SYNOPSIS

In recent years, research in materials science has shown a rapid expansion toward discoveries of suitable materials for sustainable energy. A hydrogen economy is proposed to solve the ill effects of using hydrocarbon fuels in transportation and other end-use applications, where carbon is released to the atmosphere. In this context the storage of hydrogen poses the biggest challenge in a new hydrogen economy because the storage medium must meet the requirements of high gravimetric and volumetric density, fast kinetics and favorable thermodynamics [1-5]. Although molecular hydrogen has very high energy density on a mass basis, as a gas, at ambient conditions, it has very low energy density by volume. If it is to be used as fuel stored on board in the vehicle, pure hydrogen gas must be pressurized or liquefied, which in addition to being energy intensive will also bring complications in terms of safety aspects. Considering all these issues, solid-state materials offer a practical alternative, and a lot of efforts have been devoted in finding efficient solid state hydrogen storage materials.

There are different candidate materials for solid state hydrogen storage [6-12]. The most conventional and practical one is metal hydride, where different transition metal based and light weight alloys are being considered. Transition metal based alloys are quite promising for their good hydrogen absorption desorption kinetics and favorable thermodynamics whereas light metal alloys shows higher hydrogen absorption capacity but unfavorable kinetics and thermodynamics. The suitability of alloys for hydrogen storage applications can be judged from their hydrogen storage properties such as hydrogen reversible capacity, plateau pressure, plateau slope, hysteresis, sorption kinetics and thermodynamics of dissolved hydrogen.
Other exclusively studied hydrogen storage materials include metal organic framework, carbon nanostructures etc. Metal organic frameworks (MOF) can absorb hydrogen by physisorption, but it requires operating at cryogenic condition. Carbon nanostructures are one of the most promising solid-state materials for hydrogen storage because of its porosity, high surface area and high gravimetric hydrogen storage properties. Nanotubes, nano scrolls, nano fibers, fullerenes and graphene sheets are among the different well studied structures. Though the experimental results obtained for hydrogen storage on carbon nanotubes are contradictory because of the presence of metal nano particle impurities and defect structures but still theoretical and experimental research is going on to see its nature of interaction with hydrogen, curvature effect and the effect of doping on the hydrogen absorption properties.

In the present scenario there is a need for the development of hydrogen storage materials with high gravimetric and volumetric hydrogen storage capacity and fast enough kinetics of loading and unloading of hydrogen gas. Existing drawbacks of transition metal based systems should be addressed carefully and meticulously to minimize the practical difficulties. A systematic research work is required on the determination of hydrogen storage capacities, isotherms, and critical thermodynamic and kinetic properties of different solid state hydrogen storage materials using different experimental techniques and improvement upon them. To make the hydrogen economy viable, another principle goal should be the understanding of physical and chemical properties of efficient light weight hydrogen storage materials, especially magnesium, which can provide platform for experimental studies. Till now no hydrogen storage material could show performances close to practical requirements. Therefore in addition to the existing hydrogen storage materials, there is an urgent need to explore new materials with improved performances compared to the existing one. Among various ways, theoretical
modeling of materials is one of the most cost effective routes to explore new materials with tunable properties.

In the present thesis the focus has been made on the investigation of the absorption and desorption behavior of hydrogen on metal and carbon based systems using both experimental and theoretical techniques. For this purpose, the hydrogen storage properties of various transition metal based elements were investigated in detail using different experimental techniques. Along with that, the first principle based calculations were done on magnesium based system to see the effect of size and transition metal doping on the hydrogen absorption properties. Also calculations were carried out on carbon based nanomaterials to find prospective new hydrogen storage systems. The total work of the thesis has been described in nine chapters as outlined below.

**Chapter I: Introduction**

This chapter gives a broad review on hydrogen as an alternative, clean and renewable energy carrier. Different hydrogen storage methods are discussed with special emphasis on solid state hydrogen storage materials. The special aspects of different solid state materials as hydrogen storage media and the requirements for vehicular and other applications are discussed subsequently. The thermodynamics of hydrogen absorption is also explained elaborately. A brief overview is presented on the role of doping elements on the hydrogen storage properties. Finally the aim and scope of the present thesis is addressed.

**Chapter II: Instrumentation and Experimental Methods**

This chapter deals with the experimental techniques employed for the synthesis, characterization and evaluation of the hydrogen storage properties of the alloys. All the
transition metal based alloys were prepared by melting the high purity constituent elements in stoichiometric ratio, in DC arc melting furnace under Ar atmosphere in a water cooled Cu hearth. The Sievert’s type volumetric hydrogen storage setup, which had been developed in our laboratory, was used for the synthesis of the hydrides. The methods used for the activation of the alloys before hydride formation is also presented. The procedure to measure the pressure composition isotherm and hydrogen absorption kinetics in the Sievert’s type setup is discussed in detail. Various characterisation techniques were used for the characterization of the alloys as well as the hydrides during the present work, this includes X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray (EDX), Mössbauer, Electron Probe Micro-analyzer (EPMA) and temperature programmed desorption (TPD). A brief account of these techniques is presented in this chapter.

**Chapter III: Effect of Substitution on Hydrogen Storage Properties of Ti-V-Fe System**

Ti–V based alloys are considered to be promising third generation hydrogen storage materials due to their high hydrogen storage capacity. They have a great potential to replace the AB$_5$ types of alloys in the hydrogen compressor systems [13]. But Ti–V alloys suffer from certain disadvantages, such as, rigorous activation prior to hydrogen absorption, slow kinetics, sloping plateaus and high desorption temperature for the complete desorption of the stored hydrogen. Substitution of a small amount of transition elements like Fe, Co, Ni, Mn or Cr changes the hydrogen absorption characteristics of Ti–V system drastically [14-16]. In this work, to improve the performances of Ti-V system, Ti was partially replaced by Fe and the hydrogen absorption properties of Ti$_{1-x}$VFe$_x$ ($x = 0.0, 0.1, 0.15, 0.2$ and $0.4$) alloys were investigated in detail. Fe substituted Ti-V alloys were characterized by XRD and EPMA. It is evident from Fig. 1, that except Ti$_{0.85}$VFe$_{0.15}$, all the other Ti–V–Fe compositions are having mixed phase structure
composed of a body centered cubic (bcc) phase and a secondary C14 Laves phase, with bcc as the major phase. The composition, Ti$_{0.85}$VFe$_{0.15}$ contains single phase bcc structure. The lattice parameter of the bcc phase decreases with increasing Fe substitution due to the smaller atomic radius of Fe as compared to that of Ti and V (Ti: 1.47 Å, V: 1.34 Å, Fe: 1.26 Å). The corresponding hydride structures were found to have face centered cubic (fcc) structure and the lines corresponding to the secondary phase were not seen in the XRD patterns of the hydrides.

![X-ray diffraction patterns](image1.png)

**Fig. 1** (A) X-ray diffraction patterns for: (a) Ti$_{0.9}$VFe$_{0.1}$, (b) Ti$_{0.9}$VFe$_{0.1}$H$_{3.65}$, (c) Ti$_{0.85}$VFe$_{0.15}$, and (d) Ti$_{0.85}$VFe$_{0.15}$H$_{3.83}$ (the lines corresponding to the secondary phase are marked by ‘*’). (B) Electron micrographs for: (a) Ti$_{0.9}$VFe$_{0.1}$ and (b) Ti$_{0.85}$VFe$_{0.15}$ alloys

The pressure composition isotherm and kinetics of all the alloys were evaluated and the hydrogen storage capacities of Ti$_{1-x}$VFe$_x$ alloys as a function of Fe content, x, are shown in Fig. 2. It is seen that the hydrogen storage capacity of Ti$_{1-x}$VFe$_x$ increases with Fe content up to $x = 0.15$, but further increase in the Fe content brings down the hydrogen storage capacity drastically. At a high Fe concentration, the bcc phase was found to coexist with the secondary phase. The
amount of the hydrogen absorbed in this series of alloys is closely related with the amount of bcc phase present. The bcc phase in Ti–V system is reported to absorb more hydrogen than the secondary phase [17]. The composition Ti$_{0.85}$VFe$_{0.15}$ was found to have single phase bcc structure and it shows the maximum storage capacity of 3.7 wt. % among the various Ti–V–Fe compositions studied in this work.

![Fig. 2 Variation of hydrogen absorption capacity with respect to the Fe content in Ti$_{1-x}$VFe$_x$ alloys (x = 0.0, 0.1, 0.15, 0.2 and 0.4)](image)

The desorption profiles of the saturated hydrides reveal that with increasing Fe concentration the hydrogen desorption temperature decreases. This may be attributed to the fact that with increasing Fe concentration the relative stability of the hydrides decreases and hence the hydrogen desorption takes place at a lower temperature.

Further, to see the effect of Cr substitution on the activation performance, the compositions Ti$_{0.85}$VFe$_{0.15}$ and Ti$_{0.80}$VFe$_{0.20}$ were modified by chromium substitution (60 at. %) in place of V. It is found that the storage capacity decreases with Cr substitution but there was no observable change in the absorption plateau pressure up to 373 K. Among the two compositions, Ti$_{0.8}$V$_{0.4}$Fe$_{0.2}$Cr$_{0.6}$ was found to absorb hydrogen without any prior activation. It is reported that
the presence of C14 Laves phase in Ti-based bcc alloy helps in the easy activation of the alloys [18]. The XRD of the above two compositions also confirms the presence of a secondary C14 hexagonal Laves phase along with the bcc phase. Thermal desorption studies showed a sharper desorption profile for the Cr containing hydride as compared to the Cr-free hydride.

The hydrogen absorption properties of Ti$_{0.85}$V$_{0.95}$Fe$_{0.15}$ alloy was modified by Zr substitution (5 at. %) at V site to ease the activation as it is known that small amount of Zr substitution ease activation before hydrogen absorption. The alloys and the corresponding hydrides were characterized by X-ray diffraction and Mössbauer spectroscopy. The crystal structure (Fig. 3) shows that 5 at. % of Zr substitution in place of vanadium results in a bi-phasic structure consisting mainly C15 cubic Laves phase along with V based bcc solid solution. The lattice parameter of the C15 cubic Laves phase was found to be 7.36 Å. It may be noted that the C15 cubic Laves phase structure remains unchanged on hydrogenation of Ti$_{0.85}$V$_{0.95}$Fe$_{0.15}$Zr$_{0.05}$ alloy though there is an appreciable shift in the peak positions to lower 2-theta values indicating volume expansion due to hydrogenation.

![XRD patterns](image)

**Fig. 3** XRD patterns of Ti$_{0.85}$V$_{0.95}$Fe$_{0.15}$Zr$_{0.05}$, Ti$_{0.85}$V$_{0.95}$Fe$_{0.15}$Zr$_{0.05}$H$_2$ and Ti$_{0.85}$V$_{0.95}$Fe$_{0.15}$Zr$_{0.05}$H$_{3.74}$ (Δ C15 Laves phases, * V based bcc solid solution).
Comparing the hydrogen absorption capacity and the hydrogen desorption properties of Ti$_{0.85}$V$_{0.95}$Fe$_{0.15}$Zr$_{0.05}$ with those of Ti$_{0.85}$VFe$_{0.15}$, it was found that the Zr substitution improves the hydrogen absorption–desorption characteristics of Ti$_{0.85}$VFe$_{0.15}$ alloy by decreasing the hysteresis loss without affecting the maximum hydrogen storage capacity considerably. The effective hydrogen storage capacity was found to improve by 5 at. % of Zr substitution in place of V. The increase in the effective hydrogen storage capacity can be attributed to the fact that Zr substituted alloy has an additional site (as shown in the TPD profile in Fig. 4), which desorbs hydrogen at a lower temperature as compared to Ti–V–Fe system.

![TPD profiles of the hydrides Ti$_{0.85}$VFe$_{0.15}$H$_{3.83}$ and Ti$_{0.85}$V$_{0.95}$Fe$_{0.15}$Zr$_{0.05}$H$_{3.74}$](image)

**Fig. 4 TPD profiles of the hydrides Ti$_{0.85}$VFe$_{0.15}$H$_{3.83}$ and Ti$_{0.85}$V$_{0.95}$Fe$_{0.15}$Zr$_{0.05}$H$_{3.74}$**

The effect of Ce substitution on the microstructure, hydrogen absorption properties, peak current of hydrogen absorption and electrochemical behaviour of Ti$_{0.85}$VFe$_{0.15}$ system was also investigated. Substitution of Ce (2 and 5 at. %) for Ti improves the hydrogen absorption capacity of Ti$_{0.85}$VFe$_{0.15}$ alloy. The maximum storage capacity of Ti$_{0.85}$VFe$_{0.15}$, Ti$_{0.83}$Ce$_{0.02}$VFe$_{0.15}$ and Ti$_{0.80}$Ce$_{0.05}$VFe$_{0.15}$ alloys were found to be 3.7, 4.02 and 3.92 wt. %, respectively. The ease of activation of Ti-V-Fe system was found to improve by Ce substitution. EPMA studies showed the presence of CeO$_2$ phase in Ce-substituted alloys along with a third phase. The CeO$_2$ phase is responsible for the easy activation of the alloy as it suppresses TiO$_2$ phase formation.
Electrochemical studies showed increased exchange current density for Ce doped alloy indicating improved electrochemical activity for the hydrogen electrode reactions.

**Chapter IV: Hydrogen Storage Studies on Ti-V-Cr Based System**

This chapter deals with the hydrogen storage properties of Zr substituted TiVCr alloy. Stoichiometric TiVCr from the Ti-V-Cr series is reported to exhibit good hydrogen absorption capacity in the previous studies [19]. However, hydrogenation of TiVCr is reported to result in phase separation into TiH2 and TiCr1.8H5.3 when subjected to cyclic hydrogenation-dehydrogenation process [20]. In our work, the hydrogen absorption and desorption characteristics of Ti1-xZrxVCr with x = 0, 0.05, 0.10 and 1.0 were studied as an attempt to express the phase separation. The maximum storage capacities of these alloys, as a function of Zr substitution, were found to be 3.64, 3.53, 2.93 and 2.16 wt. %, respectively. While TiVCr crystallized in bcc structure, ZrVCr found to have a C15 cubic Laves phase structure and the intermediate compositions with x = 0.05 and 0.1 showed the presence of a small amount of ZrCr2 along with the main bcc phase. A small amount of Zr substitution (5 at. %) for Ti decreases the storage capacity of TiVCr system marginally, but TiH2 phase separation is suppressed, possibly leading to better cyclic hydrogen absorption capacity. Hysteresis was found to be less for Zr substituted systems. With further increase in the Zr concentration, the hydrogen storage capacity was found to decrease considerably due to the formation of the secondary Laves phase in addition to the bcc phase. Temperature programmed desorption studies showed the presence of an additional desorption site at lower temperature for Zr substituted hydrides, which desorb hydrogen at lower temperature as compared to the hydride of TiVCr, indicating higher effective hydrogen storage capacity for Zr substituted systems.
In the second part of the chapter the hydrogen absorption-desorption properties and the cyclic stability of Ti$_2$VCr alloy are discussed in detail. This alloy shows quite high hydrogen absorption capacity with a maximum storage capacity of 4.37 wt. %. The plateau pressure was found be less than 0.02 atm. at room temperature, indicating that this alloy forms a stable hydride at room temperature. The cyclic hydrogen absorbing ability decreased progressively during the first few cycles and after that it remains almost constant. The alloy shows maximum 3.5 wt. % hydrogen absorption capacity after few cycles. The kinetics of hydrogen absorption was found be fast for Ti$_2$VCr alloy without any incubation time. The desorption capacity of Ti$_2$VCr hydride were measured by heating the sample at different temperatures. It was found that the hydrogen desorption capacity at room temperature is only 1 wt. % which increases with increase in temperature. In the DSC analysis the multi-cycled hydride showed hydrogen desorption at a lower temperature as compared to uncycled hydride of Ti$_2$VCr. This may be due to the fact that with increase in cycling the particle size of the hydride decreases. Due to the high storage capacity, the studied alloy can be used in Ni-MH batteries, though the desorption temperature is quite high for the practical application. To take care of this aspect, further modification was done by substitution of 5 at. % Co and Ni, for Ti. The results show that, with Ni substitution though there is a marginal decrease in the storage capacity, but there is a decrease in hydrogen desorption temperature by 75 K.

**Chapter V: Vanadium Substituted ZrFe$_2$ as a Laves Phase Hydrogen Storage Material**

AB$_2$ Laves phases are a class of alloy that is considered to be promising candidates as hydrogen storage materials and negative electrodes for Ni-MH batteries. It is well known that many of the pseudo binary compounds like AB$_2$ show excellent hydrogen absorption-desorption properties and can be considered as potential hydrogen storage materials [21, 22]. Many of them
can absorb three hydrogen atoms per molecule and exhibit a desorption plateau pressure of around 1 atm. at room temperature. Recently, interest has been focused on Zr-based AB$_2$ alloys, because of their good storage capacity, fast kinetics and easy activation. Among this series, ZrFe$_2$ intermetallic compound is having a C15 Laves phase structure (MgCu$_2$ type) with lattice parameter of 7.064 Å. At ambient conditions, it can absorb only a small amount of hydrogen to form a solid solution with composition ZrFe$_2$H$_{0.16}$. In the present work, we substituted different amount of V for Fe in ZrFe$_2$, and demonstrated its effect on the phase formation, hydrogen absorption desorption properties, hydrogen absorption capacity and thermodynamic stability. The compositions studied were ZrFe$_{1.8}$V$_{0.2}$, ZrFe$_{1.6}$V$_{0.4}$, ZrFe$_{1.4}$V$_{0.6}$ and ZrFe$_{1.2}$V$_{0.8}$. From the structural analysis it was observed that with increase in the V content, the C15 cubic structure transforms into C14 hexagonal structure. While ZrFe$_{1.8}$V$_{0.2}$ shows a C15 cubic Laves phase structure with lattice parameter of 7.085 Å, other compositions with V content ≥ 0.4 shows C14 type hexagonal structures. It was also observed that, with an increase in the V content the cell volume increases. All the hydrides show similar structure as their parent alloys with an increase in the lattice parameter.

It was found that with the increase in V content the hydrogen absorption capacity increases significantly due to the decrease in the 3d occupation number in the transition elements. The pressure composition isotherms was studied at 300 K, 323 K, 350 K and 373K temperatures respectively using a Sievert’s type set up. It was found that ZrFe$_{1.2}$V$_{0.8}$ absorbs maximum amount of hydrogen within this series to form ZrFe$_{1.2}$V$_{0.8}$H$_{3.78}$ at around 20 atm. pressures and it shows a very low absorption plateau around zero atm. at room temperature. The other hydrides, i.e., ZrFe$_{1.8}$V$_{0.2}$, ZrFe$_{1.6}$V$_{0.4}$ and ZrFe$_{1.4}$V$_{0.6}$, absorb 2.52, 3.26 and 3.61 H/formula unit, respectively. The plateau pressure for hydrogen absorption decreases significantly with increase
in the V content, indicating higher thermodynamic stability of the hydrides. The formation enthalpies of the hydrides were found out from the van’t Hoff plot and it was found that with increase in the V content the formation enthalpy becomes more and more negative indicating more stable hydrides. The increase in the stability of the hydrides with V substitution was also reflected in the temperature programmed desorption profile, which shows that with increase in the V content the desorption temperature increases.

**Chapter VI: Theoretical Methodology**

This chapter deals with the computational methods used for the first principles based calculations on Mg and carbon based systems. This chapter provides a short overview of quantum chemical electronic structure methods namely, Hartree Fock, and Density Functional theory (DFT). The fundamentals of Hartree-Fock method, post Hartree-Fock and the associated approaches were discussed. The formation of density functional theory and its advantages over wave function based methods for electronic structure calculation in larger systems are discussed. The basic concept of Nudged Elastic Band (NEB) method is introduced, which has been used for the calculation of activation barrier for the dissociation of hydrogen molecules towards hydrogen atoms and subsequent diffusion of hydrogen atoms on Mg surfaces and nano-clusters. Finally some of the technical details and parameters used in these calculations, viz. initial guess wave function or basis set, pseudo-potentials, simulation cell, geometry optimization techniques, utilized computer systems configuration etc. is illustrated in this chapter.

**Chapter VII: Hydrogen Storage in Mg Based System**

Magnesium based systems are considered as one of the most promising hydrogen storage materials because of its low cost and high hydrogen storage capacity. Ideally, it can absorb 7.66 wt. % of hydrogen, which is sufficiently high for on board hydrogen storage [23]. But the
problems with magnesium are high thermal stability of the magnesium hydride and its slow kinetics of hydrogen absorption and desorption in bulk Mg [24]. On reaction with hydrogen at extreme condition, Mg forms MgH$_2$ and the heat of formation was estimated to be $-76$ kJ/mole of H$_2$. [25]. Due to such higher stability of MgH$_2$, the hydrogen desorption occurs at a temperature of around 360°C, which is very high for practical applications. It was found that ball milling of Mg can improve the hydrogen absorption-desorption kinetics by a factor of 10. It is also reported that transition metal elements can act as a catalyst for the adsorption of hydrogen on the Mg surface, thus improving the kinetics of hydrogen adsorption. Here, an attempt was made to provide such an understanding by first-principles calculations to investigate the structure and stability of Mg(0001) surface doped with M atoms (M = Ti, V, and Ni) and their interaction with hydrogen molecule. The chapter deals with the interaction behavior of a hydrogen molecule on the Mg(0001) surface doped with three different transition metal atoms (M = Ti, V, and Ni). In the first part of the work we investigated the stability of these M atoms at different layers of the Mg surface, and in the second part we calculated the interaction energy of hydrogen on the surfaces and the energy barriers for the dissociation of molecular hydrogen into atomic form and subsequent diffusion of atomic hydrogen when the M atoms are at the top surface and in the bulk. From the calculation, it was concluded that the substitutional energies of all the M elements are negative, indicating that M atom doping is thermodynamically favorable (Fig. 5).
More importantly, it was seen that all the M atoms prefer to substitute one of the Mg atoms from the second layer than that from the top surface layer. However, the relative stability in the first and second layers differs for different transition metal elements. For Ti and V the differences in energy are almost 0.52 and 0.425 eV, respectively, and in the case of Ni it is 0.13 eV only.

The interaction of molecular hydrogen was seen with all the transition metal (Ti, V, Ni) doped Mg surfaces, when the M atom remains in the first and second layer of the surface and the results are represented in the tabular form in Table 1.

The interaction of a hydrogen molecule with doped Mg surface suggests that when the impurity atoms are on the top layer they behave as good catalyst for hydrogen dissociation and the dissociative chemisorption of hydrogen molecule occurs spontaneously on the catalytic site. The dissociated hydrogen atoms occupy the fcc or hcp holes depending on the nature of M atom. However, they restrict the movement of hydrogen atoms further as the diffusion barrier is quite high. Here the diffusion of hydrogen atoms is the rate limiting step. The situation is reversed.
when the M atoms substituted one of the Mg atoms from the second layer. In this case the
dissociation of hydrogen molecule is controlled by a high activation barrier but once the
hydrogen is absorbed the mobility of the hydrogen atoms on the surface is easier than the
previous case. In this case, the dissociation process is the rate limiting step.

Table 1 Calculation of interaction energy of hydrogen and different activation barriers

<table>
<thead>
<tr>
<th>Surface</th>
<th>Substitution at the first surface</th>
<th>Substitution at the second surface</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hydrogen adsorption energy (eV)</td>
<td>Activation barrier for dissociation (eV)</td>
</tr>
<tr>
<td></td>
<td>Pure Mg surface</td>
<td>-0.07</td>
</tr>
<tr>
<td></td>
<td>Ti doped Mg surface</td>
<td>-0.61</td>
</tr>
<tr>
<td></td>
<td>V doped Mg surface</td>
<td>-0.67</td>
</tr>
<tr>
<td></td>
<td>Ni doped Mg surface</td>
<td>-0.37</td>
</tr>
</tbody>
</table>

From the above calculations, we understood the behavior hydrogen on the metal doped Mg
surfaces and inferred that the most desirable situation could be, if we can use two dopants, each
substituting one Mg atom from the first layer and the second layer. So we investigated the
structure and stability of the Mg(0001) surface doped with V and Ni atoms and its interaction
with hydrogen molecules. For this purpose, first we calculated the stability of the doubly doped
Mg surface by placing the dopants at different layers and found the most stable configuration,
where V and Ni are placed in the second and first layer, respectively. Once the preferred location
was established through stability criteria, we investigated the dissociative chemisorptions of
hydrogen molecule followed by diffusion of hydrogen atoms on the doubly doped Mg surface. It was found that the most stable state is one where the hydrogen atoms absorb into two nearby hcp positions and one hydrogen atom is nearer to the V atom (Fig. 6). Moreover, from the projected density of states (PDOS) of the system we found that the d PDOS of V changed significantly after the interaction with hydrogen, which suggests that there is a strong influence of V atom, also for the dissociation of hydrogen molecule. The dissociation activation barrier for the hydrogen molecule on the doubly doped structure was found to be quite low (Fig. 7). The stabilization of Ni in the first layer enhances the direct interaction of hydrogen, which results in significant lowering of the dissociation energy barrier, the most desirable property of hydrogen storage. The presence of V atom at the subsurface layer not only stabilizes Ni at the surface layer but also facilitates dissociative chemisorptions of the hydrogen molecule on the catalytic site of Mg(0001) surface. After dissociation of hydrogen molecule into two hydrogen atoms at the catalytic site in the Mg(0001) surface, two hydrogen atoms show different activation barriers for diffusion depending upon their positions. The hydrogen atom, which is away from the V atom, shows a lower diffusion barrier compared to the other hydrogen atom as a result of the lower influence of the V atom.

In the final part of the chapter, discusses the hydrogen adsorption properties of Mg cluster using first principle calculations to reveals the effect of finite size. Our calculations clearly showed that Mg_{55} cluster has less activation barrier for dissociation of hydrogen molecule than bulk Mg, hence enabling hydrogen dissociation at lower temperatures. The effect of Ti doping on the hydrogen adsorption properties of Mg_{55} cluster was also established, and we find that when Ti is substituted in the Mg_{55} cluster then, it preferably goes at the middle layer and it can decrease the dissociation barrier further by activating the surface Mg atom. The
overall decrease in the activation barrier in this case is 40% compared to pure Mg bulk. The *ab-initio* molecular dynamics calculations showed that at 300 K the Mg–H is elongated sufficiently and starts a flip-flop motion on the surface, which can be viewed as the onset of hydrogen diffusion, a preliminary step for desorption. As currently, high desorption temperatures are a major impediment; hence the projected shift toward more favorable operation temperatures is crucial for the application of Mg as a reversible hydrogen storage material.

**Chapter VIII:** Hydrogen Adsorption on Carbon Based System

In this chapter we have discussed three systems namely corannulene, SiC nano-materials and metallo-carbohedrene for their hydrogen adsorption properties. Using density functional theory, we investigated the hydrogen uptake capacity of alkali ($\text{Li}^+$, $\text{Na}^+$ and $\text{K}^+$) and alkaline earth metal ion ($\text{Be}^{2+}$, $\text{Mg}^{2+}$ and $\text{Ca}^{2+}$) doped corannulene molecules. The results showed that all
metal ions bind the corannulene ring through charge transfer complex formation. Moreover, the site preference of metal ion adsorption depends on the size of the cation. While the larger size cation prefers to bind on the concave surface, the smaller cation stabilizes on the convex surface. Subsequently, we carried out the interaction of molecular hydrogen with the clean and doped corannulene complexes. Where as, the bare corannulene absorbs hydrogen very weakly, a significant improvement of H\(_2\) binding energy on the doped corannulene was observed. This was attributed to the charge-induced polarization of the H-H bond. Based on the binding energy and hydrogen uptake considerations, it is inferred that Na\(^+\) doped corannulene is the best candidate among all metal ions considered here.

In the second part of the chapter we report the hydrogen adsorption behavior of two SiC nanostructures; a planar sheet and a nanotube (10, 0) of 1nm diameter, decorated by Ti atoms on it. The lowest energy structure of the Ti adsorbed SiC sheet shows that Ti atom distorts the sheet in such a way that one of the Si atoms goes down the plane and bind with nearest three C atoms. The interaction of this Ti decorated sheet with hydrogen suggests that each Ti atom can bind up to four hydrogen molecules (all hydrogen are adsorbed in the molecular form) with an average binding energy of 0.37 eV. For SiC nanotube, the adsorption of Ti favors the hexagonal hollow site. Moreover, on interaction of this Ti decorated tube with hydrogen, the dissociation of the first hydrogen molecule occurs first and thereafter it adsorbs hydrogen in the molecular form. The average binding energy of hydrogen molecules on this Ti decorated tube was estimated to be 0.65 eV. Based on these results, we inferred that the Ti decorated SiC nanostructures moderately bind with hydrogen molecules (within the energy window for hydrogen storage materials) and therefore, can be considered as one of the potential hydrogen storage material.
The hydrogen adsorption properties of the metallo-carbohedrene (met-car) having a formula $M_8C_{12}$ ($M = \text{Sc, Ti, V}$) was also discussed in his chapter. In the work the tetrahedron ($T_d$) geometry of met-car was considered and the stabilization energies of the pure met-car clusters were compared. In $\text{Ti}_8C_{12}$ cluster, each corner Ti atoms can bind three molecules of hydrogen, where as each face Ti atom can bind with one molecule of hydrogen. So total 16 molecular hydrogen can get absorbed on met-car by physisorption. Along with that, six hydrogen molecules get dissociated and absorbed as hydrogen atom on six C-C bond. Considering all the hydrogen atoms, the hydrogen adsorption capacity of $\text{Ti}_8C_{12}$ cluster was found to be 15.06 wt. %. The hydrogen adsorption behavior of $\text{Ti}_8C_{12}$ was compared with that of the $\text{Sc}_8C_{12}$ and $\text{V}_8C_{12}$ clusters. Molecular dynamics simulation were carried out to see the desorption behavior of hydrogen molecules.

**Chapter IX: Conclusion/Highlights of the Present Work**

This chapter discusses the summery and out come of the present thesis and also the scope for the future work both with experiment and theoretical tools. During the present thesis, different experimental techniques have been used for the determination of hydrogen storage capacities, isotherms, and critical thermodynamic and kinetic properties of solid state hydrogen storage materials. During the course of the work, several transition metal based alloys have been identified, modified by proper substitution and the results provide a suitable database for the appropriate choice of hydrogen storage materials. Further the theoretical calculations in the thesis provide proper understanding of physical and chemical properties for efficient hydrogen storage materials, which can give insight for experimental studies. In order to further explore new materials with higher hydrogen storage capacities, theoretical modeling has been carried out on carbon based system using electronic structure theory. The present work can be extended by
different other modification experimentally, and the verification of the theoretical data by experimental methods. However, efforts are to be continued, using both experimental and theoretical tools, to find newer hydrogen storage materials with suitable thermodynamics and kinetics properties, which can store higher amount of hydrogen.

References


