic and thermodynamic properties of doped-MgH$_2$[48]. PBE0 has been proved more efficient in predicting the energy gap as compared to HSE.

**2.6 Molecular Dynamics:**

Molecular dynamics simulation (MD) is the fundamental technique to study the dynamical properties of materials at specific temperature in physics, chemistry, biology and material science. Thanks to the advances in theoretical methodologies and the computational facilities MD has advanced to great extent in recent years. It can be divided into two types namely classical molecular dynamics (CMD) and ab initio molecular dynamics (AIMD), both differ in obtaining the forces acting on atoms that is the basis of MD. The basics of CMD is the solution of Newton’s equation of motion

$$F_i = m_i a_i = m_i \ddot{r}_i$$  \hspace{1cm} (2.26)

for the calculation of forces by means of the generation of model potentials [49,50]. This method allows the treatment of large systems (large number of atoms) but at the cost of accuracy as CMD fails to account for incorporating the changes like charge transfer, breaking and formation of bonds etc. As for AIMD is concerned, here ab initio methods based on DFT is used to obtain the forces and the nuclei must obey the Eq. (2.26). This approach is more accurate as compared to CMD but it is computationally expensive, so cannot treat very large system. For AIMD we will have

$$F_i = -\nabla E_i = m_i \ddot{r}_i$$  \hspace{1cm} (2.27)
In present thesis, while investigating the stabilities of different designed nanostructures for hydrogen storage, we have employed the Born-Oppenheimer molecular dynamics simulations.
3 Hydrogen Storage Methodologies

This section of the thesis deals with the brief introduction of the importance of hydrogen as energy carrier, storage problem, conventional storage methods and their drawbacks. Later on a detailed discussion on the fundamental storage phenomenon of chemisorption and physisorption is also given. Results and findings on the improvement of the thermodynamics by means of catalyst mixing and applying mechanical strain on chemisorption system specifically MgH₂ has been reported. Apart from that the nanostructures with high surface area and hexagonal structure (hydrogenated graphene, boron nitride sheet, boron carbide sheet, silicane and silicene etc.) functionalized with light metals have been presented by describing the results of our studies.

3.1 Hydrogen: Importance and Storage Problem:
The rapid growth in the demands of energy due to industrialization of the world has threatened the depletion of current sources (fossil fuels) and the energy shortage in coming years. The deteriorating effect of the exhaust greenhouse gases (associated with fossil fuels) on the environment has endangered the living organism on earth as well. This situation urgently demands a cleaner, safer, and efficient alternate of the current energy sources [51,52]. The abundant availability, highest energy content, cleaner emission and renewability has made the hydrogen (H₂) a perfect choice as alternate energy carrier to substitute current sources with so many disadvantages [1]. Though H₂ is the most abundant element on earth but instead of free state it is found in the form of water or other compounds. So, the transition to the hydrogen economy depends on finding the suitable ways of producing hydrogen. The gaseous nature of H₂ with low volumetric density (0.09 kg/m³) and the unavailability of suitable and efficient storage media is another severe challenge denying the dream of hydrogen-based economy come true [53].

3.2 Conventional Storage Methods:
Physical storage of hydrogen usually comprises of two methods (i) the storage under pressure and (ii) storage by liquefaction. As mentioned above the small volumetric density of H₂ at ambient conditions makes it impossible for its use in mobile application unless a large volume is obtained. Thus, it is
necessary to compress the gas under huge pressure (35-70MPa) for having reasonable energy density in relatively small space. This demands the material of the container keeping H₂ gas strong enough to withstand the applied pressure and also making sure that no leakage is taking place. Alternately, by liquefying H₂ gas to a certain temperature (~20 K) one can also increase the volumetric density high enough to serve the purpose for mobile and other applications. But to achieve and then to maintain the liquid at such a low temperature requires great amount of energy. A special container with extremely secure insulation will also be needed to keep the cooling. Though both of these strategies look simple, straightforward and can be employed for the large-scale storage of H₂ but not convenient when it comes to small-scale storage. Safety and economy are the other issues related with these methodologies [54,55].

3.3 Solid-State Storage Mechanism:
As clear from the discussion in the previous section, the options of conventional storage of H₂ in pressurized containers or by liquefaction have many problems associated with them. Thus, an alternate route needs to be followed in order to store H₂ efficiently. One interesting choice is the materials based solid-state storage as H₂ can interact with various materials. This can help in achieving the on-board storage for mobile application with high packing density and operation at ambient conditions. However, there are certain requirements imposed on a storage material to be eligible for efficient storage of H₂. These are:

(i) Light weight to achieve high gravimetric density
(ii) Operation at ambient temperature and pressure
(iii) Reversibility
(iv) Safety
(v) Cost effectiveness
(vi) Fast kinetics

So the successful quest of such a suitable material fulfilling above-mentioned criteria can serve the purpose of an efficient H₂ storage and help in achieving hydrogen driven economy. Usually the materials based H₂ storage follow the two basic mechanisms termed as chemisorption and physisorption. The first one is the chemical absorption of atomic hydrogen forming chemical bonds whereas the second approach describes the interaction of molecular H₂ with the surface of the host materials without being dissociated [56]. Both of these mechanisms are described in detail in the following sections.
3.4 Hydrogen Storage by Chemisorption:

One of the important characteristics of hydrogen is its reaction with other elements forming various compounds, which are distinguished by the nature of bonds between the host materials and the hydrogen. Chemisorption is basically a chemical reaction between the host materials and the incident hydrogen (atomic). It obeys the following reaction

\[ M + \frac{4}{2} \text{H}_2 \leftrightarrow \text{MH}_A \]  \hspace{1cm} (3.1)

Where M represents the host material. When the surfaces of the host materials (metals) are exposed to hydrogen molecules (H\(_2\)), the molecules undergo the dissociation while approaching the surface into H atoms forming different types of bonds depending on the host materials. The dissociated H atoms can either stay on the surface of the host material or there is also a possibility of their penetration into the interstitial sites within the host materials forming various types of chemical hydrides [57]. In case of the interaction of hydrogen with light metals, (alkali and alkaline earth metals) ionic bonds are formed resulting into the light metal hydrides LiH, NaH, BeH\(_2\) and MgH\(_2\) etc. usually termed saline hydride [58-61]. If the non-metals and the transition metals are reacted with hydrogen, the hydrides formed will be covalent and metallic (or semiconductor) respectively. [62-65]. Some complex hydrides are also formed by the reaction of hydrogen and the elements of first three groups of the periodic table for example LiNH\(_2\), NaAlH\(_4\) etc. Though the chemisorption based hydrogen storage process would allow in achieving high storage capacity, but the thermodynamic issues (in case of light metal hydrides) make it difficult for ambient condition operation. In order to utilize the absorbed hydrogen in the fuel cell, a very high temperature/pressure needs to be applied for hydrogen desorption.

3.5 Dehydrogenation from Chemisorbed System (MgH\(_2\)):

In the previous section, a brief introduction of some chemisorbed systems has been discussed. Once these material systems absorb hydrogen and form stable hydrides, the most important thing after that is to know the desorption energy required to take out hydrogen and the temperature/pressure at which desorption would take place. It is also worth knowing about the various approaches for speeding up absorption/desorption process and how to improve the thermodynamics of the system for designing new promising hydrogen storage systems as well as for the betterment of the existing ones. Here, we will describe the results of our studies on one of the most prominent member of the saline hydride family, magnesium hydride (MgH\(_2\)), which has extensively been studied in the prospective of efficient hydrogen storage materials [66-70]. A reasonably high (7%) storage capacity, reversibility, and low cost
make MgH₂ an attractive candidate for on board hydrogen storage applications. However, prepared from the direct reaction of hydrogen with Mg atoms, MgH₂ has poor thermodynamics, which causes the absorption/desorption of hydrogen at as high as 300 °C.

Thus, the thermodynamics and reaction kinetics of MgH₂ needs to be improved in order to utilize it for practical purposes at moderate temperature. Countless experimental as well as theoretical studies have been done in this regard to cope with this issue. Experimentally the reaction kinetics can be improved with size reduction by mechanical alloying of Mg powder and exposed it with hydrogen. This would result into the formation of defected crystal structure that eventually improves kinetics. A significant improvement in the adsorption/desorption of MgH₂ has been noticed by nanostructuring with the help of ball milling [71]. The doping of various adatoms has also found to be helpful in the improvement of sorption properties of MgH₂. Light as well as transition metals have been investigated in this regard [72-74]. As far as theoretical studies are concerned many successful attempts have been made in destabilizing the MgH₂ with the help of various alloying elements including Al, Ti, Fe, Ni, Cu, Nb etc. that in turn can speed up the kinetics [75]. Apart from bulk MgH₂, the different surfaces (110) and (001), have also been investigated under the influence of alloying elements (Al, Ti, Mn, Ni,) by means of density functional theory (DFT) calculations. The preferential sites of the dopants and the mechanism of destabilization were reported in detail. [76,77]. A few years ago, the effects of Al and Si on the desorption properties and electronic structure of different phases α-MgH₂, β-MgH₂, γ-MgH₂ were performed by means of DFT [20,69]. Here we present the summarized results of our works on the improvement of thermodynamics of MgH₂ by various means.
3.5.1 Al and Si doped α-, γ- and β-MgH₂:

![Image of optimized structures](image)

Figure 3.1: The optimized structures of (a) α-MgH₂ (b) β-MgH₂ (c) γ-MgH₂ (d) Al-doped α-MgH₂ (e) Al-doped β-MgH₂ (f) Al-doped γ-MgH₂. Color scheme: Orange, green and red balls represent Mg, H and Al atoms respectively.

In paper I, we have performed a detailed study on α-, γ- and β-MgH₂ phases doped with Al and Si by using both generalized gradient approximation (GGA) and hybrid functionals (HSE06, PBE0) within the framework of density functional theory (DFT). The figure 3.1 shows the optimized structures of all the three phases in pure form and doped with Al. The calculations to investigate the structural, electronic and thermodynamic properties with the prospective of hydrogen storage efficiency of above-mentioned phases have been carried out by using plane-wave basis set. In a previous study [69] the improvement in the dehydrogenation of MgH₂ caused by the dopants were related with the reduction in the energy gaps of the system. The small energy gaps in the case of Al and Si dopant were not trust worthy as the use of GGA is known to underestimate the energy gap. The importance of accurate energy gap is evident from the fact that in metallic form, metal hydrides are good candidates for high-T_c superconductivity [78-79]. The use of hybrid Hartree-Fock functionals allow to overcome the underestimation of energy gaps as predicted by GGA-PBE in case of pure MgH₂ phases, while PBE0 has proved to be better than HSE06 and even GW approach. A supercell of
2×2×2 having 48 atoms (Mg=16, H=32) in the case of α-MgH\(_2\) where 96 atoms (Mg=32, H=64) in the case of both β-MgH\(_2\) and γ-MgH\(_2\) has been generated for this study. To study the effect of dopants (Al, Si) on the heat of adsorption of the doped systems, a doping concentration of 6.25% for α-MgH\(_2\) and 3.12% for β- and γ-MgH\(_2\) phases has been achieved by substituting one Mg atom by Al and Si atoms from these systems. The structural properties in terms of lattice parameters of the pure as well as the doped systems have been calculated with GGA-PBE, HSE06 and PBE0 functionals and the obtained results compared with the experimental values. Though for the pure systems, the GGA-PBE slightly underestimate the lattice parameters in case of α and γ phases and overestimate for β phase, but still provide better approximation as compared to the two hybrid functionals, which almost double the percentage error for all the phases. The lattice parameters and the cell volumes of the Al and Si doped α, γ and β phases calculated by GGA-PBE are slightly more than HSE06 and PBE0 but the difference in magnitude is not much and is in the range of 0.01-0.04 Å. It has also been observed that Al doping tend to decrease whereas the Si doping increase the lattice parameters and hence the cell volumes in case of doped systems at the given doping concentration as considered here. Al and Si doping also cause a slight variation in the arrangements (positions) of atoms and hence the corresponding Mg-Mg and Mg-H distances differ from the pure systems. In case of pure α-MgH\(_2\), the Mg-Mg and Mg-H bonds are found to be 3.514 Å and 1.935 Å respectively. Whereas, upon Al doping a significant increase in the above-mentioned distances has been observed in the vicinity of the dopants. The corresponding Mg-Mg and Mg-H bonds change to 3.536 Å and 1.956 Å respectively. To further study the effects of dopants on the electronic properties of the MgH\(_2\), the total and partial density of states of pure and the doped systems of α, γ and β phases have been plotted by GGA-PBE, PBE0 and HSE06. For reference the results in case of α-Mg\(_{15}\)H\(_{32}\)Al are shown in figure 3.2. After energy gap analysis it has been revealed that although an insulating behavior is evident for α, γ and β phases (in pure form) even with GGA-PBE, but still it underestimates the values to a large extent when compared with the previously measured experimental values. The use of hybrid functionals improves the band gap as expected with PBE0, resulting into the best values among all the functionals used. Metallic and semiconducting behaviors have been observed theoretically in case of Al and Si doping on α, γ and β phases of MgH\(_2\) respectively.
Figure 3.2: Total and partial density of states of $\alpha$-Mg$_{15}$H$_{32}$Al calculated by (a) GGA-PBE (b) PBE0 (c) HSE06. The Fermi level is set to zero.

The improvement in the band gap by PBE0 can also be seen in figure 3.3 where charge density distribution has been plotted in case of $\gamma$-Mg$_{32}$H$_{64}$, $\gamma$-Mg$_{31}$H$_{64}$Al and $\gamma$-Mg$_{31}$H$_{64}$Si on (001) plane. The localization of charge density in case of pure system describes the ionic bonding character while after Al and Si doping, covalent character is understood due to the broadening of the elliptical red and green region.
Finally, we have calculated the heat of adsorption $\Delta H_{\text{ads}}$ by using the following relation

$$(\Delta H_{\text{ads}})(M_{g_{1-a}H_2X_a}) = E_{\text{tot}}(M_{g_{1-a}H_2X_a}) - (1 - a)E_{\text{tot}}M_g - aE_{\text{tot}}(X) - E_{\text{tot}}(H_2)$$

(3.2)

In equation (3.2) $E_{\text{tot}}$ is the total energy. $X=\text{Al, Si}$ and ‘a’ represents the doping concentrations. For $\alpha$-MgH$_2$ $a=0$ and 0.0625 whereas for $\beta$-MgH$_2$ and $\gamma$-MgH$_2$ we have $a=0$ and 0.03125. In case of H$_2$ the total energy has been calculated by the constructing a cubic cell of 15Å parameters and performed ionic relaxation in contrast to all the other systems where geometry were optimized. The complete results of $\Delta H_{\text{ads}}$ for pure and doped $\alpha$, $\gamma$ and $\beta$ phases calculated by GGA-PBE, PBE0 and HSE06 have been presented in table 3.1. For comparison the previously measured values by theory and experiment has also been mentioned to have better understanding of the dopants effect in improving the thermodynamics of MgH$_2$. From table 3.1 it is clear that in pure form both $\alpha$- and $\gamma$-MgH$_2$ possesses almost same and slightly higher values of $\Delta H_{\text{ads}}$ than $\beta$-MgH$_2$, which indicates that both of these phases are more stable than the later phase. The doping of Al and Si reduces the stability of the all the systems and improve the decomposition effect by making the $\Delta H_{\text{ads}}$ less negative. The lowest value of $\Delta H_{\text{ads}}$ corresponding to the lowest dehydrogenation temperature has been obtained in case of Si-doped $\beta$-MgH$_2$ suggesting that Si could prove to be more efficient dopant as compared to Al.
Table 3.1: Heat of adsorption $\Delta H_{ads}$ of pure and Al- and Si-doped $\alpha$, $\gamma$ and $\beta$-MgH$_2$ calculated by GGA-PBE, HSE06 and PBE0 functional.

<table>
<thead>
<tr>
<th>System</th>
<th>Dop-</th>
<th>$\Delta H_{ads}$ (eV)</th>
<th>$\Delta H_{ads}$ (eV) (Previous)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ing %</td>
<td>GGA-PBE</td>
<td>PBE0</td>
</tr>
<tr>
<td>$\alpha$-Mg$<em>{16}$H$</em>{32}$</td>
<td>0</td>
<td>-0.577</td>
<td>-0.660</td>
</tr>
<tr>
<td>$\gamma$-Mg$<em>{32}$H$</em>{64}$</td>
<td>0</td>
<td>-0.576</td>
<td>-0.656</td>
</tr>
<tr>
<td>$\beta$-Mg$<em>{32}$H$</em>{64}$</td>
<td>0</td>
<td>-0.483</td>
<td>-0.562</td>
</tr>
<tr>
<td>$\alpha$-Mg$<em>{15}$H$</em>{32}$Al</td>
<td>6.25</td>
<td>-0.459</td>
<td>-0.509</td>
</tr>
<tr>
<td>$\gamma$-Mg$<em>{31}$H$</em>{64}$Al</td>
<td>3.125</td>
<td>-0.513</td>
<td>-0.575</td>
</tr>
<tr>
<td>$\beta$-Mg$<em>{31}$H$</em>{64}$Al</td>
<td>3.125</td>
<td>-0.424</td>
<td>-0.483</td>
</tr>
<tr>
<td>$\alpha$-Mg$<em>{15}$H$</em>{32}$Si</td>
<td>6.25</td>
<td>-0.409</td>
<td>-0.453</td>
</tr>
<tr>
<td>$\gamma$-Mg$<em>{31}$H$</em>{64}$Si</td>
<td>3.125</td>
<td>-0.492</td>
<td>-0.555</td>
</tr>
<tr>
<td>$\beta$-Mg$<em>{31}$H$</em>{64}$Si</td>
<td>3.125</td>
<td>-0.404</td>
<td>-0.463</td>
</tr>
</tbody>
</table>

3.5.2 Effect of Transition metals on MgH$_2$:

In the previous section we have described the promise of MgH$_2$ as efficient H$_2$ storage material and the methods to improve its kinetics and thermodynamics. Apart from the doping of light elements, MgH$_2$ was doped with transition metals to lower the absorbing/desorption temperatures $^{[83,84]}$. The Paper II, deals with the study of structural, electronic and thermodynamic properties of MgH$_2$ doped with selected set of transition metals. The TMs dopants considered here to substitute Mg in 1×1×3 supercell of MgH$_2$ includes Sc, Ni, V, Fe, Co, Cu, Y, Zr and Nb. The structural aspects have been studied in terms of lattice parameters and the equilibrium volume, which increase in case of Sc, Zr, Y and decrease for the rest of the dopants. This change also causes a slight rearrangement of atomic positions and alters the Mg-H bonds that ultimately affect the desorption properties. In order to determine the effect of TMs on the kinetics of MgH$_2$, adsorption energies ($E_{ads}$) for all the doped systems have been calculated. The improvement showed by all the dopants take the following trend Cu > Nb > Ni > V > Zr > Co > Sc > Y.
Here, Cu proved to be the best dopant causing 1/5\textsuperscript{th} reduction in $E_{\text{ads}}$ and Fe did not show any decrease. To study the electronic structures, the total and partial density of states of pure as well as doped system has been plotted. A large band gap indicating the insulating behavior of pure MgH$_2$ matches with the previous study [48]. For Cu doping the system behaves metallic where as significant band gaps of 1.87 eV, 2.0 eV and 3.25 eV have been observed in case of Nb, Ni and V doping respectively. A correlation between the electronic properties and the $E_{\text{ads}}$ has also been made in this study.

<table>
<thead>
<tr>
<th>System</th>
<th>$\Delta H_{\text{ads}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$<em>5$H$</em>{12}$Sc</td>
<td>-0.6449</td>
</tr>
<tr>
<td>Mg$<em>5$H$</em>{12}$V</td>
<td>-0.4193</td>
</tr>
<tr>
<td>Mg$<em>5$H$</em>{12}$Fe</td>
<td>-0.8656</td>
</tr>
<tr>
<td>Mg$<em>5$H$</em>{12}$Co</td>
<td>-0.6419</td>
</tr>
<tr>
<td>Mg$<em>5$H$</em>{12}$Ni</td>
<td>-0.3979</td>
</tr>
<tr>
<td>Mg$<em>5$H$</em>{12}$Cu</td>
<td>-0.1431</td>
</tr>
<tr>
<td>Mg$<em>5$H$</em>{12}$Y</td>
<td>-0.6535</td>
</tr>
<tr>
<td>Mg$<em>5$H$</em>{12}$Zr</td>
<td>-0.4801</td>
</tr>
<tr>
<td>Mg$<em>5$H$</em>{12}$Nb</td>
<td>-0.3207</td>
</tr>
</tbody>
</table>

Table 3.3: The heat of adsorption $\Delta H_{\text{ads}}$ (eV/H$_2$) of TM doped MgH$_2$ systems calculated by PBE0 functional.
3.5.3 Strain and doping effects on MgH$_2$ Surface:

A number of the studies investigating the adsorption and desorption kinetics of MgH$_2$ have been carried out on bulk phases as compared to the nanostructures and surfaces, which are relatively less explored. The preferential site and the influence of the selected dopants (Al, Ti, Ni, Mn) on the desorption properties of MgH$_2$ (001) and (110) surfaces have been studied by mean of first principles calculation [76,77]. The mechanism of the destabilization that results into the improvement of adsorption/desorption of hydrogen has also been presented in detail. The effect of transition metals (Ti, Fe) on the hydrogen enthalpies from the semi-infinite MgH$_2$ (110) surface and nanocluster has been reported by both DFT and simulated annealing [82]. Similarly, few other surface studies of MgH$_2$ reports the attempts made to improve the kinetics and thermodynamics by destabilizing the system upon doping of different adatoms. We have employed here a unique strategy, which is the application of mechanical strain on MgH$_2$ surface in order to reduce its stability and hence improve the kinetics. In paper III we have applied biaxial mechanical strain symmetrically on MgH$_2$ (001) whereas in paper IV the MgH$_2$ (110) has been subjected to a uniaxial mechanical strain. The corresponding
effects of strain on the dehydrogenation energies (ΔH) of pure and doped systems have been investigated. The crystal structure of MgH₂ with tetragonal symmetry having lattice constant (a = b = 4.501Å and c = 3.04 Å) and supercell of appropriate size (four layers) with vacuum space of 18 Å along Z-direction has been used in both the studies of paper III and paper IV. The energy needed to take out H atom from the intrinsic MgH₂, termed as dehydrogenation energy (ΔH) has been calculated as

\[ \Delta H = \left\{ E\left( M_{g16}H_{32-n} \right) + \frac{n}{2} E(H_2) \right\} - E\left( M_{g16}H_{32} \right) \]  

(3.3)

In eq. (3.3) ‘n’ denotes the number of H atoms. The energy of M_{g16}H_{32-n} has been approximated by taking one H atom out of the optimized structure of M_{g16}H_{32} without relaxing the geometry and the coordinates. We have calculated the energy of H₂ by putting it in a box of 15×15×15. Along with considering the strain effects, we have also studied the doping and their combined effects on MgH₂ (001) and MgH₂ (110) surfaces. The value of ΔH for both the systems in pure form has been calculated and found to be 1.500 eV and 1.700 eV respectively. In case of MgH₂ (001) we apply a homogenous biaxial strain symmetrically in equal intervals within the elastic limits. It has been revealed that the system can withstand a maximum strain of 7.5% along (XY) direction. For MgH₂ (110) instead of biaxial strain, we restrict ourselves to a maximum of 7.5% uniaxial strain along X or Y-direction due to the anisotropy of orthorhombic cell. A significant decrease in ΔH measured in both the systems has been thought to be the result of elongation of Mg-H bond under the application of strain. The substitution of Mg by selected dopants (Al, Si, Ti) with doping concentration of 6.25% also help in improving the ΔH. However the most significant effect in the reduction of ΔH has been observed when a mechanical strain of 7.5% applied on Al, Si and Ti doped MgH₂ (001) and (110) surface. The corresponding values of ΔH against applied strain are shown in the table 3.2 for MgH₂ (001). The value of ΔH reduces from 1.500 eV to 0.707 eV for Al-doped MgH₂ (001) and 1.700 eV to 1.160 eV in case of Al-doped MgH₂ (110). Apart from Al, the Ti and Si have also proved useful in improving the kinetics under strain.
<table>
<thead>
<tr>
<th>System</th>
<th>Applied Strain (%)</th>
<th>Dehydrogenation energy $\Delta H$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.5</td>
<td>0.871</td>
</tr>
<tr>
<td>MgH$_2$-Al</td>
<td>5.0</td>
<td>0.796</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>0.707</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>1.337</td>
</tr>
<tr>
<td>MgH$_2$-Si</td>
<td>5.0</td>
<td>1.330</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>1.229</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>1.217</td>
</tr>
<tr>
<td>MgH$_2$-Ti</td>
<td>5.0</td>
<td>1.818</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>0.962</td>
</tr>
</tbody>
</table>

Table 3.2: Effect of biaxial symmetric strain on dehydrogenations energies of Al, Si and Ti doped MgH$_2$ (001) surface.

Figure 3.5: The optimized structures of (a) Pure MgH$_2$ (001) surface and (b) Ti-doped MgH$_2$ (001) Color scheme: Orange, green and blue balls represent Mg, H and Ti atoms respectively.
4 Hydrogen Storage by Physisorption

4.1 Introduction:
This section deals with the adsorption of H₂ retaining its molecular form without being dissociated to surface of materials. This phenomenon of physical adsorption having no chemical bonds involved and with small binding strength is termed as Physisorption. During the mechanism of physisorption, the H₂ molecule adsorb to the surface of the host material by a weak interaction (van der Waal’s) usually of small value ~10kJ/mol. For the prospective of H₂ storage, the weak interacting forces between H₂ and the host material’s surface would help in achieve a fast absorption/desorption and hence improve the kinetics that lacks in chemisorption. As physisorption takes place in materials with large surface area, thus a high H₂ storage capacity can also be achieved. Reversibility is another advantage associated with this mechanism. But on the other hand too weak interaction in chemisorption somehow makes it difficult for H₂ molecules to remain adsorbed with the surface, as little energy is needed to dislodge them from the surface. In order to deal with it, the system needs to be maintained low temperature and high pressure since high temperature and low-pressure causes desorption of H₂.

4.2 Hydrogen adsorption in high surface area materials:
Fast adsorption/desorption kinetics, safe operation at ambient conditions and high storage capacity are the key requirements for an ideal H₂ storage system. Materials with large surface area especially, carbon nanotubes, nanoribbons, fullerenes, metals-organic framework, zeolite, graphene, graphane, BN-sheet etc. have been found very promising for adsorbing high quantity of H₂ under physisorption mechanism. These materials have been extensively investigated in connection to H₂ storage in the literature [85-96]. An experimental investigation on single-walled carbon nanotubes yields a reasonably high H₂ storage capacity of more than 8wt% at feasible conditions of temperature and pressure [97]. Recently the adsorption/desorption mechanism of H₂ in titanium-doped graphene has been studied experimentally showing that desorption occurs between 400-700 K [98]. Likewise, there are many theoretical studies [90-95] based on carbon-based nanostructures in context to H₂ storage. However, one of the major shortcomings of above-mentioned nanostructures (carbon-based) is their weak binding strength with H₂ in pristine forms, which restricts their operation at ambient conditions. Thus, the onboard applications of these H₂ storage systems depend on searching for
the ways of enhancing the H₂ adsorption energies with the substrates. For this purpose various strategies like creating defects, applying electric field, doping with foreign adatoms etc. have been employed. In the following sections we will present the summarized results of our studies included in this thesis on hydrogenated graphene, silicene, silicane, BN-sheet and boron carbide sheet functionalized with different adatoms/compounds as promising H₂ storage systems.

4.2.1 Alkali and Alkaline Metal-doped Graphane:
Graphene, a chemically active atomic layer of carbon atoms has been one of the most fascinating and extensively studied materials in recent times, finding its promise in large number of fields including H₂ storage [99]. The complete hydrogen of graphene would result into another promising materials named hydrogenated graphene or graphane (CH) with different electronic properties than graphene [100-101]. Graphane is a crumpled insulating material unlike planer conducting graphene. As described in the previous section, about the weak interaction of carbon-based nanostructures with H₂ (in pristine form) can be enhanced by the doping them with suitable dopants. There exist various dopants (atoms. molecules, radicals etc.) for the decoration of nanostructures with alkali, alkaline earth and transition metals being the most common ones.

In papers V and VI, we have employed the DFT to investigate the electronic, structural and H₂ storage properties of lithium (Li) and calcium (Ca) functionalized graphane respectively. While performing the calculations for adsorption energies, along with LDA and GGA functionals, we have also taken into the account van der Waal’s correction for the better description of these weakly interacting systems. Here, the light metal adatoms (Li, Ca) have been used to functionalize graphane (CH) structure in order to attain strong metal-substrate binding. The choice of light metals for doping is due to their much smaller cohesive energies (-2eV ≤ E_{coh.} ≤ -1 eV) to avoid clustering in contrast to those of transition metals, which tend to form clusters at high doping concentrations instead of binding strongly to the substrate. Strong metal-substrate binding would allow uniform distribution of adatoms over the substrate that is highly desirable for an efficient H₂ storage material. The substitution of few H atoms by Li/Ca in CH results in the CHLi and CHCa structures, which are the starting materials for studying H₂ storage properties. We have calculated the binding energies (E_b) of adatoms (Li, Ca) on CH sheet and found to be much higher than their corresponding cohesive energies [E_b = 2.94 eV (Li), 2.4 eV (Ca)]. MD simulations have further confirmed the stability of the doped system. As both of these metal adatoms directly bonded to C atoms of CH, hence due to difference of electronegativities of Li/Ca and C, a transfer of charge would take place from the adatoms to the CH sheet. So, a fractional (+ve) charge appeared on both Li/Ca, which resulted the cationic Li⁺/Ca⁺. The doping of adatom has also converted the
insulating CH to metallic CHLi and CHCa structures as shown in the total and partial density of states plots in case of CHCa in fig.4.1.

Finally the H₂ uptake of both CHLi and CHCa has been studied by adsorbing H₂ around Li⁺/Ca⁺ in stepwise manner. For a maximum coverage, it should be preferred to introduce H₂ around each dopant vertically, maintaining a sufficient distance from the other adsorbed H₂ molecules. The following relation has calculated the adsorption energies of H₂ molecules

\[ E_{ads} = E(CH:X + nH₂) - E(CH:X + (n - 1)H₂) - E(H₂) \]  

(4.1)

In eq. (4.1), first two terms represent the total energies of CHLi/CHCa adsorbed with n and (n-1) H₂ molecules. Here X=Li, Ca and ‘n’ indicate the number of H₂ adsorbed. E (H₂) is the total energy of the H₂ molecule computed by putting the molecule in a 10×10×10 supercell. It has been revealed that 4H₂ and 5H₂ molecules can be accommodated around each Li and Ca adatoms respectively, thus reaching a storage capacity that fulfills the targets of DOE. The adsorption energies in both cases fall into the desired window for the practical applications.
4.2.2 Strain Induced Li Decorated Graphene

The optimal functionality and efficiency of metal-doped nanostructures (with high doping concentration) as H\(_2\) storage medium depends on the strong metal binding to the substrate. It has been observed that in these systems the binding energy of the dopants vary inversely with their doping concentrations, that is, the higher the doping concentration the lower the binding energy [102]. Hence to achieve high H\(_2\) storage capacity by employing small supercell of metal-doped nanostructure, the metal-substrate binding needs to be improved in order to nullify the clustering effects. One way of doing this is the substitution of some foreign atoms like boron [103]. A relatively different strategy for increasing the binding of dopants on nanostructures (graphene) is the application of strain. It has already been reported experimentally that more than 15% of strain can be induced to the graphene without distorting the structure [104]. Even the elastic properties and the variation of band gap of graphene (CH) under strain have been studied [105].

In Paper VII, we have investigated H\(_2\) storage properties and the enhancement in the binding strength (E\(_b\)) of Li adatoms on CH sheet under the application of mechanical strain. The current study performed on a relatively smaller supercell with two Li atoms substituting H atoms in CH resulting into a higher doping concentration of 25%. We have considered uniaxial, biaxial, symmetric and asymmetric mechanical strain up to 10% (within the elastic limits) on CH geometry. It has been observed that a biaxial strain of
(X=7.5%, Y=10%) has improved $E_b$ 38% of its value without strain. In case of rectangular CH structure, applied strain has yielded $E_b$ of 2.48eV, which is 52% higher than Li’s bulk cohesive energy. The variation in $E_b$ of Li in CHLi ($C_8H_6Li_2$) with applied strain has been shown in figure 4.3.

![Figure 4.3: Binding energies of Li atom in the hexagonal CHLi cell under strain calculated by LDA, GGA, and van der Waal’s induced calculations.](image)

The high value of $E_b$ indicates the stability of CHLi, which has further been confirmed by MD simulations at 400 K. Finally, we have studied the $H_2$ storage capacity of CHLi and found that each Li atom would bind a maximum of four $H_2$ molecules attaining a storage of 12.12wt%. The average $H_2$ adsorption energies lie within the range of 0.15eV-0.20 eV, which are suitable for the practical applications as depicted earlier.

### 4.2.3 Metal Functionalized Silicene and Silicane:

Despite having unique and outstanding properties in various technological fields, graphene and its derivatives like graphane have certain limitations in large-scale production and compatibility with current electronics. Considering these issues, a two-dimensional structure of silicon, called silicene have been isolated experimentally from CaSi$_2$ [106-107]. Silicene having gapless structure with zero mass Dirac fermions mimic it to the graphene [108,109]. Just as the transformation of graphene to graphane upon the complete hydrogenation, the silicene sheet has also shown the similar characteristics. Thus, the complete hydrogenation of silicene will give rise to another fascinating material called silicane (SiH), very different from silicene structurally and
electronically [110]. The hydrogenation would result in the opening of energy gap and caused the metallic silicene into a wide gap semiconducting silicane. Both silicene and silicane has found it promise in many technological fields especially in silicon-based nanotechnology.

In papers VIII and IX, we have studied the promise of silicene and silicane doped with alkali and alkaline earth metals as efficient H2 storage materials. The metal dopants considered here for the functionalization of silicene and silicane in order to increase their interaction with H2 includes (Li, Na, K, Be, Mg, Ca). As described earlier that the strong binding of metal adatoms over the substrate ensuring uniform distribution is of fundamental importance while designing H2 storage materials. The calculation of binding energies of dopant to the sheet has revealed that alkali metals bind more strongly with both silicene and silicane as compared to the other elements.

MD simulations have also confirmed the stability of the dopants (Li, Na) on both the sheets. Figure 4.4 described the electronic properties of pure as well as metals (Li, Na) doped SiH by means of total and partial density of states.
The mechanism of hydrogenation is similar as that of metal-doped graphane. Each dopant can accommodate 5H₂ and 4H₂ molecules in case of metal-doped silicene and silicane respectively yielding a storage capacity fulfilling DOE targets.
Figure 4.5. The average adsorption energies of H2 molecules on SiLi and SiNa calculated by LDA, GGA and van der Waal’s corrected functionals.
Figure 4.6: The side and top view of the relaxed structures (van der Waals corrected) of (a) SiH, (b) SiHLi, (c) CHLi+nH$_2$, (d) SiHNa, and (e) SiHNa+nH$_2$. Color scheme: Blue, red, green and yellow balls represent silicon, hydrogen, lithium and sodium atoms respectively.

4.3 Polylithiated Functionalized Nanostructures:
Apart from functionalizing the above-mentioned nanostructures (graphane, silicene, silicane) with isolated light metal dopants, there exist another class of dopants for the adsorption of hydrogen molecules under physisorption mechanism. These species contain high densities of lithium (Li) atoms and therefore termed as polylithiated molecules. Being lightweight and the ability to form strong binding with the nanostructured substrate, Li has been considered as a prominent dopant, which could result a high storage capacity by adsorbing large number of H$_2$ molecules. Hence large density of Li in polylithiated molecules made them of significant importance for the potential H$_2$ storage materials. These species can further be classified into two types, C and O based. Some of the representative members of the polylithiated group are OLi, OLi$_2$, OLi$_3$, CLi$_3$, CLi$_4$, CLi$_5$, and CLi$_6$ etc. Many of them have already been investigated both theoretically and experimentally [111-114]. In the following sections we will briefly present the summarized results of our studies of different polylithiated species functionalized on graphane, boron-nitride and boron carbide sheets.
4.3.1 Polylithiated Doped Graphane (CH):
In the pursuit of suitable material for H₂ storage, the efficient nanostructures capable of attaining high H₂ gravimetric density has been considered to be of great significance. However the weak adsorption energies of H₂ with the nanostructures in their pristine form remain a point of concern, restricting their application at ambient conditions. The functionalizing of nanostructures (graphane, silicene, silicane) with light metal adatoms as described in papers V to IX would enhance the H₂ interaction with the metal dopants. The storage capacity can further be enhanced by functionalization of polylithiated species (OLi₂, CLi₃, CLi₄) instead of isolated metal atoms. In paper X and XI we have employed DFT studies for studying the electronic structure, stability and H₂ storage capacities of graphane. Similar to the case of Ca doped graphane in paper VI, few H atoms in graphane sheet has been substituted with OLi₂ (paper X) and CLi₃, CLi₄ (paper XI). In polylithiated molecules considered here, the strong polar nature of C-Li and O-Li would allow a considerable positive charge on Li (Li⁺), which is highly desirable for the adsorption of H₂ molecules. Though OLi₂, CLi₃ and CLi₄ are stable and capable of adsorbing large number of H₂ molecules, which leads to very high gravimetric density, but to ensure the reversibility and to minimize the clustering effect of these species one needs to bind them to a substrate with sufficient binding strength. To achieve this strong dopant-substrate binding, a defected CH sheet has been investigated as a substrate for these lithiated structures. The stability of all polylithiated functionalized CH structures (CH-OLi₂, CH-CLi₃, CH-CLi₄) has been studied by means of binding energy (Eₜ) calculation and further confirmed by MD simulations. The calculated values of Eₜ for OLi₂, CLi₃ and CLi₄ on CH sheet are 2.60 eV, 3.24 eV and 2.04 eV respectively. These numbers are large enough to indicate the stability and ensure uniform distribution of adsorbets on CH without clustering. For the further confirmation of the stability of these lithiated functionalized CH, we have performed MD simulations at 400 K by considering a larger supercell of CH with two CLi₃ species on either side of the sheet. The structure remained intact even after 4 ps. The MD result is shown in figure 4.7.
The difference in electronegativities of C, O and Li would allow Li to accumulate a significant (+ve) charge by donating its charge to C and O in OLi$_2$, CLi$_3$ and CLi$_4$. Thus the cationic (Li$^+$) in each lithiated specie can adsorb the approaching H$_2$ molecules by electrostatic interactions. It has been observed that a large number of H$_2$ molecules adsorbed on these functional nanostructures resulted into a very high storage capacity. The optimized structures showing the adsorption of H$_2$ on CH-OLi$_2$ with a storage capacity of 12.90 wt% is given in figure 4.8.
Similarly, the CLi3 and CLi4 doped CH also resulted into a storage capacity more than twice as the DOE targets with adsorption energies suitable for the practical applications. The results of adsorption energies and H-H bond lengths of adsorbed H2 molecules in case of CLi3 functionalized CH resulting a maximum storage of 13.87wt% has been presented in table 4.1.
<table>
<thead>
<tr>
<th>No. of H₂</th>
<th>Adsorption energy E_{ads} (eV)</th>
<th>H-H bond ∆d (Å)</th>
<th>Storage capacity (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>LDA 0.338 0.270</td>
<td>LDA 0.810 0.770</td>
<td>3.88</td>
</tr>
<tr>
<td>6</td>
<td>vdW 0.330 0.259</td>
<td>vdW 0.807 0.780</td>
<td>7.45</td>
</tr>
<tr>
<td>12</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1: Number of H₂ molecules adsorbed (N), Adsorption energy (E_{ads}), Average H-H bond length ∆d and H₂ storage capacity of CLi₃ doped CH.

### 4.4 H₂ Storage using Boron Nitride and Boron Carbide Sheets:

The importance of nanostructures with high surface area in context to H₂ storage has been described in detail in the previous sections. The purpose of metal functionalization to them and the enhanced efficiencies of H₂ adsorption have also been presented by considering the examples of graphane, silicene and silicane. In this section we will describe the summarized results of our studies on the stability of polylithiated species OLi₂ and CLi₃ over boron nitride and boron carbide sheet and their corresponding H₂ storage efficiencies. In paper XII and XIII the structural analysis, stability, bonding mechanism, electronic properties and H₂ storage capabilities of polylithiated molecules doped BN-sheet and BC₃ has been studied respectively. Two-dimensional hexagonal BN structure exhibiting insulating behavior could replace to its analogous graphene in many field due to its unique features. Much higher thermal stability as compared to carbon-based materials enables them to withstand a temperature of 1273 K [115]. Apart from other technological fields BN nanostructures have also been a subject of various studies for H₂ storage [116-118]. By means of first principles calculations, we have investigated the adsorption site, binding strength and storage capacity of OLi₂ and CLi₃ on h-BN sheet. First the most stable configuration yielding highest binding energies of adsorbets to the sheet is found. It is observed that the OLi₂ molecule binds strongly on B-top of h-BN whereas in case of CLi₃ an N atom in BN has been substituted with C atoms to form BNC structure. So, BNC-CLi₃ would give the higher value of binding energy as compared to all the other configurations.
Figure 4.9: Isosurface of the differential charge density of (a) BNC-CLi$_3$ and (b) BN-OLi$_2$. Cyan and the yellow colors indicate the accumulations and depletion of charge respectively.

The accumulation of partial positive charge on Li in both BN-OLi$_2$ and BNC-CLi$_3$ and the mechanism of hydrogenation can be understood similarly to the case of polylithiated-functionalized graphane, as explained in previous section. It has been observed that each Li$^+$ cation can adsorb 4H$_2$ in BN-OLi$_2$ and 3H$_2$ molecules in case of BNC-CLi$_3$ resulting a sufficiently high storage capacity of 6.11 wt% and 6.80 wt% respectively.
Table 4.2: Adsorption energies $E_{\text{ads}}$, and wt% of H$_2$ molecules adsorbed on CLi$_3$ functionalized C-doped BN-sheet, calculated by LDA, GGA and Van der Waal’s corrected GGA.

<table>
<thead>
<tr>
<th>No. of H$_2$</th>
<th>Adsorption energies ($E_{\text{ads}}$) eV</th>
<th>H$_2$ capacity (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LDA</td>
<td>GGA</td>
</tr>
<tr>
<td>3</td>
<td>0.533</td>
<td>0.146</td>
</tr>
<tr>
<td>6</td>
<td>0.450</td>
<td>0.101</td>
</tr>
<tr>
<td>9</td>
<td>0.264</td>
<td>0.089</td>
</tr>
</tbody>
</table>

There are many two-dimensional structures being characterized in recent years for various novel technological applications [119-120]. Boron carbide BC$_3$ is another interesting layered material with graphite like structure formed by the reacting benzene with the trichloride. The mono sheets of BC$_3$ have also been isolated [121].

![Figure 4.10: Optimized structure of hexagonal BC$_3$ monolayer sheet (Dotted rhombus indicates the primitive cell)](image)

Though the boron-carbide cages and nanotubes were studied for H$_2$ storage in the past, but the monolayer of BC$_3$ has not been functionalized with poly-lithiated specie (CLi$_3$) [122-123]. In paper XIII we have introduced two CLi$_3$ molecules on either side of 2$\times$2$\times$1 supercell of BC$_3$ and investigated the binding strength of the decorated structure. A very high binding energy of 5.08 eV per lithiated molecule indicates the stable 2CLi$_3$-B$_8$C$_{24}$ configurations, which has further been verified by MD simulations. The electronic
properties have been studied by means of density of states of pure and lithiated BC$_3$. A semiconducting behavior in case of pure BC$_3$ sheet is observed with GGA with a band gap of 0.54 eV. However upon CLi$_3$ doping, the structure turns from semiconducting to metallic as CLi$_3$ molecules donates its electron to the BC$_3$ sheet.

Figure 4.11: Optimized structure of BC$_3$ monolayer sheet decorated by CLi$_3$ on both sides:(a) top view, and (b) side view.

After doing a careful charge analysis it is observed that the Li atoms attach to CLi$_3$ donates almost all of their charge to C due to difference of electronegativities between Li and C, which accumulates as much as 0.89 of the positive charge on each Li. These Li$^+$ would induce polarization on H$_2$ molecules and adsorb them by weak van der Waal’s interaction and Coulomb’s attractive forces. The H$_2$ molecules have been introduced around Li$^+$ in stepwise manner and after the introduction of each H$_2$ molecules, we performed a complete structural relaxation. Following relation can calculate the adsorption energies of H$_2$ on BC$_3$-CLi$_3$

$$E_{ads} = \left[ \langle E(B_8C_{24} + 2CLi_3 + nH_2) \rangle - \langle E(B_8C_{24} + 2CLi_3) \rangle - nH_2 \right]/n \quad (4.2)$$

Along with GGA functional the adsorption energies of H$_2$ have also been calculated by means of van der Waal’s corrected GGA for the better description. At the most 4H$_2$ molecules could be adsorbed on each Li in case of CLi$_3$ functionalized BC$_3$ resulting into a storage capacity of 9.83wt%. The calculated adsorption energies are considered to be reasonable for reversible adsorption/desorption of H$_2$ at ambient conditions. Hence we conclude that the polylithiated functionalized boron-carbide sheet is promising material for efficient hydrogen storage.
Figure 4.12: The calculated average adsorption energies of H$_2$ molecules on polylithiated BC$_3$ monolayer by GGA and GGA+vdW methods (the relaxed structures of H$_2$ molecules physisorbed on polylithiated BC$_3$ sheet are provided in the in set.)
In the present thesis, first principles calculations based on DFT have been extensively employed to study the hydrogen storage properties of various materials. The systems under investigations storing hydrogen by chemisorption and physisorption mechanism include metal hydride (MgH₂), high surface area two-dimensional materials like graphane, silicene, silicane, BN-sheets, BC₃ sheets etc.

We have investigated the H₂ storage properties of MgH₂ and adopted various approaches to improve the adsorption/desorption mechanism for operation at feasible conditions. The structural, electronic and thermodynamic properties of pure as well as Al and Si-doped α-, γ- and β-MgH₂ phases have been reported with context to hydrogen storage. The use of hybrid functionals HSE06 and PBE0 not only presented good description of energy gaps and structural parameters but also yielded better heat of adsorption as compared to GGA. The dopants used proved helpful in improving the thermodynamics of the system. We have also employed PBE0 functional to study the effect of selected transition metals (Sc, V, Mn, Fe, Co, Ni, Cu, Y, Zr, Nb) on the desorption energies of α-MgH₂. The calculations revealed that except Fe all the dopants improve the thermodynamics of MgH₂ with Cu, Nb, Ni and V emerged as the most promising ones as compared to the others.

A systematic investigation has been performed to analyze the dehydrogenation energies of MgH₂ (001) and (110) surfaces under the application of mechanical strain, doping of Al, Si and Ti and their combined effect. The reduction in dehydrogenation energies was thought to be the result of destabilization in MgH₂ surfaces caused by the concerted action of doping and strain. Al doping coupled with a maximum of 7.5% mechanical strain reduced dehydrogenation energy the most.

On the other hand, two-dimensional nanostructures with high surface area and capable of adsorbing molecular hydrogen (H₂) through physisorption mechanism have also been explored thoroughly. The weak interaction of H₂ with these nanostructures in pristine form is greatly enhanced by metal functionalization. Light metal adatoms have been considered to dope graphane; silicene and silicane nanostructures for the efficient storage of H₂ with adsorption energies lie in range of practical applications.

The choice of light metals as dopant over the nanostructures result into a strong metals-substrate binding which is highly desirable for uniform distribution of dopants minimizing the clustering effect that reduces the storage
capacity. We have also observed that the 10% of mechanical strain has increased 52% of Li-graphane binding with respect to its bulk’s value resulting into a very high storage capacity of 12.12wt%.

Finally, we have studied the H₂ storage properties of special class of species having higher densities of Li atoms termed as polyliithiated molecules. To ensure reversibility and avoid clustering these species (OLi₂, CLi₃, CLi₄) have been functionalized over different substrates like graphane, BN-Sheet and BC₃ sheet. Strong polar nature of both O-Li and C-Li bonds would cause the electric charge to transfer from Li to O and C, resulting a sufficient positive charge on Li in these species. These cationic Li⁺ polarize the approaching H₂ and adsorb them through van der Waal’s and electrostatic interactions. We have observed that these species resulted into a very H₂ high storage capacity with adsorption fall into the window of practical applications.
Efterfrågan på energi i världen öka exponentiellt samtidigt som de ödesdigra effekterna av nuvarande fossila bränslen har tvingat oss att minska beroendet av dessa, och istället hitta renare, billigare och förnybara alternativ. Väte finns i rikliga mängder, samtidigt som det är rent, effektivt och förnybart och kan därför föras fram som en av de bästa ersättarna för de sinnande och skadliga fossila bränslena. Men förändringen mot en väte-baserad ekonomi hindras av saknaden att på ett passande sätt att lagra vätet. I motsats till värets höga energinnehåll per massa, så är densiteten av väte endast 0.09 kg/m³ eftersom det är en gas, vilket gör det väldigt svårt att lagra stora mängder väte i en liten volym. Vanligtvis för att lagra väte används två olika angreppssätt (i) lagring under tryck eller (ii) lagring genom konvertering till vätska. Dock innehåller båda dessa metoder flertalet nackdelar och är därför olämpliga. I den första metoden sätts väte-gasen under ett tryck på hundra-tals (700) bar för att komprimera den till en densitet av 42 kg/m³ i motsats till de 0.09 kg/m³ den har under normaltryck. I den andra metoden krävs kryogeniska temperaturer av ett fåtal Kelvin för att vänet ska kondensera till vätska vid normaltryck. För att nå en väte-densitet på 70 kg/m³ behöver temperaturen vara så låg som -253 grader Celsius. För att undvika dessa nackdelar kan istället lagring i material i fast tillstånd vara ett intressant och fungerande alternativ.

I den här avhandlingen används första princips beräkningar baserade på tätethetsfunktionalteori för att studera vätelagringsegenskaper hos olika material. De undersökta systemen är bland annat metallhydrider (MgH₂) och två-dimensionella material med stor yt-area (graphane, silicene, silicane, BN-flak, BC₃-flak, etc.) där lagring av väte antigen sker genom kemisk eller fysisk adsorption. Tack vare den höga lagringskapaciteten, tillgängligheten samt den låga kostnaden anses metallhydriden (MgH₂) som ett lovande alternativ för vätelagring. Dock har även de en nackdel då vänet binder väldigt starkt i dem under kemisk adsorption vilket gör dem olämpliga att använda under normalt tryck och temperatur. Olika strategier har använts för att förbättra de termodynamiska egenskaperna vid adsorption bland annat genom att dopa olika faser av metallhydriden med lätt- och övergångs-metaller. Energin som krävs för att lösgöra vänet kan påverkas genom mekanisk påfrestning tillsammans med dopning av MgH₂ (001) och (100) ytorna med Al, Si och Ti vilket i slutändan förbättrar temperaturerna för adsorption. Minskningen i energin för att lösgöra vänet resulterar från destabilisering av MgH₂.
ytan orsakad av samordnade effekter från dopningen och deformationen. Dopning med Al tillsammans med en maximal deformation av 7.5 % från mekaniska påfrestningar gav den största minskningen i energin för att lös-göra vätet.

Fortsättningsvis, har även två-dimensionella nanomaterial med stor yta-areal som med hjälp av fysisk adsorption kan binda väte i molekylär form (H₂) utforskats. För nanostrukturerna i dess orörda form är växelverkan med H₂ svag men den kan förstärkas genom funktionalisering med metaller. Undersökningar med lättmetall-atomer dopade på ytan av graphane, silicene and silicane har visat att de ger adsorptionsenergier inom gränsen för praktiska tillämpningar. Valet att dopa nanostrukturerna med lättmetall atomer resulterar i en stark metal-substrat bindning som är viktigt för att få en uniform fördelning av dop-atomer över ytan, och minimera klustrings-effekter som reducerar lagringskapaciteten. Resultaten visar också att en deformation med 10 % ökar Li-graphane bindningen med 52 % jämfört med den orörda vilket ger en mycket hög lagringskapacitet på 12.12 vikt-%.

Till sist har vi studerat vätelagringsegenskaper för en speciell klass av material som har högre densitet av Li atomer, som kallas poly-litium molekyler. För att säkerhetsställa en reversibel reaktion och undvika kluster har de här föreningarna (OLi₂, C Li₃, CLi₄) funktionaliseras över olika substrat som graphane, BN-flak och BC₃-flak. Bindningar i O-Li och C-Li är starkt polära vilket medför överföring av elektrisk laddning från Li till O och C, vilket ger en förhållandevis stark positiv laddning på Li i de här föreningarna. De positivt laddade Li⁺ polariserar närmande H₂-molekyler och adsorberar dem genom van der Waals krafter och elektrostatisk växelverkan. Vi har sett att de här föreningarna ger en väldigt hög lagringskapacitet samtidigt som adsorptionsprocessen ligger inom gränserna för praktiska tillämpningar.
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