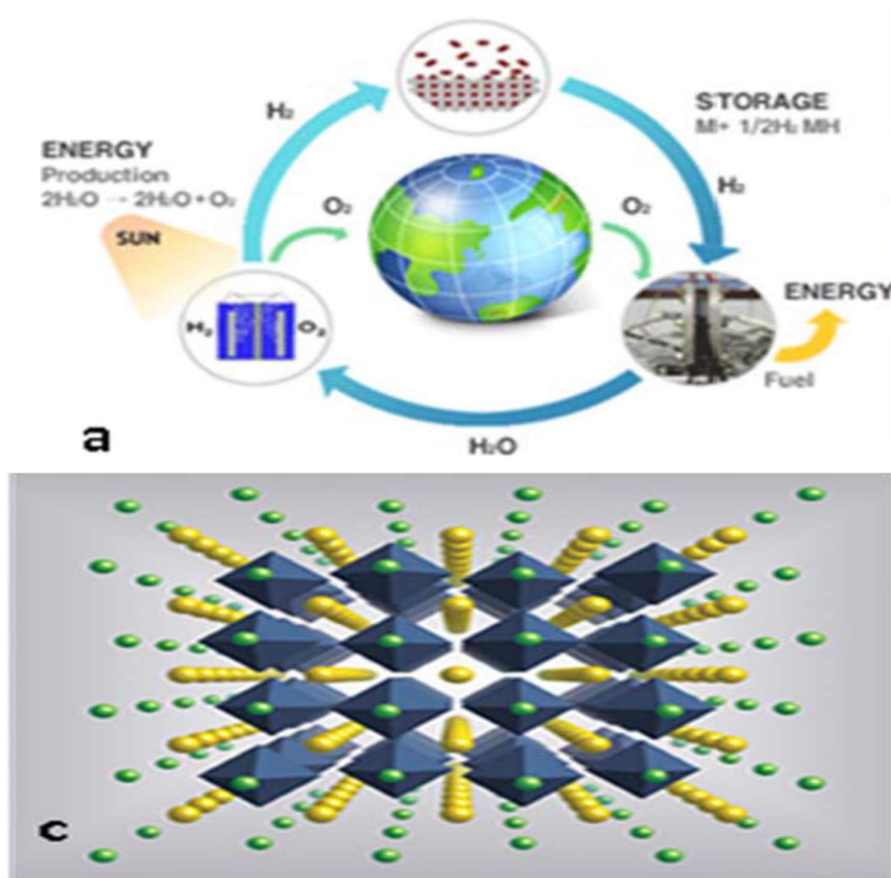
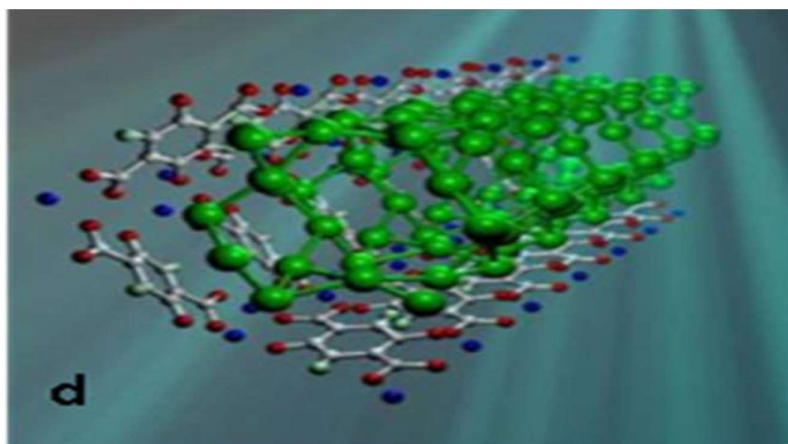


SOLID STATE HYDROGEN STORAGE OPTIONS



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PREFACE

Energy conversion and distribution appears to be essential components of sustainable society. Among the options available for energy sources, hydrogen, the lightest element appears to occupy a unique position. In the past 50 years or so, various research efforts are made to make this energy source available for societal use. However, there are bottlenecks in energy conversion, storage and also in distribution. The components of the energy chain have to be properly stitched together for the society to derive maximum efficiency.

Energy storage is the middle component in the energy chain and it has received considerable attention in recent times. This monograph is an attempt to examine the possibility of storing the energy carrier, Hydrogen in solid state materials. This subject is a vast one and covering all the aspects in one volume is not feasible or it is not also desirable. Therefore, only a few aspects of this problem are taken up for discussion and it must be remarked that not only the selection but also coverage is not comprehensive.

It is hoped that this attempt will be useful in a small measure for those who are interested in this topic. Any suggestions and remarks will be gratefully received.

Our grateful thanks are due to the members of NCCR for their support. We are also grateful to MNRE (Ministry of Non-conventional and Renewable Energy) and Department of Science and Technology, (DST) Government of India for supporting NCCR's programme on these topics

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CHAPTER: ONE

INTRODUCTION

1.1. Energy Sources

Energy resources and energy conversions are the two factors that are essential for a sustainable society. The search and identification of energy sources are directed from the points of view of sustainable availability, affordable cost and environmental acceptability. The possible energy conversion processes that can be exploited must be such that it should yield maximum efficiency, least polluting the atmosphere and also should be easily processable. Human civilization has tried various forms of matter (solid, liquid and gas) to meet their need for energy, and their predictions on the change over from one form of matter to another during the evolution of human civilization. One such projection taken from literature for the recent centuries is shown in Fig.1.1.

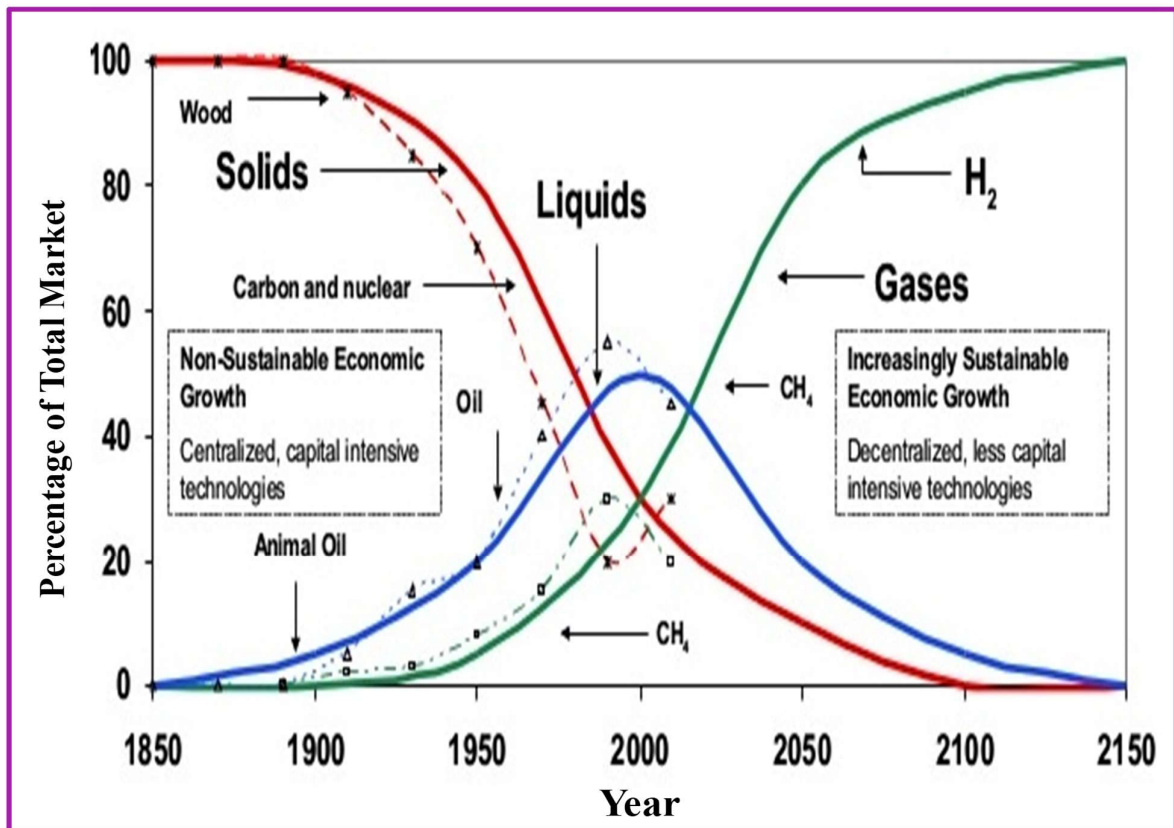


Fig.1.1. Evolution of state of fuel in the recent centuries [Figure reproduced from Dunn, S, International Journal of Hydrogen Energy, 27,235-264 (2002)].

It is on the basis of the generalization of this observation, that it is believed the immediate future lies in the gaseous state for the possible fuel sources. It is therefore natural to expect that natural gas (in the immediate future) and hydrogen (sustainable source) can be the alternate fuel sources or carriers in the future. There can be many other arguments for this expectation and these can be found vociferously expressed in many current literature.

First the essential features of hydrogen as a possible energy carrier in the near future.

- It is the lightest and most abundant element. (mostly in combined state)
- It can burn with oxygen to release (large amounts) of energy.
- Hydrogen has a high energy content by weight.
- It has a low energy density by volume at standard temperature and atmospheric pressure.
- Like any other gas, the volumetric density can be drastically lowered by storing compressed hydrogen under pressure or converting it to liquid hydrogen.
- Hydrogen burns when it makes up 4 to 75% of air by volume.
- Many pollutants are formed when hydrogen is burnt in air because of the high nitrogen content of the air.

Hydrogen is a good choice for a future energy source for many reasons. Some of these reasons include:

- Hydrogen has the potential to provide energy to all parts of the economy namely industry, residences, transportation, and mobile applications.
- Hydrogen can be made from various sources, water, fossil fuels and other sources as well
- It is completely renewable as of now.
- The most abundant and cleanest precursor for hydrogen is water.
- Hydrogen can be stored in many forms, from gas to liquid to solid.
- It can be stored in various chemicals and substances such as methanol, ethanol, and metal hydrides and in various solid state matrices
- It can be produced from, and converted to, electricity with (high)reasonable efficiencies.
- It can be transported and stored as safely at least as any other fuel.
- It can eventually aid in the release of oil-based fuels used for automobiles. The change of economy base.
- It is an attractive solution for remote communities that cannot access electricity through the grid.

- One of the fundamental attractions of hydrogen is its environmental advantage over fossil fuels, however, hydrogen is only as clean as the technologies used to produce it. The production of hydrogen can be pollutant-free if it is produced by one of three methods:
- Through electrolysis using electricity derived solely from renewable energy sources or nuclear power.
- Through steam reforming of fossil fuels combined with new carbon capture and storage technologies.
- Through thermochemical or biological techniques based on renewable biomass.
- A major disadvantage of processing hydrocarbons is the pollution and carbon dioxide, which eliminates one of the main reasons for using hydrogen in the first place. The best low-pollution alternative for creating hydrogen is a process involving electrolysis of water by electricity. This method creates no carbon dioxide or nitrous or sulfurous oxides emission.

In Table 1 relevant properties of hydrogen, methane, methanol, ethanol, propane, and gasoline—all of which can be used as fuel are compared.

Table 1.1. Hydrogen Compared with Other Fuels, based on fossil fuels.

Property	Hydrogen	Methane	Methanol	Ethanol	Propane	Gasoline
Molecular Weight (g/mol)	2.016	16.043	32.040	46.063	44.100	~107.00
Density (kg/m ³ at 293 K and 1 atm)	0.08375	0.6682	791	789	1.865	751
Normal Boiling Point (°C)	-252.8	-161.5	64.5	78.5	-42.1	27 - 225
Flash Point (°C)	< -253	-188	11	13	-104	-43
Flammability Limits in Air (volume %)	4.0 - 75.0	5.0 - 15.0	6.7 - 36.0	3.3 - 19	2.1 - 10.1	1.0 - 7.6
Carbon dioxide production per Energy Unit	0	1.00	1.50	N/A	N/A	1.80
Auto-Ignition	585	540	385	423	490	230 - 480

Temperature in Air (°C)						
Higher Heating Value (MJ/kg)	142.0	55.5	22.9	29.8	50.2	47.3
Lower Heating Value (MJ/kg)	120.0	50.0	20.1	27.0	46.3	44.0

Even though we have seen the properties of hydrogen as a fuel or energy carrier in comparison to most other fossil fuel-based compounds, it is necessary to compare hydrogen with other energy sources such as electricity as well as LPG or CNG. These data have been assembled in literature and are available at [www.afdc.energy.gov/].

1.2. Sources of Hydrogen:

For any substance to be considered as a fuel, its sources are important. In the same way if hydrogen is to be considered as an energy carrier, one must ensure the available sources of hydrogen. Even though we will not deal with the technology and exploitation of sources of hydrogen in this presentation, it is better at least to list the possible and available sources of hydrogen. Hydrogen can be obtained from various sources and also by various technologies. These possibilities (though not exhaustive) are given in Table 1.1.

Table 1.1. Possible hydrogen production technologies

<ol style="list-style-type: none"> 1. Steam reforming of naphtha 2. Partial oxidation of hydrocarbons 3. Thermal decomposition of hydrocarbons 4. Thermochemical cycles Iron-Halogen, Sulphur-Iodine cycles 5. Electrolysis 6. Electrochemical method 7. Photolysis method 8. Photochemical process 9. Photoelectrochemical method 10. Biological Method 11. Biochemical method 12. Photobiological method
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1.3. The Hydrogen-based Economy

The use of hydrogen as an energy carrier may reduce in the coming years the dependence of fossil fuels and other energy sources, one such scenario is pictorially shown in Fig.1.2.[2]. Many similar predications may be available in literature.

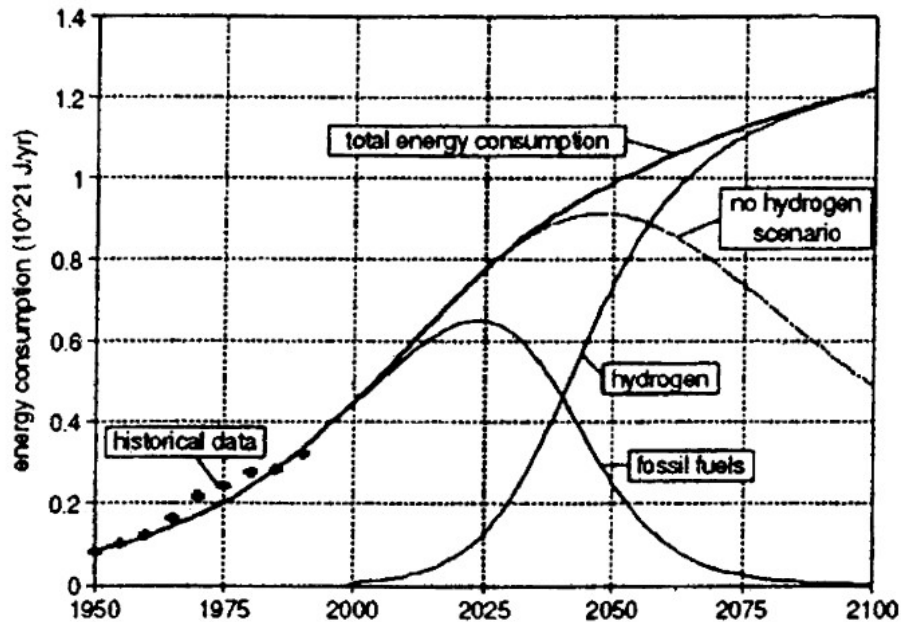


Fig.1.2. Energy Consumption pattern over the years [Reproduced from ref.2].

The basis for looking to hydrogen economy is that during the 19th century, the characteristics and potential uses of hydrogen were considered by clergymen, scientists, and writers of science fiction and possibly the common men as well. In one of the sources, an engineer in Jules Verne's 1874 novel 'The Mysterious Island' informs his colleagues, "Yes, my friends, I believe that water will one day be employed as fuel, that hydrogen and oxygen which constitute it, used singly or together, will furnish an inexhaustible source of heat and light, of an intensity of which coal is not capable.... Water will be the coal of the future" [3]. There are many attempts to turn to hydrogen economy in selected areas. The tiny South Pacific island of Vanuatu has even tried to prepare a feasibility study for developing a hydrogen-based renewable energy economy as early as 2000. Similar exercises were carried out in Hawaii, Iceland. In addition, automobile manufacturing giants like Ford, and others also formed a consortium to turn over to the hydrogen-based economy.

Hydrogen by itself cannot solve various aspects of the complex problems of fuel supply, increase in population, explosion in transport vehicles use. But hydrogen

could provide a major hedge against these risks. By employing hydrogen in fuel cells and their use in vehicles can dramatically cut emissions of particulates, carbon monoxide, sulfur and nitrogen oxides, and other local air pollutants. By providing a secure and abundant domestic supply of fuel, hydrogen would significantly reduce oil import requirements by various nations and also the energy independence and security that many nations crave for. One should not think that we turn to hydrogen-based economy simply because our fossil fuel sources are depleting. There is a statement by Don Huberts, CEO of Shell Hydrogen. He, has noted: “The Stone Age did not end because we ran out of stones, and the oil age will not end because we run out of oil.” It is only our anxiety to be ready with alternate energy sources for the future of humanity.

Without going into details, electrolysis and electrochemical processes may lead to a clean hydrogen-based energy cycle. One such cycle is shown pictorially in Fig1.3.

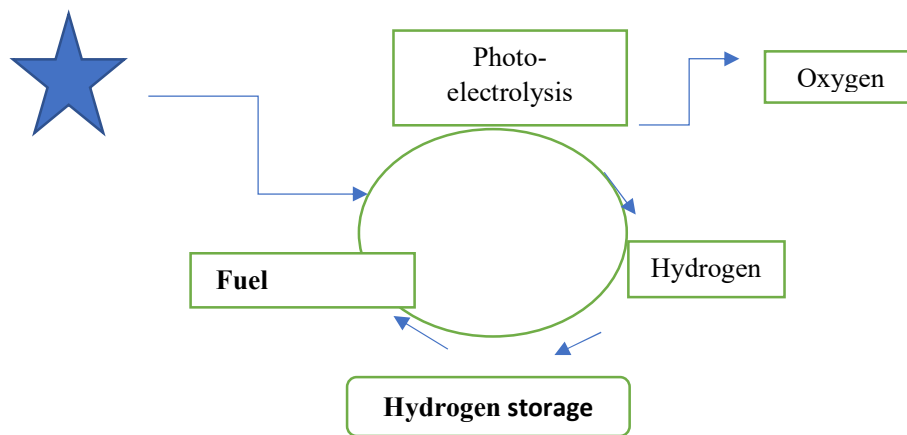


Fig.1.3. A possible hydrogen cycle that will emerge in the near future

There are various aspects of hydrogen-based economy on which further knowledge is required. A complete tracing of the origin and the development of hydrogen economy has been done by Seth Dunn in his publication [1]. In this publication, he concludes that there are risks and costs to a program of action as stated by President John F. Kennedy some years before. “ But they are far less than the long range risks and costs of comfortable inaction”. Thus, there are risks and costs involved in building hydrogen-based economy but they are far less than the costs and risks involved in continuing on hydrocarbon-based economy. In this publication many other aspects of hydrogen-based economy have been considered. The impression one gets from these arguments is that we cannot avoid turning to hydrogen-based economy even though the transition may be slow. There can be various reasons for this delay, among these, the possible feasible and cost-effective storage of hydrogen is one of the stumbling blocks and that is what is considered in this monograph. There has been many attempts to

store hydrogen in all the states of matter, but however, the storage capacity required could not be achieved in solid state storage which is one of the options for hydrogen to be used as fuel for transport sector. This being the most important aspect of the future hydrogen economy and thus forms the subject matter of this monograph.

1.4. Hydrogen Storage: Issues and Targets

Hydrogen is an ideal clean energy carrier since hydrogen is both carbon-free and pollution-free and its only product of combustion is water. Hydrogen is one of the most abundant natural resources in the universe. However, storing H₂ in an efficient, economical, and safe way is one of the main challenges. In general, hydrogen can be stored either as liquid H₂ via liquefaction, in compressed gas cylinders, or in solid state as chemical hydrides or absorbed in porous materials. Potential hydrogen storage materials can be classified according to the type of binding involved in the hydrogen sorption process. Among the various approaches to Hydrogen storage, various materials have been explored as the candidates namely, metal hydrides, metal-organic frameworks, porous polymer, and porous carbon in consideration to the fast kinetics, excellent cyclability, and high adsorption/storage capacity.

The hindrance to utilizing hydrogen as the alternative fuel is the absence of appropriate storage medium. The challenges and demands faced for the storage of hydrogen can be surmounted if the following aspects are adequately addressed

- ❖ Investigation and development of new materials for the storage of hydrogen.
- ❖ Developing suitable and reproducible experimental techniques to identify the storage capacity.
- ❖ The existing storage medium can be improved considerably and the cost and size of the storage medium can also be reduced.

For stationary systems, the weight and volume of the system used for hydrogen storage are not key factors. However, for mobile applications such as fuel cell for electric vehicles or hydrogen-fueled (internal combustion) cars, a hydrogen storage system has to be compact, safe, and affordable. In 1996, the International Energy Agency established the “Hydrogen Storage Task Force” to search for innovative hydrogen storage methods and materials. The US Department of Energy (DOE) hydrogen plan has set a standard for this discussion by providing a commercially significant benchmark for the amount of reversible hydrogen absorption. The benchmark requires a system weight efficiency (the ratio of stored hydrogen weight to system weight) of 6.5 wt% hydrogen and a volumetric density of 62 kg H₂/m³. Because a vehicle powered by a fuel cell would require

more than 3.1 kg of hydrogen for a 500 km range. There are various storage options that meet long-term needs like liquid or solid state storage. Current high-pressure hydrogen tanks and liquid hydrogen meet some although clearly not all near-term targets. The hydrogen storage materials for 2007 targets were based on systems such as solid-state (metal hydrides) or liquid systems. The focus of the DOE was on materials technologies to meet 2010 targets and with potential eventually to meet 2015 targets, as given in **Table 1.2**, although these have not yet been realized. The targets include a 20% penalty for the assumption that hydrogen storage systems (unlike conventional gasoline tanks) are not conformable and have limitations regarding how they may be packaged within the vehicle [5]. The targets also assume a factor (2.5 to 3 times) in terms of efficiency improvement in using a fuel cell power plant compared with a conventional gasoline based internal combustion engine. If efficiency improvements are not as high as projected, this would clearly dictate even more challenging requirements for on-board hydrogen storage to achieve a comparable driving range. The development of a high-capacity lightweight material that could be used to store hydrogen reversibly under ambient conditions seems to be attainable. A viable on-board automotive hydrogen storage system must be compact, lightweight, low-cost, and safe. It must be capable of storing enough hydrogen to provide a reasonable traveling range and good dormancy (ability to retain hydrogen for long time without leakage) [6.7].

Hydrogen storage can be achieved in a number of ways. Among these possibilities, solid state hydrogen storage appears to be promising from various points of view. Regarding solid state storage of hydrogen, many targets have been fixed in the past but none of them could be achieved within the time scales prescribed by Department of Energy (DOE). One such expectation is given in given in **Table 1.2**.

Table 1. 2. Department of Energy (DOE) On-Board Hydrogen Storage Targets

Storage Parameter	Units	2017	Ultimate
System Gravimetric Capacity: Usable, specific energy from H ₂ (net useful energy/max system mass)	kWh/kg (kg H ₂ /kg system)	1.8 (0.055)	2.5 (0.075)
System Volumetric Capacity: Usable energy density from H ₂ (net useful energy/max system volume)	kWh/L (kg H ₂ /L system)	1.3 (0.040)	2.3 (0.070)
Gravimetric hydrogen density	Wt %	5.5	7.5
Cycle life	Cycles	1500	1500
Min/max delivery temperature	°C	-40/85	-40/85

Charging/Discharging Rates			
Charging/discharging Rates	min	3.3	2.5
System fill time (for 5 kg)	kg H ₂ min	1.5	2.0
Minimum full flow rate	(g/s)/kW	0.02	0.02
Start time to full flow (20 °C)	s	5	5
Start time to full flow (-20 °C)	s	15	15

In the use of hydrogen as fuel, the differences in the volumetric and gravimetric densities contribute to the search for an appropriate storage medium. From this point of view solid state hydrogen is preferred to other forms of hydrogen storage. The data given in **Table 1.2** is one of the many targets fixed by DOE and these are frequently changed depending on the progress made on the research side on selection of solid-state material. Pictorial representation of the comparison of volumetric and gravimetric densities of hydrogen on typical storage media is given in **Fig.1.4**. There are other forms of this representation in literature and hence this figure should not be considered as unique one. The most moderate level of storage namely 6.25 weight percent is also denoted in the figure and it appears to be in the midst of the storages that are possible but only other considerations like cost, availability and other factors have to be taken into account in the final selection of material for hydrogen storage.

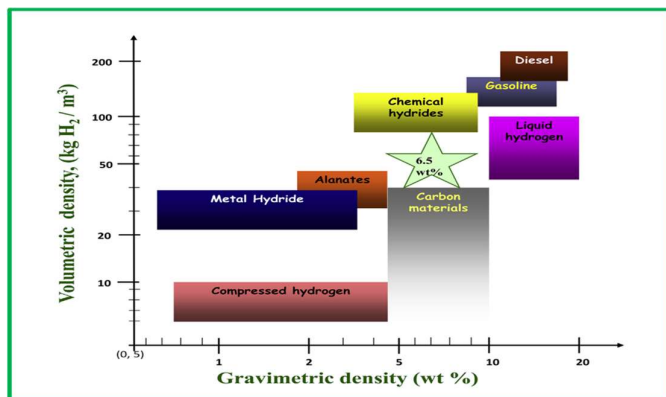


Fig.1.4. Comparison of Volumetric and Gravimetric Density of Hydrogen with Various Storage Media. Reproduced from Reference number [4].

The transition to hydrogen-based economy depends on production, transport, storage and utilization and a pictorial sequence is shown in **Fig.1.5.**

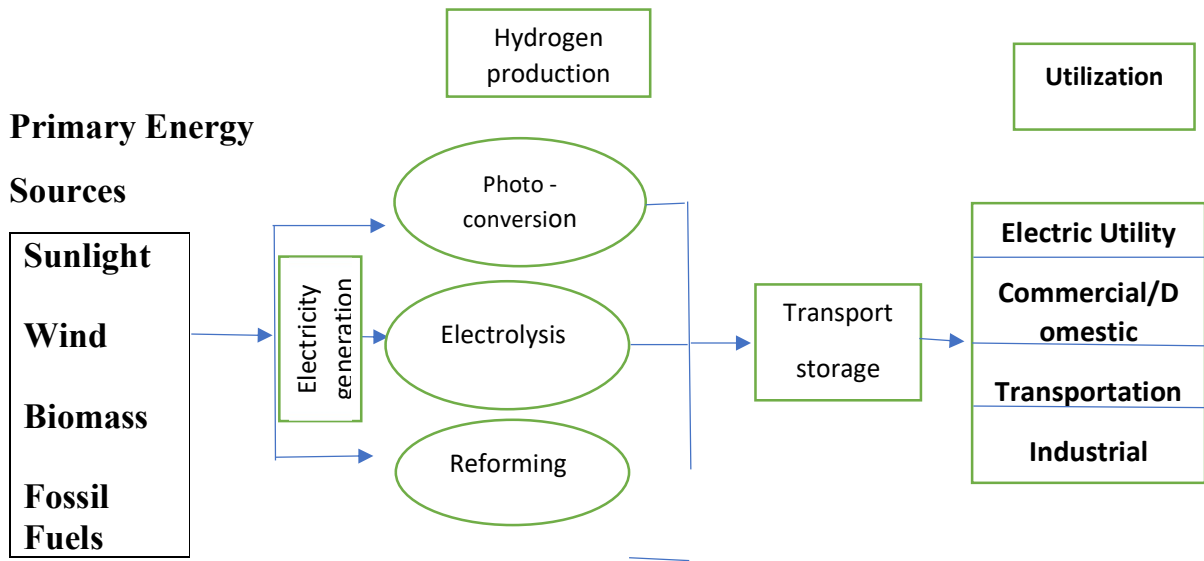


Fig.1.5. Hydrogen energy system a simple manifestation

It is seen that there are alternate possibilities exist in the production and storage of hydrogen as seen from this figure. The method that can be employed depends on various factors like cost and sustainability and these factors will decide which method can be adopted for this two steps in hydrogen economy.

1.5. Fundamentals of Hydrogen Storage

1.5.1. Adsorption

Adsorption is the accumulation of atoms, or molecules from the gas, liquid, or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of the adsorbent. This process differs from absorption, in which a fluid (the adsorbate) is dissolved by or permeates a liquid or solid (the adsorbent), respectively. Adsorption is a surface-based process while absorption involves the whole volume of the material. The term sorption encompasses both processes, while desorption is the reverse of it.

1.5.2 Chemisorption

Chemisorption (or chemical adsorption) is adsorption in which the forces involved are the valence forces of the same kind as those operating in the

formation of chemical compounds. The problem of distinguishing between chemisorption and physisorption is basically the same as that of distinguishing between chemical and physical interaction in general. No absolutely sharp distinction can be made and intermediate cases exist, for example, adsorption involving strong hydrogen bonds or weak charge transfer.

Some features which are useful in recognizing chemisorption include:

- The phenomenon is characterized by chemical specificity.
- Changes in the electronic state may be detectable by suitable physical methods.
- The chemical nature of the adsorptive (s) may be altered by surface dissociation or reaction in such a way that on desorption the original species cannot be recovered; that is mostly chemisorption may not be reversible.
- The elementary step in chemisorption often involves an activation energy.
- Since the adsorbed molecules are linked to the surface by valence bonds, they will usually occupy certain adsorption sites on the surface and only one layer of chemisorbed molecules is formed (monolayer adsorption), in monolayer adsorption all the adsorbed molecules are in contact with the surface layer of the adsorbent.

In the case of hydrogen chemisorption (**Figure.1.6.**), the H₂ molecule dissociates into individual atoms, migrates into the material, and binds chemically with a binding energy. The bonding is strong, and desorption takes place at higher temperatures. Thus, chemisorption may not useful for the practical storage of hydrogen.

1.5.3. Physisorption

Physisorption (or physical adsorption) is adsorption in which the forces involved are intermolecular forces (Van der Waals forces) of the same kind as those responsible for the imperfection of real gases and the condensation of vapors, and which do not involve a significant change in the electronic orbital. The term van der Waals adsorption is synonymous with physical adsorption.

The adsorption of hydrogen in carbonaceous materials corresponds to the amount of hydrogen adsorption which takes place near the carbon surface only due to the physical forces.

Some features which are helpful in recognizing physisorption include:

- The phenomenon is a general one and occurs in any solid/fluid system, although certain specific molecular interactions may occur, arising from particular geometrical or electronic properties of the adsorbent.
- Evidence for the perturbation of the electronic states of adsorbent and adsorbate is minimal.
- The energy of interaction between the molecules of adsorbate and the adsorbent is of the same order of magnitude as, but is usually greater than, the energy of condensation of the adsorbate.
- Under appropriate conditions of pressure and temperature, molecules from the gas phase can be adsorbed in excess of those in direct contact with the surface (multilayer adsorption or filling of micropores, In multilayer adsorption, the adsorption space accommodates more than one layer of molecules and not all adsorbed molecules are in contact with the surface layer of the adsorbent).

In the case of physisorption (**Figure.1.6**), hydrogen remains molecular and binds on the surface with a binding energy in the meV range. Hence, it desorbs even at low temperatures.

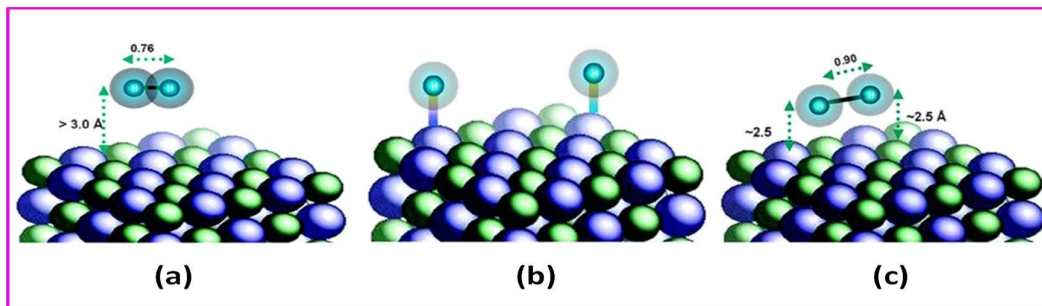


Figure 1. 6. Adsorption of hydrogen on solids, (a) physisorption, (b) chemisorption, and (c) quasi-molecular bonding. Reproduced from the reference number [13].

The physisorption of gases follows two basic rules: the monolayer adsorption mechanism, and the decrease of the amount adsorption with the increasing temperature. It follows that the adsorption capacity of hydrogen on a material depends on the specific surface area of the material and that higher temperatures will lower the adsorption capacity. The total storage capacity in a porous solid is, however, not only the adsorption capacity, but also the sum of contributions due to adsorption on solid surface and that due to compression in the void spaces [9,10].

The third form of binding is where the bond between H atoms in a H_2 molecule is weakened but not broken. The strength of binding is intermediate between physisorption and chemisorption (binding energy in the 0.1-0.8 eV range) and is ideal for hydrogen storage under ambient pressures and temperatures. This form

of quasi-molecular binding has two origins. Kubas et al., has shown that charge donation from the H₂ molecule to the unfilled d orbitals of transition-metal atoms and back-donation of electrons from the transition-metal atom to the antibonding orbital of the H₂ molecule is responsible for this quasi-molecular bonding [11]. This interaction is due to donation of charge from the highest occupied orbital of the ligand (H₂) to the empty metal orbitals and a subsequent back-donation from filled d-orbitals into the lowest unoccupied orbital of the ligand [12]. On the other hand, Niu et al., have shown that the electric field produced by a positively charged metal ion can polarize the H₂ molecule, which can then bind to the metal cation in quasi-molecular form. In both cases, multiple hydrogen atoms can bind to a single metal atom [13].

Yet another method to store hydrogen is '*Spillover*': Additives act as a catalytic active center for the dissociation of hydrogen. The dissociated hydrogen atoms then can *spillover* from the additive sites to the carbon or other network and finally become bound to surface atoms. Besides the high polarizability and the high surface areas, adsorption can be increased by a curving of the structure. The curved surface leads to an overlap of the potential fields of surface atoms and therefore to an increase of the adsorption energy, up to 30 kJ mol⁻¹ [12].

1.6. Hydrogen Storage

Current on-board hydrogen storage approaches involve compressed hydrogen gas tanks, liquid hydrogen tanks, cryogenic compressed hydrogen, metal hydrides, high-surface-area adsorbents, and chemical hydrogen storage materials. Storage as a gas or liquid or storage in metal hydrides or high-surface-area adsorbents constitutes "reversible" on-board hydrogen storage systems because hydrogen regeneration or refill can take place on-board the vehicle. For chemical hydrogen storage approaches (such as a chemical reaction on-board the vehicle to produce hydrogen), hydrogen regeneration is not possible on-board the vehicle; and thus, these spent materials must be removed from the vehicle and regenerated off-board.

Although hydrogen appears to be a possible replacement for fossil fuels, it does not occur in nature as fuel. Rather, it occurs in the form of chemical compounds like water or hydrocarbons that must be transformed to yield hydrogen. One of the basic elements of nature, hydrogen is the universe's simplest element, with each atom composed of just one proton and one electron. It is the most abundant element as well. More than 30 percent of the mass of the Sun is atomic hydrogen. Considering the transport sector, to achieve a comparable driving range and performance as with modern diesel vehicles, a breakthrough in on-board vehicle hydrogen storage technology may still be required. Conventional storage such as

compressed gas cylinders and liquid tanks can be further improved and strengthened, become lighter and less expensive. Additional research and development work are required to appropriately evaluate and further advance the performance of hydrides. [14].

1.7. Ways of Hydrogen storage

Hydrogen in some form is all that is required for a fuel cell to run a hydrogen fueled car. In vehicles, hydrogen can be stored as a cryogenic liquid or a pressurized gas. However, liquefying hydrogen is expensive and storing this extremely cold fuel in a vehicle is a difficult engineering task. Storing hydrogen requires significant energy expenditure for compression, stringent safety precautions, and bulky, heavy storage tanks. Natural gas is used as a hydrogen source in some fuel cell designs for large stationary electricity generating stations. However, this also prevents many of the drawbacks of cryogenic liquefaction or compression when considering mobile applications with weight and space limitations. Metal hydride storage of hydrogen is possible. However, weight constraints currently limit the potential range of a vehicle with this particular hydrogen storage technology. Carbon nanofibers or tubes as hydrogen storage also have been proposed; however, this technology is far from commercial development. Intermetallics, carbon materials, porous solids, and metal organic frameworks are some of the options being considered for hydrogen storage purposes. This is also another area of research which is at the crossroads without a proper direction toward the desired goal. The desired goal is the weight percent storage capacity (taken to be around 6.5 weight % on the basis of various considerations like the range of a vehicle with current fuel storage capacity). This expected percentage of hydrogen storage capacity has not been achieved in any of the solid-state storage materials under the desired temperature and pressure conditions (namely near room temperature and atmospheric pressure conditions). The various options that are currently considered are given in **Figure 1.7**.

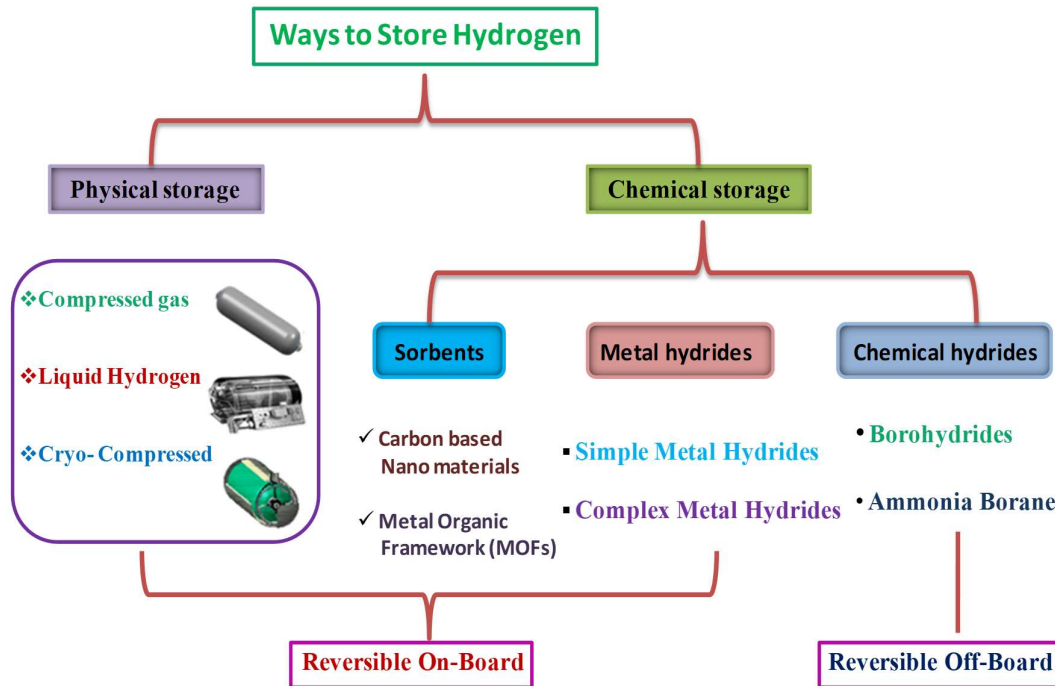


Figure.1.7. Various options for hydrogen storage.

Solid State Hydrogen Storage

The gas and liquid states of storage of hydrogen have considerable energy and weight penalty in addition to safety issues. However, these two forms of storage have been in practice for a long time.. From various points of view, solid-state hydrogen storage appears to be advantageous and may become a viable option [15].

For solid-state hydrogen storage, the following characteristics are expected for the system.

- ❖ Favourable thermodynamics: that, is the storage and release should take place without much heat requirement.
- ❖ The kinetics of adsorption and desorption should be fast enough to be useful for applications on hand.
- ❖ The extent of storage should be sufficiently large enough so that it can be adopted for mobile applications (volumetric and gravimetric density).
- ❖ The material employed should withstand a sufficient cycle number for both adsorption and desorption.
- ❖ The material of choice should have sufficient mechanical strength and durability.

- ❖ The system chosen should be capable of functioning as a good heat transfer medium.

Metal Organic Framework (MOFs)

The metal–organic frameworks (MOFs) are a class of porous materials that were discovered about 40 years ago by polymer scientists. In 1989 Hoskins and Robson proposed a class of solid polymeric materials later known as MOFs [16,17]. For example, the structure of MOF-5 is shown in **Fig 1.8** (a). These materials are crystalline, infinite networks assembled by linking metal ions with various organic linkers through strong bonds [18]. In a basic level, MOFs typify the gorgeousness of chemical structures and the authority for the combination of organic and inorganic chemistry, two disciplines frequently regarded as dissimilar [19]. These MOFs have emerged as an extensive class of crystalline materials with low density unite both high surface areas extending ahead of 6000 m²/g and ultrahigh porosity (up to 90% free volume) tunable pore size, and modifiable internal surface [20]. These properties, make MOFs find application in clean energy storage for gases such as hydrogen and methane and also as adsorbents. Further applications in membranes, catalysis, and biomedical imaging are gaining significance. More recently, it was realized that a few of them can be shown as potential candidates for hydrogen storage materials [21-23]. Interestingly, in particular, the MOF-177, a structure consisting of tetrahedral [Zn₄O]⁶⁺ clusters linked by the tritopic link BTB (1,3,5-benzenetribenzoate), was shown to adsorb reversibly up to 7.5 wt % H₂ at 77 K and 70 bar [24]. However, the majority studies of H₂ adsorption in MOFs were performed at very low temperatures (mostly at 77 K). However, no significant hydrogen uptake on the MOFs have been obtained at room temperature [25]. In addition, systematic studies on the effects of structural and surface properties, e.g., metal oxides, organic linking units, surface areas, and pore volumes, on the hydrogen storage capacities are insufficient, particularly at room temperature [22, 26-30]. As a possible hydrogen storage material MOFs are still in its infancy and the work is yet to be individually confirmed.

Covalent Organic Framework (COFs)

An addition to the family of crystalline microporous materials are the Covalent organic frameworks (COFs). These are a class of crystalline materials built from organic “linkers” which are made up of light elements (C, O, B, and Si) and held together by strong covalent bonds. For example, COF was synthesized by condensation of 1,3,5-tri(4-aminophenyl) benzene (TPB) and 2,5-dimethoxyterephthalaldehyde (DMTP) under solvothermal conditions. The

structure is shown in **Fig. 1.8 (b)** it's called TPB-DMTP-COF [31]. Particularly, due to the absence of characteristically weaker metal-ligand bonds, which is responsible for the metal-organic frameworks chemically and thermally unstable, covalent organic frameworks generally demonstrate surprising thermal and chemical stability, in several ways resembling some high melting-point amorphous polymers [32]. The covalent organic frameworks (COFs) are different from other organic polymers, however, they are crystalline and have a well-organized macromolecular structure. They exhibit low density high porosity and they contain high surface area making them attractive candidates for hydrogen storage. Because of their significantly lower density compared to MOFs, COFs have an advantage in the hydrogen gravimetric storage capacity [32-34]. Interestingly, Omar M. Yaghi and William A. Goddard III *et al.* reported COFs as exceptional hydrogen storage materials. They predicted the highest excess hydrogen uptakes at 77 K as 10.0 wt % at 80 bar for COF-105, and 10.0 wt % at 100 bar for COF-108. This is the highest value reported for associative hydrogen storage of any material [35].

Metal Hydrides

Another means of hydrogen storage is that of metal hydride storage, hydrogen can be combined with many metals to form hydrides that will release hydrogen upon heating. Many metals, intermetallics compounds and alloys react with hydrogen and form mainly solid metal-hydrogen compounds. Hydrides exist as ionic, polymeric covalent, volatile covalent and metallic hydrides. Fig 1.8(d) shows the structure of NaAlH_4 . The demarcation between the various types of hydrides is not sharp, they merge into each other according to the electronegativities of the elements concerned. Hydrogen reacts at elevated temperatures with many transition metals and their alloys to form hydrides. Metal hydrides are composed of metal atoms that constitute a host lattice and hydrogen atoms trapped in interstitial sites. The chemisorption accounts for compounds containing hydrogen such as metal hydrides, chemical hydrides, complex hydrides, nitrides and related compounds, from which H_2 can be released under specific conditions, usually via heating at high temperatures. The basic principle is that certain metals alloys absorb hydrogen to form a metal hydride. Therefore, chemisorption is basically an activation process that requires additional energy to break the chemical bond between H and other elements, which makes the recovery of H from those materials, energy-inefficient and the recycling of such hydrides is problematic. For example, magnesium hydride, one of the most extensively investigated, low cost and natural abundant compounds, has a high hydrogen storage capacity of up to 7.6%; but heating up to 300°C is needed to release the H_2 , which corresponds to up to 2.4 wt% of stored H_2 to be used to feed the high endothermic reaction, leaving only 5.2 wt% H_2 available for use. Therefore, the high thermodynamics, slow kinetics combined with poor

cyclabilities have prevented the widespread adoption of magnesium hydrides for practical application. Metal hydrides are effective to store large amounts of hydrogen in a safe and compact way. All the reversible hydrides working around ambient temperature and atmospheric pressure consist of transition metals; therefore, the gravimetric hydrogen density is limited to less than 3 mass %. Thus, with the promising results observed to date, metal hydrides clearly have potential as hydrogen storage systems with the limits of this potential yet to be fully defined.

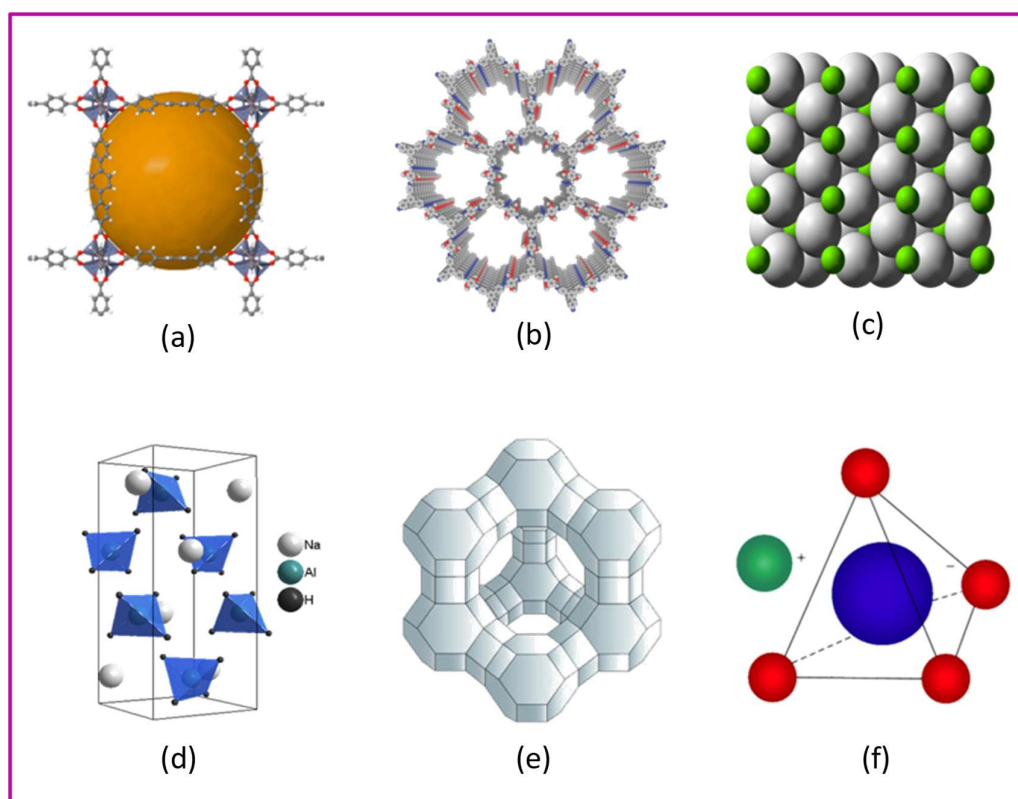


Fig.1.8. Various solid-state possibilities of hydrogen storage (a) MOF-5, (b) TPB-DMTP-COF, (c) Magnesium hydride, (d) NaAlH₄, (e) Zeolite-Y and (f) NaBH₄

Complex hydrides

The first second and third group light elements, e.g. Li, Mg, B, Al, build a large variety of metal-hydrogen complexes. They are especially interesting because of their light weight. The main difference between complex hydrides to metallic hydrides is the transition to an ionic or covalent nature of the bond between the metal and hydrogen. The hydrogen in the complex hydrides is often located in the corners of a tetrahedron with boron or aluminum in the center. The negative

charge of the anion, $[\text{BH}_4]^-$ and $[\text{AlH}_4]^-$ is compensated by a cation e.g. Li or Na. The hydride complexes of borane, the tetrahydroborates $\text{M}(\text{BH}_4)$, and of alane the tetrahydroaluminate $\text{M}(\text{AlH}_4)$ are interesting storage materials, however, they were known to be stable and decompose only at elevated temperatures. The compound with the highest gravimetric hydrogen storage density at room temperature known today is LiBH_4 (18 mass%). Therefore, this complex hydride could be the ideal hydrogen storage material for mobile applications. LiBH_4 desorbs three of the four hydrogen in the compound upon heating at 280°C and decomposes into LiH and boron. The desorption process can be catalyzed by adding SiO_2 and significant thermal desorption was observed starting at 100°C [36]. Recently it has been shown, that the hydrogen desorption reaction is reversible and the end products lithium hydride and boron absorb hydrogen at 690°C and 200 bar to form LiBH_4 [37]. The scientific understanding of the mechanism of the thermal hydrogen desorption from LiBH_4 and the process of absorption remain a challenge and more research work needs to be carried out. A little is known about $\text{Al}(\text{BH}_4)_3$ a complex hydride with a very high gravimetric hydrogen density of 17 weight % and the highest known volumetric hydrogen density of $150 \text{ kg}\cdot\text{m}^{-3}$. Furthermore, $\text{Al}(\text{BH}_4)_3$ has a melting point of -65°C and is liquid at room temperature. Beside of the covalent hydrocarbons, this is the only liquid hydride at room temperature. However, the required temperatures and reaction rates for operation of sodium alanates are inadequate for potential application. Some of the common complex hydrides for their hydrogen storage capacity are given in Table 1.3.

Table 1.3 Common Complex Hydrides for Hydrogen Storage Applications.

Hydride	Hydrogen content (Wt %)
LiAlH_4	10.5
NaAlH_4	7.5
KAlH_4	5.7
$\text{Be}(\text{AlH}_4)_2$	11.3
$\text{Mg}(\text{AlH}_4)_2$	9.3
$\text{Ca}(\text{AlH}_4)_2$	7.7
$\text{Ti}(\text{AlH}_4)_4$	9.3
LiBH_4	18.0
NaBH_4	10.4
$\text{Al}(\text{BH}_4)_3$	17.0

ZEOLITES

The crystal structure of zeolites is composed of channels and cavities which form a pore system large enough for diffusion of molecules. Zeolites have large micropore volumes and thus forms potential candidates for the storage of hydrogen. An example of the pore structure of zeolite Y is shown in Figure 1.8. (e). Hydrogen storage in zeolites can be encapsulation and adsorption. The process involves the diffusion of hydrogen molecules into channels and cages (voids) of the structure. Fraenkel *et al.* reported zeolites as potential materials for the encapsulation of hydrogen [38,39]. In the following years, many different ion-exchanged zeolites were tested as potential hydrogen storage materials [40]. The uptake of hydrogen by adsorption is below 0.5 wt% at ambient temperature conditions and below 2 wt% at 77K and at elevated pressures. For all systems, at low hydrogen loadings, the cell volume of the zeolites decreases due to attractive forces between adsorbent and adsorbates [41]. However, even though at first glance microporous zeolites seemed to be promising materials for hydrogen storage, the capacities and experimental requirements are unfavorable to make them real storage materials [42].

Glass Spheres

Glass spheres are small hollow glass micro balloons whose diameter varies from about 25 to 500 μm and whose wall thickness is about 1 μm . The microspheres are filled by heating in high-pressure hydrogen to temperatures sufficient for rapid diffusion of hydrogen into the microspheres. Upon cooling the low diffusivity of hydrogen at ambient temperature causes the gas to be retained in the microspheres. Hydrogen is then released when needed by reheating the microspheres. Because of the inherently poor thermal conductivity of inorganic glasses, a problem further exacerbated by the morphology and size of hollow microspheres, poor hydrogen release rates have limited further development and implementation of this hydrogen storage method. A possible solution to the poor hydrogen release rates has been realized with the discovery of photo-induced outgassing in which a high-intensity infrared light is used to elicit hydrogen release in selectively doped glasses. This process results in faster response times for the release of hydrogen in glasses than can be obtained by normal heating and may provide a path to superior performance for hydrogen storage in glass microspheres. However, high pressures and high temperatures are stumbling blocks to the use of glass spheres as a hydrogen storage medium for mobile applications. The storage capacity of spheres is about 5—6 wt% at 200—490 bar in favourable cases.

Chemical Storage

Chemical hydrogen storage may offer options with high-energy densities and potential ease of use, particularly if systems involve liquids that may be easily dispensed using infrastructure similar to today's gasoline refueling stations. Most of these reactions are irreversible. Therefore, the spent storage material would have to be regenerated off-board the vehicle because they cannot be reconstituted simply by applying an overpressure of hydrogen gas at a modest temperature and pressure. A number of chemical systems using both exothermic and endothermic hydrogen release are currently under investigation. Chemical compounds containing hydrogen can also be considered a kind of hydrogen storage. These include methanol, sodium, ammonia, and methyl cyclohexane. For an example of the pore structure of NaBH_4 is shown in Figure 1.8. (f). Under STP conditions all of these compounds are in liquid form and thus the infrastructure for gasoline could be used for transportation and storage of these compounds. There is a clear advantage compared with gaseous hydrogen, which demands leak-proof, preferably seamless piping and vessels. The hydrogen storage capacity of these chemical compounds is good: 8.9 wt% for methanol, 15.1 wt % for ammonia, and 13.2 wt % for methylcyclohexane. These figures do not include the containers in which the liquids are stored. Because the containers can be made of lightweight composites or even plastic in some cases, the effect of the container is negligible especially with larger systems. A number of processes have been tried to release hydrogen from ammonia borane in the solid state and in solution. Catalysts, including a range of acids and transition metal complexes, have been demonstrated and are being optimized to enhance the amount of hydrogen released as well as the overall kinetics for hydrogen release. However, efficient and cost-effective regeneration of the spent fuel resulting from the dehydrogenation of ammonia-borane is critical to the successful application of ammonia-borane as an on-board hydrogen storage material [43,44].

The chemical storage of hydrogen also has some disadvantages. The storage method is irreversible, the compounds cannot be charged reproducibly with hydrogen. The compounds must be produced in a centralized plant and the reaction products have to be recycled somehow. This is difficult especially with ammonia, which produces highly environmentally unfavorable nitrogen oxides. Other compounds produce carbon oxides, which are also unfavorable.

Carbon Materials

The element carbon is present in nature in a variety of allotropes that can be classified based on its hybridization (See Figure 1.9). Carbon allotropes have been widely investigated for their unique features, like thermal and electrical conductivity, optical and mechanical properties. For instance, sp^3 -hybridization is responsible for the structure and properties of diamond, while sp^2 -

hybridization characterizes graphite, carbon nanotubes, and graphene, which is a single layer of carbon atoms arranged in a 2D hexagonal lattice. Depending on the atomic hybridization, the macroscopic properties of carbon-based materials can dramatically vary for each allotropic form. The sp -hybridization comes next in the series, and the corresponding carbon allotrope is known under the name of carbyne which has the feature of extending in one dimension. Because of this property, carbynes are also named carbon nanowires, representing at the nanoscale mono-dimensional atomic chains. Carbon have these uniqueness for creating different types of allotropic forms and hence can show a variety of applications.

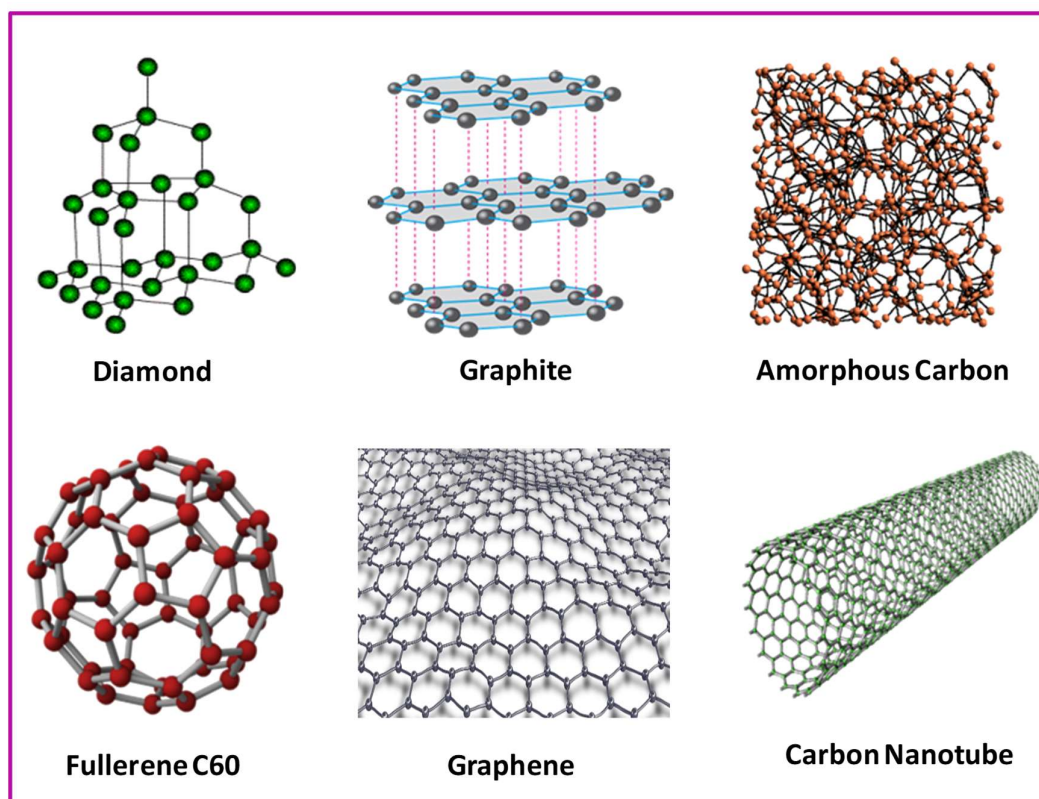


Fig.1.9. Some of the possible allotropic forms of carbon

Carbon Materials for Hydrogen Storage

Carbon materials are another set of candidates for hydrogen storage because of their combined adsorption ability, high specific surface, pore microstructure, and low mass density. Hydrogen sorption by carbon materials has assumed considerable importance especially in the context of these properties in recent times.

Carbon clusters that can be formed can be varied with the cluster size starting from 2 to 2000 carbon atoms. The three well-known forms of carbon are diamond,

graphite, and fullerenes. In diamond each carbon has four bonds to its neighbors and forms a three-dimensional lattice. Graphite is built of two-dimensional hexagonal sheets of carbon atoms in which the carbon-carbon distance in the plane is 1.42 Å and the distance between the sheets is 3.35 Å.

Various morphologies are promoted by carbon, which form sheets in the case of graphite, whereas a hard crystalline solid is found in diamond. Carbon materials with different morphologies such as cone, onion, belt, and sphere are also known.

Although a variety of morphologies are possible, the covalence of the carbon atoms is maintained. The strong covalent in-plane bonding and weak Van der Waals interplane bonding result in anisotropic physical properties that are useful for applications in lubrication and other processes requiring “slippage” between layers. The in-plane carbon-carbon bonds are shorter than those of diamond but the interlayer distance is larger.

The existence of variable hybridization states is possible in carbon from sp^3 . Variable valency states of fractional values are also possible. The classical example is the difference between sp^3 and sp^2 bonding properties seen in diamond and graphite. Variable valency states of fractional values are also possible. For diamond the three-dimensional, fourfold coordinated sp^3 structure is rigid and almost isotropic in its properties. In contrast, the sp^2 bonding in graphite is planar and threefold coordinated in the planes with weak bonding between planes. Besides the usual hybridization (sp^3 , sp^2 , and sp), structures involving more than a single type of hybridization (mixed forms) and intermediate hybridization of the type sp^n (with $3 > n > 1$, $n \leq 2$) are included.

The former cover mixed short-range order carbon species with more or less randomly distributed C atoms, whereas the lattice describe a structure in which curvature introduces strains responsible for the mixture of a different hybridization. For example, the structure of fullerene C_{60} facilitates attribution of intermediate hybridization of sp^2 and sp^3 to the carbon atoms.

Various geometric forms can be obtained, such as platelets, sheets, and disks, flowers, cones and ball shapes.

Carbon can form meta stable compounds in which the most stable form is graphite. However, the hardest substance with a crystalline nature (diamond) is a meta stable state.

Similarity to Biological Architecture: “Haeckelites” Biological structures are formed by carbon materials such as the helical structure of DNA, and an equal number of hexagons and heptagons can lead to the formation of different morphologies.

The minimum storage capacity for economic commercial application has been estimated to be 6.5 wt% as postulated by DOE. It is necessary to recall that hydrogen storage up to 67 weight % has been reported in exotic carbon materials, though the reliability of this result has been doubted at various stages [45,46]. Since carbon material was first applied to hydrogen storage in the 1980s, various carbon materials, including activated carbon, CNTs, template carbon, carbon fiber, and even graphene have been extensively explored as hydrogen storage media. The introduction of these nanomaterials may have manifold impacts: improved cyclability, better stability, ease of fabrication and handling, higher electronic conductivity, higher power density and so on. Hydrogen sorption by carbon materials has been investigated from a variety of points, like physisorption at low temperatures (77 K), the relationship between surface area of carbon and adsorption capacity, the methods of synthesis and activation of carbon to enhance the surface area and sorption capacity, manipulative carbon materials in a variety of dimensional architectures

Activated carbon is a synthetic carbon containing small graphite crystallites and amorphous carbon. It is a form of carbon that has been processed to make it extremely porous and thus to have a very large surface area available for adsorption or chemical reactions. The pore diameters are usually less than 1 nm and possess a specific surface area up to 3000 m²/g or even higher. Activated carbon is produced from carbonaceous materials like nutshells, wood and coal. It can be produced in one of the following processes: Advanced carbon is prepared from carbon-rich organic precursors by a thermal method (dry distillation) to form carbonized organic precursors, which can be activated to increase the pore volume either thermally or chemically. Chemically activated carbon materials are synthesized via heat treatment of a mixture of carbon samples and chemical activation agent at a distinctive temperature between 450°C and 900°C. Numerous activating agents are proposed in the literatures. KOH, NaOH, H₃PO₄, and ZnCl₂ are the most employed agents. Strong bases like KOH and NaOH do not frequently supply as dehydrating agents, but as oxidants, where as ZnCl₂ and H₃PO₄ act as dehydrating agents. Although KOH chemical activation is proven to be a universal way to develop the pore structure in carbons, the mechanism of chemical activation has not been fully understood due to the process complexity and variable process parameters such as the ratio of KOH/C, activation time, and activation temperature. The properties enable the activated carbon materials to be useful in a variety of fields such as gas storage (H₂, CH₄, or CO₂) and power storage i.e., battery or supercapacitor. In the early 1980s the first work was started to investigate the potential of hydrogen storage in the capillaries of activated carbon at low temperatures. The gravimetric measurements resulted in less than

2 wt% adsorption at 77 K or room temperature with a specific surface area of 2600 m²/g. Experimental results on activated carbon show a linear dependence of the excess hydrogen absorption capacity on the specific surface area of the activated carbons. Those values not sufficient for DOE desired hydrogen storage capacity.

Fullerene is a spheroidal or polyhedral-shaped carbon molecule. It can be described as a sphere and is composed of 20 triangular equilateral faces with 12 apices, each at the junction of 5 triangles. Fullerene was discovered in 1984 by Harry Kroto and Richard Smalley at Rice University [47, 48]. The fullerene molecule closely resembles a soccer ball. It has 20 hexagons and 12 pentagons. Structural studies of C₆₀ have shown it to possess a face-centered cubic lattice. The lattice parameter is $a = 14.17 \pm 0.001 \text{ \AA}$, with a Vander Waals space of 2.9 Å. Because of the high symmetry of the molecule, the ¹³C-nuclear magnetic resonance spectrum and the infrared absorption spectrum are particularly simple [49]. C₆₀ has been the most thoroughly studied member of fullerenes since it is produced abundantly in the carbon soot by the arc discharge of graphite electrodes, has high symmetry, less expensive, somewhat inert under mild conditions, and it shows negligible toxicity. Fullerenes have been investigated as a potential hydrogen storage material based on their capability to react with hydrogen [50,51]. According to theory a maximum of 60 hydrogen atoms can be attached both to the inside (endohedrally) and outside (exohedrally) of the fullerene spherical surface and a stable C₆₀H₆₀ isomer can be formed, which accounts for a storage capacity of 7.7 wt% hydrogen. Although the storage capacity of fullerenes is high, the hydrogenation of fullerene currently requires high pressures and temperatures for the reaction to take place by overcoming the reaction barrier. To overcome this potential barrier, high temperatures (>673 K) and pressures (>60 MPa) are required [52].

Nanostructured carbon materials synthesized via simple processes and which use readily available and low-cost precursors are now considered as key materials for the generation and storage of sustainable energy and for environmental remediation [53]. In this regard biomass and biomass wastes are potential precursors for a large variety of carbon materials with different morphology, highly porous and high specific surface area. However, carbon nanogel derived from polymeric resin and also the polymeric precursor based porous materials have been widely studied as potential sorbents for hydrogen due to their high surface area, large pore volume, light weight, good chemical stability, and the ease with which their porosity can be tailored. In general, the H₂ storage capacity of porous carbon material is proportional to the specific surface area and micropore volume [54]. Moreover, the size and the shape of the pores play a

crucial role in hydrogen uptake. Sevilla *et.al.* reported porous carbide derived carbon material with KOH activation. Interestingly after the KOH activation process the hydrogen storage property is increased simultaneously. In this regard, the activated carbons exhibit an enhancement of up to 63% in hydrogen uptake from 3.8 wt% for the carbide derived carbon to 6.2 wt% at 77K and 20 bar. At 1 bar the super activated carbide derived carbon (CDC) store 2.7 wt% hydrogen, which is amongst the highest values for activated carbon [55]. High surface area carbon (3500 m²/g) materials have been obtained via chemical activation of polypyrrole with KOH. The carbons show hydrogen storage capacity of up to 7.03 wt% at 77K and 20 bar [56]. Tian *et al.* prepared KOH-activated carbon material derived from resorcinol and furfural, displaying a hydrogen uptake of 5.2 wt% at 77K [57]. More recently, Robertson and Mokaya *et al.* prepared activated carbon from resorcinol and formaldehyde through KOH activation process. The obtained activated carbon materials exhibit 3.5–4.3 wt% hydrogen storage at –196°C and 20 bar. [58]

Hydrogen storage in pure (undoped) carbon materials

Several reports both experimental and theoretical attribute the uptake of hydrogen to physisorption on carbon. The mechanism of hydrogen storage on carbon nanomaterials still remains unclear (For typical data of hydrogen uptake by carbon materials See Table. 1.4).

Table 1.4 Literature Data on Hydrogen Storage on a variety of Carbon Materials

Adsorbent	Temperature (K)	Pressure (MPa)	Weight % of Hydrogen	Ref
MWNT	300	12	0.3	[59,60]
	77		2.27	
SWNT	77	0.1	0.8	[61]
SWNT treated	Acid 77	3.1	1.8	[62]
	303	11.5	0.26	
ACF	303		<0.2	
CNT				

Wood based carbon	303			<0.3	[63]
CA800	77	2		3.9	[64]
CB850	77	2		5.5	
Amorphous carbon	299	1		0,05	
Fishbone CNF	299	1		0.03	[65]
Platelet CNF	299	1		0.03	
Ribbon CNF	299			0.02	
Nanofibers (Pd/C)		0.1 to 10		0.04-0.33	[66]
AC	77-303	2-10		0.85-5.5	[67]
CNF	303	10		0.35	
A-CNF	303	3-10		0.33-1.03	
ZIF templated carbon	77	2		2.6-3.1	[68]
				3.9-6.2	

MWNT -Multiwall nanotube; **SWNT**- Single wall nano tube; **CNT**- carbon nano tube; **ACF** activated carbon fiber

Enormous efforts to achieve the desired levels of storage of hydrogen in solid-state materials have not yielded expected results. Possibly this has given rise to some frustration regarding the possibility of achieving the required levels of storage. Nature has shown that in carbon materials hydrogen storage can vary from low values to 25 wt% in methane. However, this level of storage involves covalent bonding and hence requires sufficient energy to release the hydrogen back. To achieve the desired levels of hydrogen storage capacity in carbon materials or in any other solid-state material, one has to resort to a configuration and morphology of solid state materials in such a way that each constituting atom

should be capable of generating more than one void volume in the solid, and this may be possible only if architecting solids becomes possible. Among the solid-state materials, lightweight metals and carbon appear to be the appropriate choice if both the thermodynamics and kinetics of hydrogen absorption and desorption considered. To date, this seems to be a far cry from reality.

Alternatives to store hydrogen for DOE desired level

The work related to hydrogen storage in nanostructured carbon materials and particularly heteroatom (N, B and P) containing carbon materials have been pursued [69-72]. The introduction of heteroatoms like nitrogen, boron and phosphorus in carbon materials has been shown to produce activation centres for dissociation of molecular hydrogen and thus possibly increase in hydrogen storage by virtue of the possibility of dissociative activation of hydrogen at heteroatom centres. Heteroatom substituted carbon materials have been proposed as alternate option for hydrogen storage application. Even though reversible nature of the hydrogen absorption/ desorption process on/in carbon-based materials and high surface area sorbents has been realized, they suffer from lower hydrogen storage capacity, especially under desirable operating conditions. However, irrespective of their high surface area, the presence of heteroatom on the surface of carbon materials has been regarded as an attractive feature to increase the hydrogen storage capacity [73-80]. It is necessary to examine how the hetero atom substituted carbon materials appear to be suitable for hydrogen storage applications. The essential points in relation to this question are:

- Heteroatom substitution provides appropriate centres for the dissociation of molecular hydrogen. Since hetero-atoms take up substitution positions in the lattice, there is facile transport of hydrogen atoms on to the carbon surface.
- The possibility of generating layered configuration in carbon materials (graphene) offers additional advantage in terms of appropriate sites in layered configurations. This configuration possibly not only generated residual valency required for hydrogen migration but also provides enough active centres for hydrogen storage.
- The heteroatoms may segregate and thus generate a core shell configuration which may be providing sites which are both geometrically and electronically suitable for the hydrogen activation and transport. This type of modified surfaces may not be generated in other materials. In fact, that a surface is formed means automatically there is shell around the core bulk and hence surface atoms behave differently with respect to the atoms in the bulk. This configuration may be one of the reasons for the surface atoms to behave differently with respect to the atoms in the bulk.

- The substituted heteroatoms in a carbon layer provide nearly equipotential sites facilitating the free transport of hydrogen over the layers.
- The possibility of dimensionality in carbon materials especially possibility of generating one or two-dimensional architectures may be appropriate for hydrogen sorption behavior.

It is hoped that the scene will soon change and that reproducible, reliable storage capacity will be achieved.

Heteroatom-Doped Carbon Materials for Hydrogen Storage

Heteroatoms doped Graphene

The fascinating properties of pristine graphene (single atom-thick layer of sp² bonded carbon atoms tightly packed into a 2D honeycomb lattice) are now largely understood and well-recognized through extensive research in the past years. Although the lack of intrinsic bandgap and catalytic abilities seem to greatly limit the practical applications of pristine graphene, the interest on this 2D material is going to continue owing to its structural transformability and highly tunable properties. A large variety of methods have already been developed for the synthesis of graphene materials, from which various doping strategies can be derived. The methods for heteroatom insertion can be categorized into in situ approaches and post treatment approaches. In situ approaches, which simultaneously achieve graphene synthesis and heteroatom doping, include chemical vapor deposition (CVD), Hydrothermal, ball milling, and bottom-up synthesis. Post-treatment methods include wet chemical methods, thermal annealing of graphene oxides (GO) with heteroatom precursors, plasma and arc-discharge approaches.

Modifying the graphene surface has been considered as one of the techniques for accomplishing higher hydrogen storage capacity. As discussed in this section, heteroatom doping can endow graphene with various new electromagnetic, physicochemical, optical, and structural properties, depending on the dopants and doping configurations. Different approaches have been developed for heteroatom doping. Doping type, level and configurations are critically determined by the chosen precursors, starting graphene material, reaction time, temperature, etc. Even though the remarkable progress has been made thus far, it is, however, still a current challenge to precisely control heteroatom doping. Based on both experimental and theoretical studies, we have discussed the distinct effects induced by particular dopant, different bonding configurations of a given dopant, and synergistic action between co-dopants. However, the current understanding on the properties of doped graphene materials is still far from complete and sometimes even contradictory because of

the large and uncontrolled heterogeneity of the materials obtained from the synthesis approaches adopted [81].

In addition, the physicochemical and electronic properties of graphene can be drastically altered by molecular and atomic doping. Because boron (B) and nitrogen (N) have similar sizes and valence electron numbers as carbon (C), it is reasonably easier to incorporate them into graphene. However, V. Tozzini *et al* [82] reported modifying graphene materials with metal nanoparticles can improve the gravimetric storage capacity via the polarization-induced interaction between metal and hydrogen atoms. But, decorated nanoparticles suffer from aggregation and poor stability. Parambath *et al* [83], reported the heteroatom doping can help nanoparticle dispersion and high coverage on graphene material, as well as hydrogen adsorption. It shows the hydrogen capacity around 7 at% at 25°C and 2 MPa. Therefore, it is desirable that the adsorbed H atoms bonded with the C atoms near the doped N atom can diffuse to the other C atomic sites, and subsequently the adsorbed H atoms can be easily desorbed to form H₂ molecules once the electric field is removed.

Interestingly, nitrogen-doping is nowadays an extensively applied concept in graphene materials. The chemical nature of the other heteroatoms might not be as absolutely appropriate for incorporation into a carbonaceous backbone, as is the case for nitrogen. In the following discussion an overview of highly advanced graphene materials, doped with boron or phosphorus is given.

At the same time, Miwa *et al* discussed B-doping-induced graphene polarization and electron deficiency is also favorable for hydrogen adsorption, which is even more effective than graphitic-N doping [84]. E. Beheshti *et al.* reported theoretical calculations show a high H₂ storage capacity (8.38 wt%) of Ca-decorated B-doped (12 at%) graphene. Further, the desirable interaction between H₂ and B, Ca-decorated graphene makes H₂ storage possible even at room temperature and ambient pressure [85]. For instance, the presence of substitutional boron atoms on graphene improves the hydrogen adsorption on the carbon atoms neighboring the boron substitutional sites [84]. Furthermore, only limited reports are available for the synthesis of phosphorous substituted graphene and used as hydrogen storage material [86]. However, some reports has been found so far on whether or not the P-doping can improve the activity and the hydrogen storage capacity of graphene material [87]. Theoretical studies have predicted the influence of P-doping on the band gap of graphene, and also the incorporation of phosphorus should be energetically more favorable. Furthermore, calculations have also shown that P-doping improves the electron-

donor properties of a graphene material which is beneficial to enhance the hydrogen storage capacity.

Heteroatoms doped Carbon Nanotubes (CNTs)

Carbon nanotubes were thought to have been discovered in 1991 by Sumio Iijima [88]. New findings reveal, however, that two Soviet scientists were the first to observe a hollow nanometer carbon tube in 1952 [89]. The first specimens observed would later come to be known as single walled nanotubes (SWNTs) because they are simply one layer of graphite. After Iijima the discovery of multi-walled nanotubes (MWNTs) followed. MWNTs are simply several layers of graphite which are then rolled into a cylinder. The layers of graphite form concentric circles if the tube were to be viewed from either end. Carbon nanotubes are long cylinders of 3-coordinated carbon, slightly pyramidalized by curvature from the pure sp^2 hybridization of graphene, toward the diamond-like sp^3 . Infinitely long in principle, a perfect tube is capped at both ends by hemi-fullerenes, leaving no dangling bonds. A single walled carbon nanotube (SWNT) is one such cylinder, while multiwall tubes (MWNT) consist of many nested cylinders whose successive radii differ by roughly the interlayer spacing of graphite (see SWNT is limited by curvature-induced strain to ~ 0.4 nm [90]. MWNT may have outer shells >30 nm in diameter, with varying numbers of shells, affording a range of empty core diameters. Lengths up to 3 mm have been reported [91]. Nanotubes are distinguished from less-perfect quasi-one-dimensional carbon materials by their well-developed parallel wall structure [92]. Nowadays carbon nanotubes are prepared using CVD, laser ablation, arc discharge and pyrolysis of hydrocarbons [93].

Among nanostructures, tubular materials are particularly attractive that their morphology is assisted by an inherent multifunctionality that arises from four different contact regions: a tube opening, outer surface, inner surface, and interstitial region. These properties show potential for the realization of highly functional, effective and resource saving nano-devices such as sensors, capacitors, or storage and release systems. Surprisingly, despite their relatively small surface area and pore volume, CNTs and carbon nanofibers may have a high hydrogen storage capacity [94,95].

For decades, CNTs have been examined with a particular attention at the level of their potentiality to adsorb hydrogen in their regular nanometric microstructure. A number of publications are devoted to the experimental and theoretical study of gas adsorption on different adsorbent structures. In 1997, Dillon *et al.* found that single wall carbon nanotube (SWNTs) soot could absorb about 5 to 10 wt% of hydrogen at 133 K and 300 torr [96]. Chambers *et al.* observed that at 120 atm

and room temperature, graphite nanofibers (GNFs) with herringbone structure could store 67 wt% of hydrogen [97]. These relatively promising results lead to the development of many studies on adsorption of hydrogen in carbon nanotubes by molecular simulations and by experiments.

Subsequently there have been a variety of reports in the literature to substantiate these observations and none could achieve the expected 6.5 wt% or even repeat the original adsorption capacity reported. Inelastic neutron scattering experiments have shown that pure carbon surface cannot activate hydrogen. It has been proposed by us that hetero-atoms may be the alternate centers for hydrogen activation and this activated hydrogen may migrate to the carbon surface. The selection of heteroatoms has been made on the basis of a variety of parameters like the redox behavior of the hetero atom and the possibility of incorporating the hetero atom in the carbon nanotube framework [98,99]. Even among the various heteroatoms like N, P, and B there exists differences in their behavior. Chen L. *et al* reported the nitrogen-doped carbon nanotubes with bamboo-like structured materials exhibit maximum hydrogen storage capacity of 1.21 wt% at 77 K and 7 bar and 0.17 wt% at 298 K and 19 bar [100]. Sankaran *et al.* reported the boron substituted carbon nanotube (BCNT) prepared by using polymer as the carbon precursor showed different chemical environments for boron. The maximum of 2 wt% of hydrogen storage capacity has been achieved by the BCNT at 80 bar and 300 K. The microporous B/C material with B content > 7% and surface area > 700 m²/g has been prepared, which shows a reversible hydrogen physisorption capacity of 0.6 and 3.2 wt % at 293 and 77 K, respectively, under 40 bar of hydrogen pressure. Alternately by choosing appropriate heteroatom containing polymers the substitution of the heteroatom can be achieved in the carbon nanotube structure. This configuration has a bearing in hydrogen sorption characteristics of heteroatom doped carbon nanostructured materials.

Nitrogen doping in Carbon Materials

Nitrogen is the most abundant (80%) element in the terrestrial atmosphere. Molecular nitrogen is stable and has a minor role in the lower atmosphere. In contrast, minor constituents such as N₂O, NO, NO₂, nitric acid and ammonia are chemically active. N-doped carbon materials currently present the much-studied area in energy storage materials. Nitrogen is a neighbor of carbon and it is comparatively simple to chemically combine both the atoms together, which makes N-doped carbon. It is quite stable and popular for a variety of applications. Depending on the type of N bonding within the carbon matrix, nitrogen can share one to two π -electrons with the π -electron system of the carbon. This sharing of electron causes an *n*-type doping if N atoms directly

substitute the C atoms in the graphitic lattice. N-doping in carbon generally manifests itself in three different forms namely, pyrrolic-N, pyridinic-N, and quaternary-N, and each form varies the carbon electronic band gap differently. The band gaps of pyrrolic-N, pyridinic-N, and quaternary-N-doped carbons are reported to be 1.20, 1.40, and 1.39 eV, respectively [101-103]. On the other hand, a number of synthesis methods as well as chemical vapor deposition, ball milling, and bottom-up synthesis and thermal annealing have been developed for the synthesis of nitrogen doped carbon nanomaterials [104-107].

Particularly, all materials obtained by these techniques have a nitrogen content lower than 10 at % because of the high temperature environment that were used in carbonization. In this context, an alternate synthesis method needs to be developed that enables the preparation of carbon material with high nitrogen content and at the same time they should be stable at high temperatures. It will be beneficial if one can adopt a polymerization and low temperature growth process to create nitrogen doped carbon materials [108, 109].

Nitrogen is essentially introduced into the carbon matrix in two ways, either by the carbonization of N-containing precursors or by post-modification methods. The common nitrogen containing precursors are urea, melamine, cyanide, polyacrylonitrile and particularly ammonia [110-113]. Another resourceful approach has been reported for the synthesis of N-doped carbon materials based on naturally (and sustainable) nitrogen containing precursors such as amino-carbohydrates or other N-enriched polymers, amino acids, proteins, N-ionic liquids, waste crab shells [114-116]. An additional possible way is to pyrolyze the nitrogen and carbon-containing precursors, such as heterocycles or melamine, by which a direct incorporation of the nitrogen atoms into the forming of carbon backbone becomes possible [117-119]. One of the established procedure for deriving N-doped carbon is hydrothermal treatment of carbohydrate-rich biomass [120, 121]. Using nitrogen-containing biomass-related precursors and hydrothermally treating them yield nitrogen-containing carbonaceous materials that offer tremendous possibilities for further treatments and energy applications [122,123]. The application of nitrogen doped carbon materials has been extensively investigated as material for hydrogen storage at room temperature and ambient pressure [124]. *Yang et al.* reported nitrogen-enriched graphitic carbon material exhibits a hydrogen storage capacity of 0.34 wt% at room temperature under 100 bar [125]. *Cai et al.* reported addition of N-species in mesoporous carbons showed hydrogen adsorption capacity of 1.1 wt% at room temperature and 100 bar pressure [126]. *Badzian et al.*, reported microwave plasma CVD process enables the growth of specific nanostructured nitrogen doped carbons. Nitrogen incorporation into these forms of carbon is

approximately 1 at.%. It shows gravimetric hydrogen storage capacity of 0.7–0.8 wt.% under 300 K and 0.1–7 MPa [127]. Hydrogen adsorption on nitrogen-doped carbon xerogels showed maximum hydrogen uptake of 0.28 wt% at 35 °C [128].

Phosphorus-doping in Carbon materials

The changes in the physical properties of sp^2 carbon motifs after the addition of phosphorous into their lattice are considered in this section. However, it has a larger atomic radius and higher electron-donating ability, which makes it an option as a dopant to carbon materials. Phosphorus is not a commonly encountered element in carbons, although it is present in carbons obtained using phosphoric acid activation. Due to the addition of P in the carbon matrix, the density of states near Fermi level is also found to increase, which increases with the increase in P-doping level[129]. In these reactions, the formation of phosphate and polyphosphate bridges provokes the expansion and cross linking of the carbon matrix, driving to an accessible pore structure after the removal of the acid . The chemical state of phosphorus in carbons is a rather controversial issue. Some experimental evidences using different analytical techniques (FTIR and XPS) have shown that the most abundant P species introduced in carbons by phosphoric acid activation are –C–P– or –C–O–P bonds in phosphate and phosphonate-like structures. The XPS analysis further allowed for an insight into the binding states, proving the true incorporation of the phosphorus atoms into the graphite sheets, besides some P–O binding sites, most likely on the surface of the material. The existence of pentavalent phosphorus and elemental phosphorus is very infrequently detected, except when high temperatures are applied. Recent studies have reported that P-containing groups might be significant for the progress of graphitic crystallites which contrasts with so far reported role of P as inhibitor of carbon graphitization. Yang *et al*[130] reported that phosphorous-doped ordered mesoporous carbon were synthesized by co-pyrolyzing a phosphorus-containing source and a carbon source collectively using ordered mesoporous silica (SBA-15) as a template without the use of any metal components. More recent approaches have recognized dissimilar synthetic pathways in the direction of phosphorus-doped carbon materials, proving themselves as promising candidates for energy storage applications. It has been shown in the previous section that carbon materials with substitution by heteroatoms like N, S, and B, show hydrogen sorption capacity. However, the effect of substitution of phosphorus in carbon materials has not been investigated to the same extent.

Boron-Doping in Carbon materials

Boron is an element with unique properties within the periodic table. It is thus an interesting candidate for the doping of carbon materials, modifying the properties

of pure carbons. Several researchers have started focusing not only on basic studies on B-doping, but also on applying the obtained materials and exploiting their favorable properties in energy-related applications. Due to its three valence electrons, B is well thought-out as a good dopant. Substitutional boron enhances the graphitization of carbon. It has been found that boron atoms are favored to be substituted in the graphite lattice. The existence of B–C bonds in the carbon framework can lower the Fermi level of the structure and then tune the properties of oxygen chemisorption and electrochemical redox reactions. The synthetic procedure, in which elemental B and graphite powder served as precursors, yielding a mixture of different B-containing carbon nanostructures, such as thin graphitic sheets, tubes, and filaments. The substitutional doping of carbon atoms in sp^2 and sp^3 configuration with boron can modify the electronic and structural properties of the resulting carbon. Over the years boron-doped carbons have been synthesized by standard CVD process using BCl_3 . Substituted boron atoms in the carbon lattice accelerate the graphitization and suppress the oxidation of carbon materials, which seems promising for their use as reinforcement materials in aerospace applications. The positive effect of boron-doping on diamond and carbon electrodes and in the field of hydrogen storage has also been reported [131], although further optimization of the boron doping environment seems yet to be needed.

The storage of hydrogen in carbon nanomaterials requires appropriate chemical activators in suitable geometry. Sankaran *et.al.* reported a different types of carbon materials employed for the hydrogen sorption capacity. The storage capacity of 2 wt% at 298K and 80 bar pressure is obtained for boron substituted carbon nanotube. Its higher compared to different types undoped carbon materials.[69]. However, a maximum storage capacity of 2 wt% is attained at 80 bar and 300 K for boron containing carbon nanotubes (BCNT) whereas pure carbon nanotubes (CNT) show only 0.6 wt% at 300K and 80 bar[69]. In addition, they compared this storage capacity for B-doped bulk carbon material (PBC) it shows only 0.2 wt% [69]. Mike Chung *et al.* reported the microporous boron substituted carbon (B/C) materials that show a significantly higher hydrogen binding energy and reversible hydrogen physisorption capacity of 0.6 and 3.2 wt % at 293 and 77 K, respectively, under 40 bar of hydrogen pressure[132]. B-containing polymeric precursors and pyrolysis were employed to synthesize microporous B/C materials with a high B content (7.2%) and high surface area (780 m^2/g). The substitutional B elements in B/C material serve as internal p-type dopants and polarize the C surface, which exhibit a significantly higher hydrogen binding energy[133]. For efficient hydrogenation and hydrogen storage, these boron atoms should be incorporated geometrically and chemically

into the carbon network. Wang et al. reported that B- and N-doped microporous carbon had a hydrogen storage capacity of 0.55 wt % at 298 K and 10 MPa. By doping 6.0 wt % Ru metal on the B- and N-doped microporous carbon, the hydrogen uptake at 10 MPa was increased to 1.2 wt %, i.e. The improvement of hydrogen storage was due to the spillover of atomic hydrogen from the Ru metal particles to the B-and N-doped microporous carbon [134].

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CHAPTER TWO

HYDROGEN STORAGE IN INTERMETALLIC SYSTEMS

The interaction of hydrogen molecules with metals, alloys and intermetallics have several points to consider. When hydrogen molecule comes in contact with the reactive surface of a solid the hydrogen molecules are bound to the surface of the the solid possibly as atoms on the material associatively. Catalytic interaction between the metal atoms on the surface of metals, alloys or intermetallics and the hydrogen molecule results in breaking of the covalent H-H bonds to produce two hydrogen atoms bound to the surface metal sites of the solid material. This process is usually called the nucleartion, which grows to form a uniform layer. After completion of the uniform layer, hydrogen atoms are introduced into the lattice either by chemisorption or absorption by the solid state diffusion. This incorporation into the lattice or accomodation in the interstitial sites decided the composition of the hydride that is formed. However, the choice bewtween the hydrogen occupying the lattice position or accomodated at an interstitial site is decided by the consieration of the energy of the resulting system which should be minimum. These two options for the occupation of hydrogen atoms in the lattice or interstitial positions of the lattice are pictorially shown in Fiig.2.1.

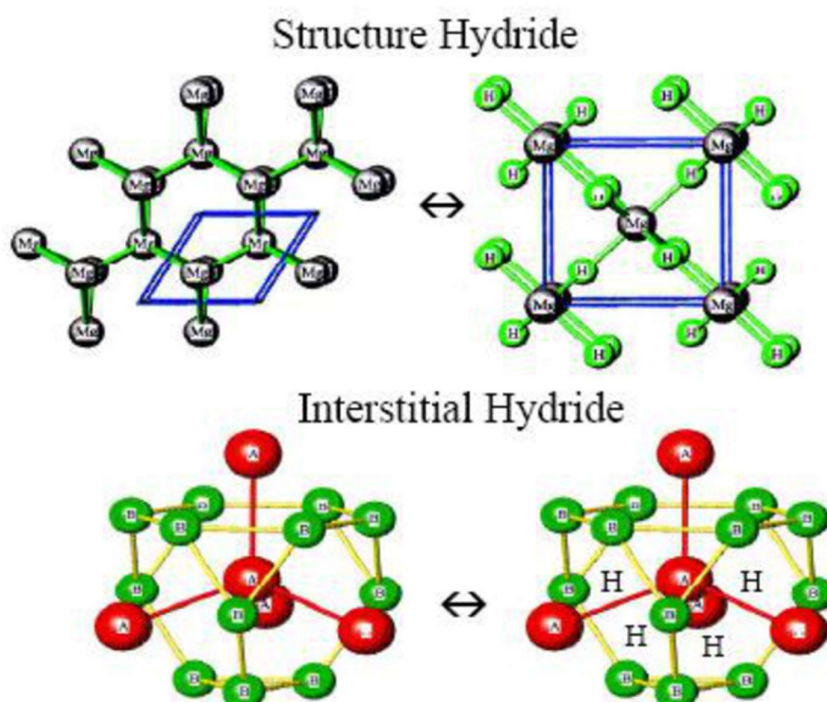


Fig.2.1. Structural and interstitial hydride formation in metals, alloys and intermetallics. [Figure reproduced from ref.1]

When the H atoms occupy a crystallographic site, then the resulting system is a hydride phase structurally different to the non-hydride phase. When the hydrogen atoms take up the interstitial positions, there is alteration of the unit cell parameter. This will be one of the criteria to distinguish between the formation of a compound hydride or hydrogen being taken up by the solid in the interstitial position.

The next point to consider is when hydrogen sorption will yield a separate hydride and when hydrogen sorption will yield interstitial hydride formation? This may be dependent on the composition of the intermetallic systems. Consider an intermetallic consisting of two elements A (stable hydride forming) and B (element not favouring stable hydride formation). Let both A and B are primarily assumed to occupy tetrahedral sites. This is only one assumption; this may not be true in every case. When the lattice is occupied by only A element stable hydride will be formed, on the other hand when the lattice is primarily made up of B element alone then one can expect interstitial hydride formation. In essence, the A/B ratio decides whether a stable hydride is formed or interstitial hydride formation is favoured depending on the A/B ratio is high or low. The statements made so far are to a limit arbitrary. This can be represented by a plot of composition ratio and bond order ratio as shown in Figure 2.2. This plot shows the stable hydride forming region and also unstable hydride forming region.

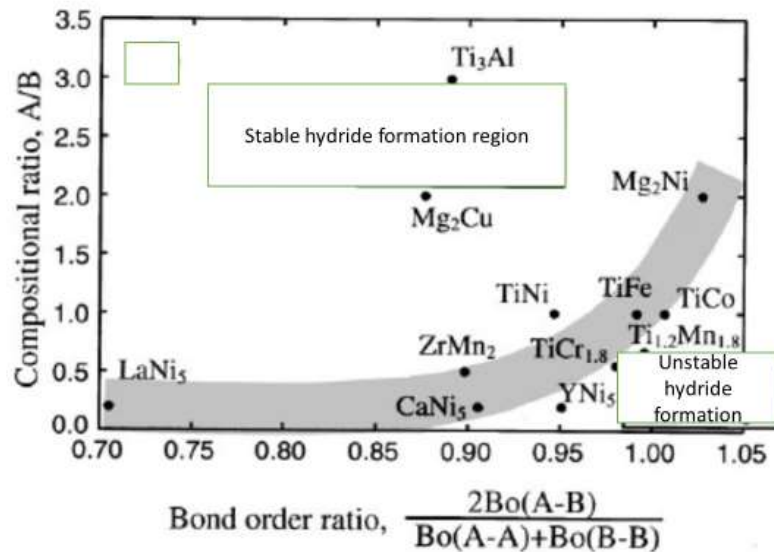


Figure 2.2. Relationship between composition ratio and bond order ratio for the various known intermetallics. [Reproduced from reference 1.]

There are three generic classes of intermetallics which are AB, AB₅, and A₂B (FeTi, LaNi₅, Mg₂Ni) compositions. The data on hydrogen storage characteristics of these three generic systems are compared with other typical systems and the data are assembled in Table 2.1

Table 2.1. Generic Intermetallic and other typical systems and their hydrogen storage properties

<i>Type</i>	<i>Composition</i>	<i>Hydride</i>	<i>Crystal structure</i>	<i>Hydrogen storage Mass%</i>	<i>Experimental conditions</i>
<i>Elemental</i>	<i>Pd</i>	<i>PdH_{0.8}</i>	<i>Fm3m</i>	<i>0.56</i>	<i>0.020 bar 298K</i>
<i>AB₅</i>	<i>LaNi₅</i>	<i>LaNi₅H₆</i>	<i>P6mmm</i>	<i>1.37</i>	<i>2 bar, 298 K</i>
<i>AB₂</i>	<i>ZrV₂</i>	<i>ZrV₂H_{5.5}</i>	<i>Fd3m</i>	<i>3.01</i>	<i>10⁻⁶bar, 323 K</i>
<i>AB</i>	<i>FeTi</i>	<i>FeTiH₂</i>	<i>Pm3m</i>	<i>1.89</i>	<i>5 bar, 303 K</i>
<i>A₂B</i>	<i>Mg₂Ni</i>	<i>Mg₂NiH₄</i>	<i>P6222</i>	<i>3.59</i>	<i>1 bar, 555K</i>
<i>BCC</i>	<i>TiV₂</i>	<i>TiV₂H₄</i>	<i>BCC</i>	<i>2.6</i>	<i>10 bar, 313 K</i>

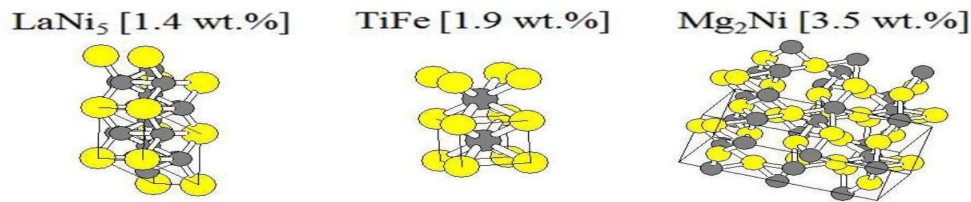
Generally, the following types of intermetallics have been studied for hydrogen storage applications, A₂B, AB, A₆B₂₃, A₂B₇, AB₃, AB₂, AB₅ but none of them could satisfy the necessary storage expected. Normally it is given a value of 6.25 weight percent. They have different kinetics and critical operating parameters like pressure and temperature for hydrogen storage. Intermetallic compounds are designed by combining an element forming a stable hydride with an element forming a nonstable hydride. As for the metallic hydrides, the dissociative chemisorption of hydrogen is followed by diffusion of hydrogen into the interstitial site.

Among the AB₅ type alloys, due to their low working temperature and pressure (Storage in La Ni₅ based systems operating under moderate temperature does not exceed 1.4 weight percent) LaNi₅ has been extensively studied [2-6].

Among the generic hydrides, AB₅ type LaNi₅ finds extensive study and it can be 90-95% reversibly hydrogenated to final composition LaNi₅H₆ at 300 K and 2 atm pressure. LaNi₅ has hexagonal CaCu₅ structure type with a = 5.0228 Å and c = 3.9826 Å. This alloy can store up to 1.4 weight percent as this is not sufficient, other alloys which are cheaper are being developed based on light elements like magnesium-based alloys. AB type alloy TiFe has a storage capacity of 1.8 weight percent with lattice parameter a=2.9789 Å and has a CsCl structure however, this material is susceptible to poisoning by oxygen, water and carbon monoxide. Third common solid state material is Mg₂Ni and this alloy is capable

of storing up to 3.6 weight percent with C36 Laves Phase with lattice parameters $a=b=4.824\text{\AA}$, $c=15.826\text{\AA}$. When Mg_2Ni is hydrogenated and characterized as Mg^{2+} and $[\text{NiH}_4]^{4+}$ and hence has strong affinity of the lattice for hydrogen. This hydrogenation is an exothermic reaction (-32.3 kJ/mol H) and high desorption temperatures $520\text{-}570\text{ K}$. The hydrogenation of the powdered Mg_2Ni takes place at 623 K . In order to improve the sorption characteristics of generic systems, attempts have been made to substitute with electropositive or electronegative elements in these three generic systems. However, none of these new systems, could store greater than 3 weight percent which does not satisfy the necessary storage for mobile applications. In Figure 2.3, the structures and storage capacities of common known generic alloys are shown.

Figure 2.3. Structures and storage capacities of common known alloys



Hydrogen sorption in metallic systems can be considered as dissolution (α phase) and hydride phase (β Phase). This is perceptible from pressure-composition-temperature plots for typical system LaNi_5 shown in Fig.2.4.

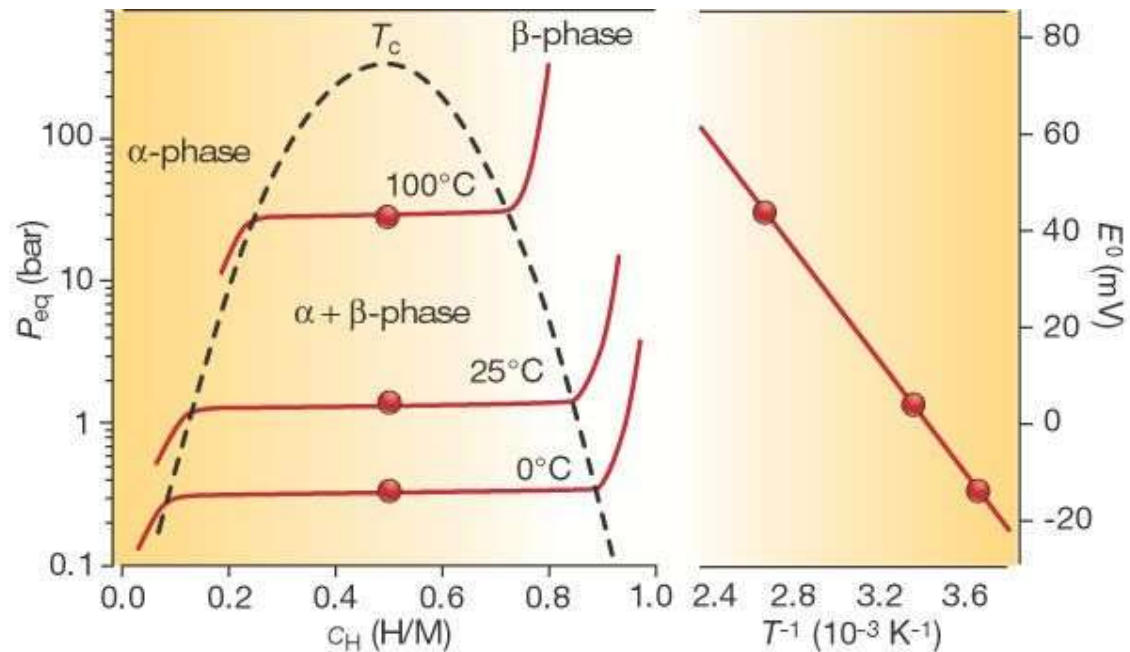


Fig.2.4. Pressure-composition-temperature curves and at the right van't Hoff plot (plot of logarithm of the equilibrium pressure versus inverse temperature for the beta phase formation; a plot to deduce the heat of hydride formation reaction). The van't Hoff plot can be used to compute the heat and entropy of the hydride formation reaction [Reproduced from ref.7]

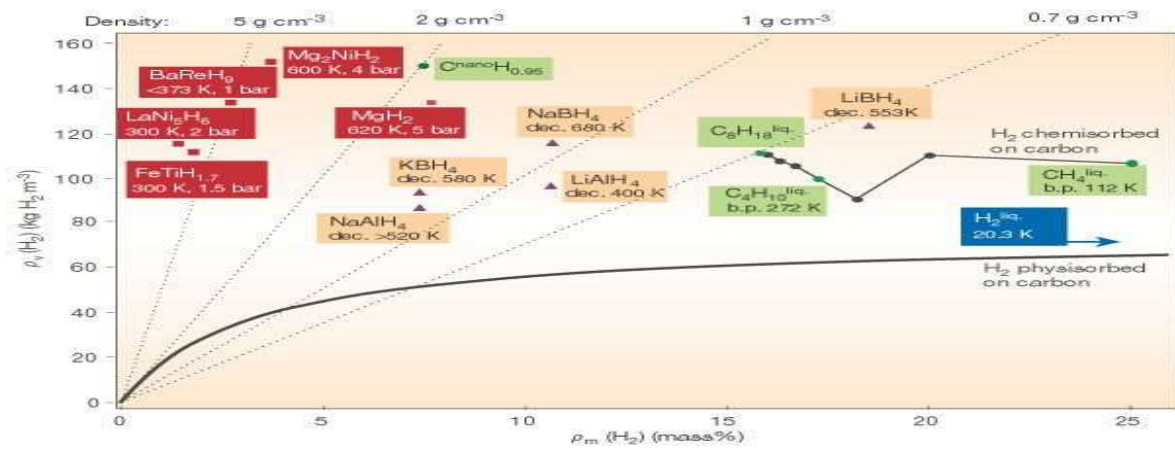


Figure 2.5. Comparison of metal hydrides, carbon nanotubes, petrol and other typical hydrocarbons. [Reproduced from ref.7]

Many of the metals and alloys are capable of reversibly absorbing amounts of hydrogen by charging using molecular hydrogen gas or hydrogen atoms from an electrolyte. Molecular hydrogen is dissociated at the surface sites before absorption; two H atoms recombine to molecular hydrogen during the desorption process. Pressure–composition isotherms of hydrogen sorption can be used to derive the thermodynamic parameters like enthalpy and entropy factors (Fig.2.4). Initially the metal dissolves some hydrogen as a solid solution (α -phase). As the hydrogen pressure together with the concentration of Hydrogen in the metal is increased, interactions between hydrogen atoms become important, and nucleation and growth of the hydride (β) phase take place. While the two phases coexist, the isotherms show a flat plateau, the length of which determines how much H_2 can be stored reversibly in the β -phase. It is also possible multiple plateaux can be formed and multiple complex hydrides (multiple β phases) can be formed. The storage capacity in metal hydrides, carbon materials and typical organic substrates is shown graphically in Fig.2.5.

One of the stipulated aims according to US DOE in hydrogen storage is to attain 6.5 weight percent storage (as already stated) with the decomposition of the

hydride should be between 60 and 120°C. These limits have been changing periodically depending on the results obtained [8]. However, the original stipulation is based on cost and range of utility of stored hydrogen in mobile applications.

There have been many attempts to store hydrogen in metals and related systems under moderate temperature and pressure. These systems appear to be promising since the storage is safe and possibly can attain the storage capacity for on-board applications even though at present the storage capacity falls short of the expected value (say ~ 6.5 weight percent). There are a number of reflections on storage of hydrogen by intermetallics in literature [9-12].

It is at this stage to look into the possibility of attaining the required storage in metallic/intermetallic systems. Most of these systems crystallize in cubic or hexagonal lattices and in this sense they can at most create or possibly account for one void space per atom and this void space can be assumed to be occupied by a hydrogen atom. If this is the situation, depending on the atomic weight of the metal (say around 50 for typical transition metals) then in the case of transition metals or higher atomic metals can store approximately ~2 weight percent while light weight metals like Mg and other group 2 and 3 light metals possibly can store a greater percentage. However, it is not only the storage capacity but also the kinetics and desorption temperature are also essential issues for considering a particular system for hydrogen storage applications. In the later cases, the light atomic weight metals may not be satisfying the conditions based on kinetics and thermodynamic considerations.

AB₅ intermetallic compounds

These systems as stated above, have hexagonal crystal lattice (prototype LaCu₅). These systems were first introduced at the Philips Eindhoven around 1969, when they were investigating magnetic alloy SmCo₅. In these systems, the A element can be one or more of the lanthanides or other elements like Ca, Y, Zr and the B element mostly consist of Ni, though substitutional elements such as Co, Al, Mn, Fe, Cu, Sn, Si or Ti are also possible. Lanthanide mixture namely misch metal can also be used as A element in these systems. The plateau pressure is variable over at least three orders of magnitude depending on the composition of the intermetallic. Hydrogen storage capacity is generally low on reversible basis it does not exceed 1.4 weight percent. These systems can be easily activated but can be *mildly* pyrophoric that means safety considerations have to be taken care off.

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CHAPTER THREE

HYDROGEN STORAGE BY CARBON NANOMATERIALS

1. Introduction

Several hydrogen storage technologies for subsequent utilization have been examined with various criteria and these are based on a variety of physicochemical and other approaches. However, due to the chemical nature of hydrogen, chemical materials that reversibly adsorb hydrogen by means of chemical reactions usually receive much attention. Most of the research on hydrogen storage has focused on storing hydrogen in light weighted materials that can maintain hydrogen in a compact manner for mobile devices. Hydrogen storage and transport as compared to other hydrocarbons are difficult due to various reasons. Though hydrogen has a considerable energy density with respect to mass, its volumetric energy density is very low and hence, it requires larger (heavier) storage vessels in comparison to the smaller hydrocarbon storage tanks required to deliver the same amount of energy. Storage of hydrogen under pressure or as liquid (boiling temperature is 20.268 K) involves significant energy loss in the process. Secondly, 1 liter of pure liquid hydrogen contains (nearly 63%) less hydrogen as compared to 1 liter of gasoline. It has been estimated by Chahine and Benard [1] that a 6.5 wt % hydrogen storage capacity is required to power a hydrogen-fueled car to achieve a range of 500 km.

Commonly available methods, namely in high-pressure gas cylinders (up to 800 bar) and as liquid hydrogen in cryogenic tanks (at 21 K) are inefficient and also not safe for certain applications. Hydrogen adsorption on materials with high specific surface area and chemically bonded in covalent and ionic compounds appears to be attractive [2]. Materials such as metal hydrides, alloys, complex hydrides and high surface porous materials are showing affinity for absorbing large amounts of hydrogen. However, each method suffers from some particular drawbacks.

In the solid-state hydrogen storage, hydrogen is bonded by either physical forces, e.g., MOF and carbon based materials, or chemical forces, e.g., hydrides, imides and nitrides. Physisorption has the advantages of higher energy efficiency and faster adsorption/desorption cycles, whereas chemisorption results in the adsorption of larger amounts of gas but in some cases, is not reversible and requires higher temperatures to release the adsorbed gas. In this chapter, we shall deal with only carbon materials and the scope of these materials for this application since there are a variety of these materials and nature has shown that this is one of the potential storage media for hydrogen (in the form of

hydrocarbons) and also shown that storage can go up to 25 weight percent (as in methane). However, one must be aware these hydrocarbon molecules are covalent in nature and thus may not be readily released when required as in transport applications. These aspects will be dealt with subsequently.

2. Carbon Materials

The microporosity of carbon materials is not directly related to hydrogen storage application but a nearly linear relationship has been realized with respect to BET surface area, typical plots can be seen in the following references [3-7]. There have been many attempts to modify the surface of carbon materials so that the storage capacity can be increased. One such attempt deals with the presence of heteroatoms on the surface of carbon materials for various reasons like the possibility of dissociating molecular hydrogen or facilitating the spill-over process [8-11]. However, the current situation with respect to hydrogen storage in carbon materials with heteroatoms can be stated that typically N-doping is only apparent when considering the hydrogen uptake as a function of microporosity (rather than total porosity). This possibly leads to the conclusion that pores larger than micropore size range have a lesser role in hydrogen storage capacity.

The advanced design and testing of carbon materials for energy storage devices appear to be important. The main shortcomings of these materials are related to the irreversible capacity loss, big voltage crosstalk, and low density [12]. Novel composites containing multifunctional nanostructured-carbon and other dopants can synergistically take advantage of the combination of ordered building block units with other desired properties. Since mostly physisorption is involved in this process of hydrogen storage, only a small amount of hydrogen could be stored even at a pressure of 90 bar. Obviously, temperature will have almost negligible effect on hydrogen storage capacity [13].

3. Graphene

The Hydrogen Adsorption/Desorption Isotherm The hydrogen adsorption/desorption isotherm of the nitrogen doped graphene, Graphitic Oxide and Graphite powder is shown in Figure. The hydrogen adsorption isotherm has been carried out 298 K and 90 bar pressure. The nitrogen doped graphene material showed nearly ~1.5 wt% hydrogen storage capacity at room temperature and 90 bar pressure. In this context the graphitic oxide (GO) showed ~0.21 wt% hydrogen storage capacity at room temperature and 90 bar. This value is less than that of nitrogen doped graphene material. However, nitrogen doping of graphene materials takes up substitution positions in the carbon lattice, there is transportation of hydrogen atoms on to the graphene surface. Furthermore, these results reveal that the nitrogen doping on graphene materials can extensively

modify the catalytic effect of the graphene materials for hydrogen dissociative adsorption, foremost for the improvement of the dissociative hydrogen adsorption [14]. This observation suggests that the nitrogen atoms possibly take part in a role in the hydrogen adsorption capacity at room temperature. A previous study recommended that the presence of nitrogen atoms in graphene sheets increases the enthalpy of hydrogen adsorption [15] [16]. Potentially almost all the adsorbed amount can be desorbed which is an interesting characteristic expected for hydrogen storage materials. Various attempts have been made to modify or adopt different preparation procedures for graphene materials and it has been shown that N and P doping in graphene does not improve the materials' hydrogen storage capacity [17,18].

4. Activated Carbon Materials

For conventional Activated carbon materials, the hydrogen uptake is proportional to the surface area and pore volume; and normally the data are fitted well with the Langmuir isotherm model (monolayer adsorption). High adsorption capacity is only obtained at extremely low cryogenic temperature and high pressure [19]. Hydrogen adsorption on various types of commercial and modified activated carbon products has been extensively studied [20]. Experimental results show that products with micropore volumes greater than 1 mL/g are able to store ca. 2.2 wt % of hydrogen due to physisorption and it is expected that optimization of the adsorbent and sorption conditions could lead to a storage capacity of 4.5–5.3 wt %. Agricultural waste materials such as coconut shell, coconut fibers, jute fibers, nut shells and oil seeds, etc. [21–28], are popular raw materials for producing activated carbon materials. Carbon materials and their activation have been extensively discussed in ref [29]. Jin et al. [30] prepared Activated carbons with different porosities using chemically activated coconut shell. They reported a maximum hydrogen adsorption capacity of 0.85 wt % at 100 bar and 298 K. Sharon et al. [22] produced activated carbon fibers (ACF) using soybean and bagasse. The authors measured hydrogen storage capacities of 1.09– 2.05 wt % at a pressure of 11 Pa and room temperature. Another form of AC, the advanced AC monoliths, with good mechanical strength (maximum compression strength of 22 MPa), high volume of micropores (up to 1.04 cm³ /g) and high density (up to 0.7 g/cm³) have been shown to adsorb 29.7 g/L of hydrogen at 77 K and 4 MPa [21]. Mechanically milled AC consists of some form of defective nanostructure, which increases the specific surface area. Research findings have revealed that after 10 h of milling, the hydrogen storage capacity increases from 0.90 wt % to ca. 1.7 wt % [31]. Studies have shown that loading of precious metals, e.g., Pt, on to AC increases the adsorption capacity [32]. The merging of the two adsorption phenomena, i.e. chemisorption (on the Pt surface) and physisorption (on the carbon surface) gives rise to a significant amount of spillover hydrogen.

5. Carbon Nanotubes

Ever since the discovery of carbon nanotubes was reported in 1991, there has been various attempts to use this new type of carbon materials for hydrogen storage. These studies have led to some unexpected levels of storage up to nearly 60 weight percent or even more. However, the consensus now is that these reports claiming over 60 weight percent are flawed by experimental aberrations.

Table 1 Selected data (for comparison) on the storage of hydrogen by Carbon nanotubes

Sample	Temp (K)	P (MPa)	Hydrogen storage (Wt %)	Ref
Herring Bone GNFs	RT	11.35	67.6	35
Platelet GNFs	RT	11.35	53.68	35
Graphitic Nano Fibers	RT	101	10	36
Graphitic Nano Fibers	RT	8-120	10	37
SWNTs (low purity)	273	0.4	5-10	38
SWNT (high Purity)	80	70-80	8.25	39
SWNT (high purity + Ti Alloy)	300-600	0.7	3.5-4.5	40
	473-673	1	20	41
Li-MWNTs	473-673	1	2.5(1.8)	42
Li-MWNTs(K-MWNTs)	RT	Ele.Chem	<1	43
MWNTs	RT	1-100	0.1-0.7	44
CNF	300-520	1	0.1	45
SWNTs	RT	35	<0.1	46
Various CNM	RT	0.8	0	47
SWNTs (+Ti Alloy)	RT	10	4.5	48
SWCNT	295	0.1	0.93	49
SWCNT	RT	4.8	1.2	50
SWCNT	323	-	4.77	51

SWCNT	-	3	0.8	52
SWCNT	-	0.005	2	53
MWCNT	77	0.1	0.54	54
MWCNT	298	10	0.2	55
MWCNT	425	3	3.8	56
MWCNT	143	7.5	3.5	57
MWCNT	RT	--	1.5-2.1	68
MWCNT	-		2.7-3.8	69
MWCNT	RT	1-3.4	5.73-12.79	78
MWCNT	77 (RT)	1.73 (1.23)	10	79
SWCNT	-----	3.5	140 Bar	80
SWCNT/MWCNT	-----	4.77	-----	81
SWCNT	323	0.298	20 bar	82
Ni-MWCNT	-----	2.8(1.2)		83
Ni-MWCNT		1.7	12	84
CNT				

Only limited data are given in Table 1. For more extensive compilations, one is directed to references [58-66]. Various nanotubes like carbon nanotubes, boron nitride nanotubes, silicon carbide nanotubes, carbon nano-scrolls, pillared Graphene and porous nanotube network materials have been extensively investigated and the final suggestion is that one should design novel materials with the following key parameters namely high accessible surface area, large free pore volume and strong interactions [67].

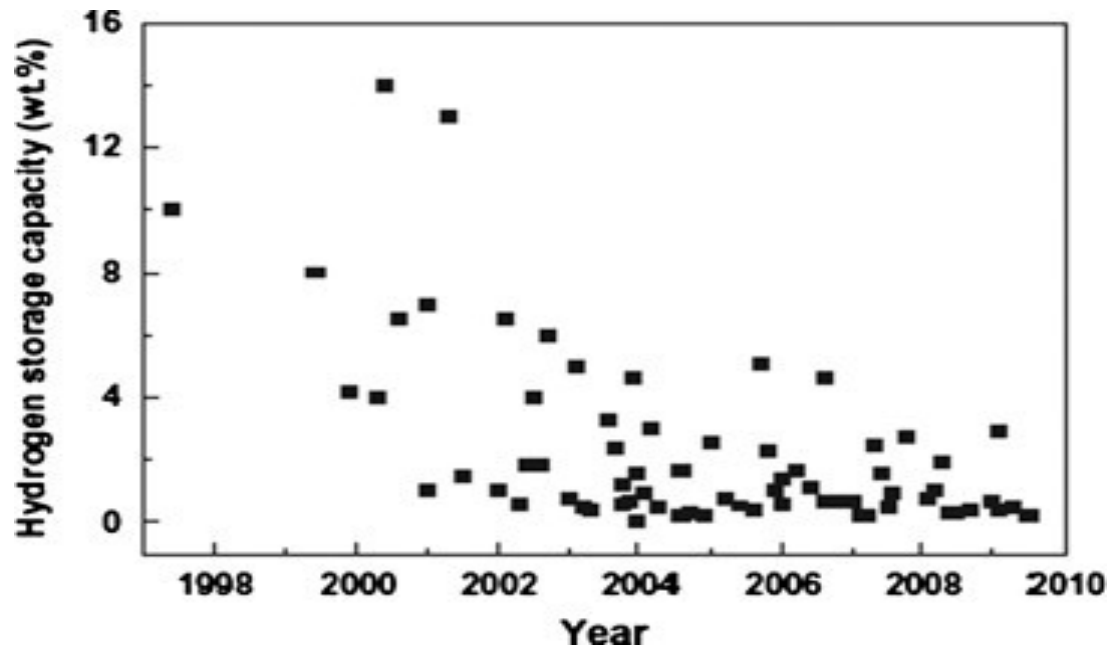


Fig.1. Reported hydrogen storage capacities of CNTs as function of the year of publication {reproduced from reference [62]}

In a recent review, Jinzhe lyu et al [70] propose that “a detailed study of the optimum number of metal atoms without aggregation on CNT should be performed, at the same time suitable preparation methods for realizing controllable doping site and doped configurations should be devised; (2) The material synthesis, purification, and activation methods have to be optimized; (3) Active sites, molecular configurations, effectively accessible surface area, pore size, surface topology, chemical composition of the surface, applied pressure and temperature, defects and dopant, which are some of the important factors that strongly affect the hydrogen absorption in carbon nanotubes” should be elucidated. In contrast, Rui Lobo et al [71], propose carbon nanostructures are promising materials for hydrogen storage applications. They emphasize that hydrogen can be physisorbed in carbon nanotube bundles on various sites such as external wall surface, grooves, and interstitial channels. Therefore, it can have a large energy density (as required for mobile applications). It is also known that by tuning the adsorption conditions, hydrogen can be either chemisorbed or physisorbed in carbon nanotubes. In a review, Seul-Yi Lee et al [72] and others [73] propose that more detailed understanding of the interfacial interactions between adsorbent and adsorbate should be evolved and the phenomenon of spill-over can contribute on adsorbent surfaces to achieve the desired levels of hydrogen storage.

6. Perspectives

First, let us try to specify the standards that one wishes to achieve in storage of hydrogen [74-76].

- Gravimetric H density in the range 5–10 wt % H₂,
- Corresponding to an energy density of 1.6–3.2 kWh/kg.
- Volumetric H density > 50 kg H₂ m⁻³,
- Corresponding to an energy density > 1.6 kWh/L.
- Thermodynamics: T 0 < 85 °C (transport applications) or < 200 °C (stationary applications).
- Kinetics (tank level): fill time 3–5 min; H₂ release flow 1.6 g/s.
- Durability: 1500 cycles (1/4 tank to full)

It is obvious that the current level of achievement in this exercise is far from satisfactory. This is the reason that the DOE has been periodically altering their specifications for hydrogen storage. One of the recent specifications and the time period to achieve them are assembled in Table 2.

Table 2 Technical system targets for on-board hydrogen storage for light duty fuel cell vehicles [extracted Data from ref. 77]

	2020	2025	Ultimate
Usable specific energy from H ₂ [kWh/kg]	1.5	1.8	2.2
Net usable energy/mass system mass [kg H ₂ /kg system]	0.045	0.055	0.065
Usable energy density from H ₂ [kWh/L]	1.0	1.3	1.7
Net usable energy/max system volume [kgH ₂ /L system]	0.030	0.040	0.050
System cost [USD/kWh net]	10	9	8

Of all the available hydrogen storage materials, why carbon materials are preferred option? What is the maximum hydrogen storage capacity that can be expected and what will be the limit that can be practically achieved? It may be remembered that nature mostly provide hydrogen source in combined form with carbon and oxygen though other elemental compositions are also possible. So, it is natural to expect that carbon materials can be one of the options for solid state hydrogen storage. If the carbon materials can be obtained in atomic state, then the maximum storage capacity can be expected to be around 25 weight percentage. However, since it is not possible to get atomic materials at the desired levels, the carbon materials can be obtained at the limit with one vacant valency in carbon in two-dimensional material and hence the maximum storage one can

expect is to be 6.25 wt %. This limit is arrived at assuming that hydrogen is held by the solid by valence forces. If hydrogen is stored or retained by other forces, this limit may not hold good.

If the stored hydrogen were to occupy the interstitial sites in carbon materials, then the energetics of storing and releasing should also be considered for any practical application as the release of hydrogen is energy consuming process.

Since, normally carbon materials are microporous in nature, hydrogen may be held in these pores by condensation forces and hence one can hope for higher storage capacity, however, the experimental variables for this process namely Temperature and Pressure have to be different from normal ambient conditions. Physisorption has been already advocated as a method for hydrogen storage in carbon materials but this process requires lower temperatures.

The questions to be answered include:

- (i) Whether the storage of hydrogen occurs in carbon materials in atomic state or molecular state? That is either Physical or chemical adsorption is involved in this process.
- (ii) If it is in atomic state what are the centres and mechanism by which the dissociation of molecular hydrogen takes place?
- (iii) If molecular adsorption takes place, what are the binding forces?
- (iv) If the storage is in atomic state, is the process by occlusion?
- (v) Is hydrogen stored on the walls of the nanotubes or in between the nanotubes.
- (vi) What are the binding forces preferred for hydrogen storage application?
- (vii) If hydrogen is stored by chemisorption forces, what will be the energy benefit or loss in desorbing hydrogen subsequently?
- (viii) Will there be any dimensional changes to the nanotubes due to hydrogen sorption? If so, what will be the limits of changes that can be expected?

The progress of introduction of hydrogen storage in carbon nanomaterials is pictorially shown in Fig.2.

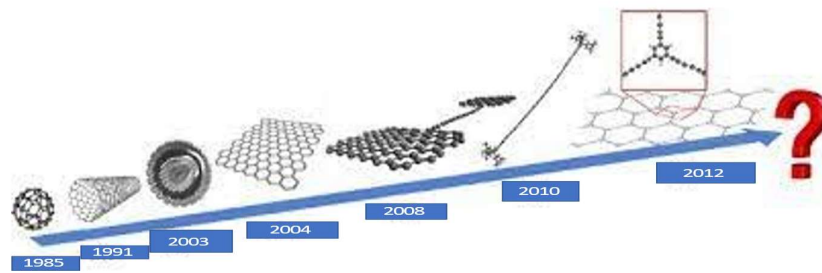


Fig.2 Starting from fullerene to graphene all kinds of nanomaterials studied for hydrogen storage

From bonding schemes from sp^3 hybridized carbon to various carbons are also shown in Fig 3.

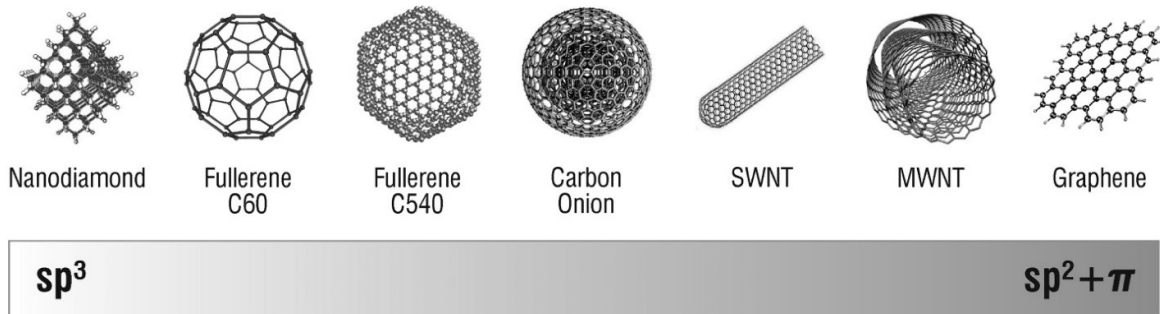


Fig.3. The various nanocarbons are shown based on bonding scheme.

Spill-over is one the phenomenon invoked to the transport of hydrogen (possibly other species as well) from the site of impact to other normally inactive sites. This phenomenon has been investigated and is now commonly accepted alternate way of surface transport. This transport has to have a transporting medium and in the case of hydrogen it is usually associated with water and its fragments. In the case of carbon, this transporting medium can be either adsorbed water species or the carbon species themselves. The role of spillover in hydrogen sorption and storage need more information and thus deserves a separate treatment.

It appears that modification of carbon materials may be necessary for hydrogen storage applications. Rostami et al [85] compiled a table wherein they have listed all the modifications so far tried for improving the storage capacity of carbon materials. In this compilation, modification using metallic components alone is given. It may be because, metallic sites may promote the activation of hydrogen molecule. However, it must be remarked that storage capacity so far reported on these modified carbon materials has yet to reach the levels specified by DOE.

Another aspect on which some remarks may be necessary. Varying storage capacities up to nearly 70 weight percent have been reported in literature but these results require independent verification. Some theoretical studies have even predicted storage possibility above the DOE specifications but so far, no reproducible results have been reported on these values proposed.

It seems only further careful research alone can provide evidence for the possibility of carbon materials for hydrogen storage option. However, there is scope for optimism and it may be worthwhile to embark on this research with more precision and care.

If one considers that hydrogen adsorption takes place on the surface, then uptake of around 1 weight percent per gram can be expected. This estimate is reflected in the so-called Chahine rule [86,87]. This estimates possibly shows that carbon materials with surface area around $3000 \text{ m}^2\text{g}^{-1}$ may be required and this exercise has already started and there are now carbon materials having surface area over $3000 \text{ m}^2\text{g}^{-1}$ have been prepared [88]. Even though, there are indications that hydrogen sorption capacity is correlated with BET surface area, limitations in this postulate has been pointed out [88]. Microporosity may become relevant for adsorption at 77K and adsorption energy may be increased from 4 kJ Mol^{-1} to $\sim 10 \text{ kJ mol}^{-1}$ in these adsorbents.

It is obvious that the available results on carbon materials are varied in nature. The pore size limit of 0.6 nm has been suggested even though the final word has yet to evolve. The reported adsorption energy limit is also variable among the results reported. The effect of heteroatom doping and metal loading has been also studied but these studies have not led to the desirable levels of storage. These inconsistencies may be due to various synthetic procedures adopted and also the variety of carbon materials that one can obtain. It can be stated that carbon materials may appear to be strong contenders for hydrogen storage application but they are yet to evolve as the solution for practical application. All these conclusions are evident from the presentation given in reference [88].

Carbon materials for hydrogen storage applications have to be prepared and activated suitably so that the porous architecture is fully usable for hydrogen storage. In literature, various methods to architecture the porous texture of carbon materials have been proposed [89] and also various activating procedures both physical and chemical methods have been reported in literature [90,29].

Hydrogen physically or chemically stored into nanomaterials in the solid-state is a desirable prospect for effective large-scale hydrogen storage, which has exhibited great potentials for applications in both reversible onboard storage and

regenerable off-board storage applications. Its attractive points include safe, compact, light, reversibility, and efficiently produce sufficient pure hydrogen fuel under the mild condition. In order to overcome the short comings of these materials, attempts are focused to increase the available surface area and also to introduce functional sites to activate and store hydrogen.

Among the options available, namely

1. The simplest is compressed H₂ gas. It is possible at ambient temperature, and in- and out-flow are simple. However, the density of storage is low compared to other methods.
2. Liquid H₂ storage is also possible: from 25% to 45% of the stored energy is required to liquefy the H₂. At this method the density of hydrogen storage is very high, but hydrogen boils at about -253°C and it is necessary to maintain this low temperature (else the hydrogen will boil away), and bulky insulation is needed.
3. In metal hydride storage the powdered metals absorb hydrogen under high pressures. During this process heat is produced upon insertion and with pressure release and applied heat, the process is reversed. The main problem of this method is the weight of the absorbing material – a tank's mass would be about 600 kg compared to the 80 kg of a comparable compressed H₂ gas tank.
4. More popular at this time is carbon absorption: the newest field of hydrogen storage.

So, it should be mentioned that even mobile hydrogen storage is currently not competitive with hydrocarbon fuels; it must become so in order for this potential environmentally life-saving technology to be realized on a great scale. However, among the currently available candidates for hydrogen storage, most of them cannot meet the DOE targets for automotive applications (5.5 wt.% by 2025) by considering not only the weight of the adsorbent but that of the entire system. Indeed, the DOE targets are valid for ambient temperature, at which excess uptakes of only 1 wt.%, on average, were found at 298 K for the majority of the reported carbon adsorbents for a pressure range up to 20 MPa. Even though the use of metallic catalysts to promote the hydrogen spillover has been proposed as a mechanism to enhance hydrogen storage on nanostructured carbons at 298 K, it seems that hydrogen uptakes higher than 5 wt.% can be ensured quite exclusively at cryogenic temperatures. Under these conditions, the hydrogen adsorption strictly depends on textural properties, such as specific surface and pore size distribution of the adsorbent material [91].

Various activated carbon materials from waste materials of agro-industries and different other sources have been examined with a variety of activation procedures and it has been shown that activation with LiOH and also different microwave irradiation are favourable for increased storage capacity of hydrogen [92]. Hydrogen uptake by residues from waste and natural materials under different conditions have been examined and was shown that cigarette butts obtained exhibited high value of hydrogen storage (11.2 wt % at 77K and 5 MPa) [93].

The advantages of employing graphene materials due to its light weight, high surface area, edge defects and curvature effect, as supports for metal hydride systems have been advocated [94]. An extensive compilation of hydrogen storage capacities by activated carbon material with details on the precursors, surface area, pore volume, hydrogen storage capacity and measurement methods employed is provided in tabular form in reference 95.

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CHAPTER FOUR

INTERMETALLICS AND CATALYSIS

Intermetallics appear to evolve as a new -class materials for catalyzing reactions [1-4] and for energy storage applications. In some literature, intermetallics and alloys are employed interchangeably. This means that one has to clearly see the difference between intermetallics and alloys. It is well known for long time that melting two or more metals together followed by cooling to re-solidify leads to the formation of new materials with properties distinct from that of the constituent metals. For example bronze consisting of 88% Cu and 12% Sn which was found to be harder and suited for making tools and weaponry than pure Cu.[5]. Among the various alloys steel ranks on the top.

Differences between alloys and Intermetallics

An intermetallic is a solid phase containing at least two metal atoms having a well-defined crystal structure with fixed and specific atom positions and site occupancies leading to long range ordering. An alloy is a random substituted solid solution of at least two metals where the atomic site distribution of the constituent elements is not fixed. Figure 1 represent an intermetallic and random alloy.

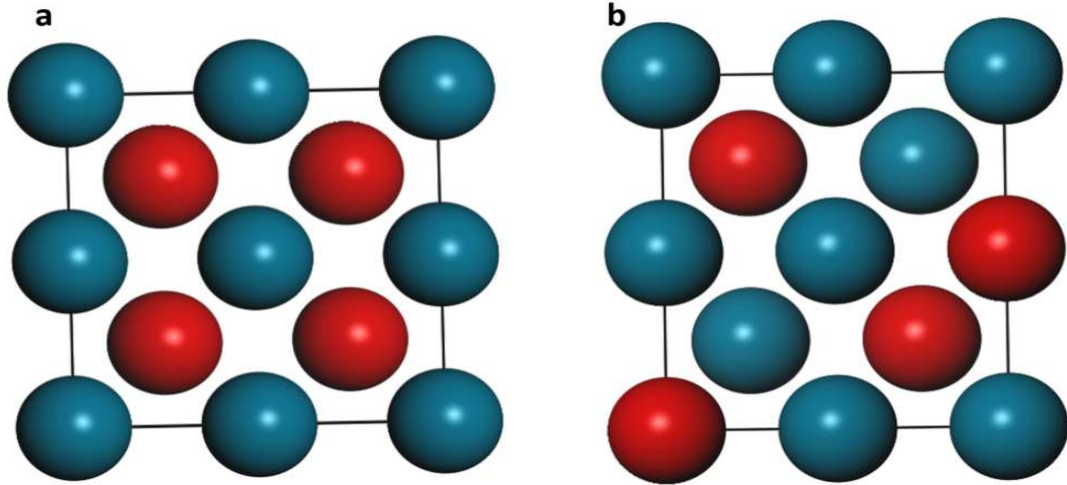


Fig.1. (a) the geometric arrangement of an intermetallic and (b) that of an alloy. One can recognise the ordering of atoms in (a) with a specific crystallographic space group (with distinct lattice positions and random distribution in (b) an alloy

The reason for the well-defined periodicity of intermetallics is the strong ionic/electronic interaction between the constituents. These interactions possibly promote formation of unique and complex crystal structures different from either of the parent metals, whereas in an alloy the crystal structure of the more abundant parent material (solvent) is expected to be retained.

Hume-Rothery has postulated that the crystal structure of most of the intermetallics are determined by the **valence electron concentration** (vec), which is defined as the number of valence electrons/atom in a unit cell. Valence electron charge is based only on the number of valence s and p electrons. For the value of $vec = 1.5$, the structure is bcc, for $vec = 1.61$ it is γ -brass and for $vec = 1.75$ the structure is hcp. Many intermetallics follow these guidelines and are called Hume-Rothery phases. The stability of Hume-Rothery phases arise from the electronic density of state (DOS) of the specific compounds. However, the necessary conditions for Hume-Rothery phases are not fully understood. A detailed discussion on the origin of the stability of Hume-Rothery phases is presented elsewhere [6, 7]. It may be

remarked that the conditions for Hume-Rothery phases need not be strictly adhered to. The concept of electronic factor in catalysis is a well-accepted concept and most intermetallic catalysts used to date are Hume-Rothery phases.

The application of alloys in catalysis possibly dates back to the work of Schwab and his co-workers. Alloying can affect the catalytic properties of a material by modifying both the active site morphology (geometric effect) and electronic structure as these two concepts are often discussed in the field of catalysis. The geometric effect of alloying essentially stems from the fact that many commercially important reactions are either structure sensitive at an atomistic level or requires a certain chemical environment at the gas-solid interface for better performance. It is therefore intuitive that a suitable bi-metallic (or multi-metallic) alloy may have significant catalytic applications due to geometric or ensemble effect.

Apart from geometric effects (i.e., crystallographic site isolation or ensemble), change in electronic structure (due to charge transfer and hybridization effect as a result of different coordination environment) during alloying can also affect the interaction of the surface with the reactants which may in turn influence catalytic properties. It is possible to postulate that geometric effect may predominate in catalysis by intermetallics though it is not general concept.

Typically, both geometric and electronic effects occur simultaneously as a result of alloying. The primary concern was electronic effects can alter interaction of the surface with the reactants, but they cannot provide positive correlations between adsorption energy of desired and undesired intermediates which is the main cause of non-selectivity in catalysis. However, geometric effects can break such correlations and have a much stronger impact on selectivity.

It is even more advantageous to use an intermetallic than an alloy because the unique crystal structure and long-range atomic ordering in an intermetallic ensures homogenous and reproducible active site

morphology and allows greater control on catalyst design. This essential difference between the two types of phases pure bi (multi)-metallics is the motivation for specifically calling intermetallics as model catalysts. At this point it is worth highlighting that the surface composition may vary with respect to the bulk and the long-range periodic order in the crystal lattice may be perturbed at the surface depending on reaction temperature and chemical atmosphere. The exact relationship between bulk and surface (active site) configurations in intermetallics has not been studied in detail and is likely difficult to achieve as the surface morphology can be altered even in the presence of a few ppm of an impurity such as oxygen.

In addition to greater atomic ordering, intermetallics can also form unique crystal structures which are not commonly demonstrated by alloys and may be advantageous to catalysis due to favorable geometric or electronic effects. For example, the γ - brass phase seen in many transition metal phase diagrams has a distinct crystal structure leading to unique coordination geometries and hence active site morphology.

It was shown [8] two $\text{Cu}_{0.6} \text{Pd}_{0.4}$ catalysts were tested with Pd being considered to be the “active element”. Despite having identical compositions, one bimetallic was a disordered alloy (prepared by heating at 1023 K) with an FCC structure (similar to the solvent, Cu) while the other crystallized (heated at 473 K) into an ordered CsCl structure (intermetallic). The intermetallic had a higher Pd-Pd separation (0.29624 nm compared to 0.26436 nm) resulting in greater extent of site isolation and higher ethylene selectivity (90% versus 75% at ~90% acetylene conversion).

Such direct comparison between alloy and intermetallic of same composition is rare and it is common to compare alloy/intermetallic systems with their pure constituent elements. Interestingly, a certain intermetallics may have identical DOS as a third catalytic metal and may be used as a direct replacement for catalyzing relevant chemistries. For example, the performance of PdZn and PdCd for methanol steam

reforming is exactly similar to pure Cu (due to similarity in the DOS of the three materials) and distinctly different from Pd.

An additional advantage of intermetallics is their well-defined periodic arrangement makes them tenable for density functional theory (DFT) calculations. In fact, intermetallics have also been used as quasi-crystal models and approximants because of the ease of computing associated with their long-range order.

Intermetallics are typically mechanically hard and brittle, have properties distinct from the parent metals. Over the past four decades, intermetallics have been used in a wide variety of mechanical, electrical and thermal applications with its most common chemical application being hydrogen storage [9] and corrosion resistance. In recent times, intermetallics have enjoyed exponentially increasing popularity as catalysts in academia and industry. Table 1 summarizes a number of intermetallic compounds and the relevant chemistry they catalyze better than the respective traditional catalysts [10].

Table 1. Examples of intermetallic catalysts and potential advantage over constituent metals. [2,4]

Reaction	Intermetallic systems tried	Conventional catalyst systems	Remarks
Hydrogenation of acetylene	PdZn, PdIn, Pd ₂ Ga, PdGa, Ga ₇ Pd ₃	Pd, Ni	Higher selectivity and yield of ethylene
Butadiene to butene	PdSn, PdPb, Pt ₃ Ge	Pd	Selectivity advantage
CH ₄ + CO ₂ → 2CO + 2H ₂	NiSc	Ni	Activity and selectivity improved
CO ₂ + H ₂ → C ₁ + C ₂	NiGa, Ni ₃ Ga	Cu	Higher activity
CO ₂ + H ₂ → CH ₃ OH	Ni ₃ CA ₃	Cu/ZnO	Low pressure reaction
CH ₃ OH + H ₂ O → CO ₂ + 3H ₂	PdZn	Cu/ZnO	CO ₂ selectivity
HCOOH → CO ₂ + H ₂	PdZn, PtBi	Pt	CO ₂ selectivity
C ₆ H ₁₂ → C ₆ H ₆ + 3H ₂	Pt ₃ Sn, PtGe	Pt	Higher selectivity
C ₄ H ₁₀ → C ₄ H ₈ + H ₂	Pt ₃ Sn, PtGe	Pt	Higher selectivity

Intermetallics in Catalysis – Survey of results from the literature

Schwab was the first to recognize anomalous activation barriers in the case of unsupported alloy and intermetallic catalysts compared to their pure metal

constituents [11,12] and studied the effect of compositional variation within the same phase as well as between different crystallographic phases for formic acid dehydrogenation as early as 1946. Since the late 1980s, the interest in intermetallic catalysts has garnered significantly more attention and efforts with increased commercial incentive of synthesizing low cost and high performing catalysts [1-3].

Formic acid dehydrogenation:

Formic acid dehydrogenation is a model reaction because of the simple nature of the substrate as well as its practical importance in modern fuel cell technology. Schwab et al. initially studied the activation barrier for this model system (on a large number of Ag-M and Au-M' catalysts) and determined different Hume-Rothery phases had markedly different activation energies. It was determined to be an electronic effect (establishing the applicability of Hume-Rothery's *vec* concept in catalysis) as the barrier was strongly correlated with intrinsic properties commonly associated with the valence shell electronic configuration of metals, such as electrical resistivity and hardness.[12] More recently, it has been found that the selectivity of formic acid dehydrogenation is also an important consideration since the formation of CO (as by-product) can poison typical fuel cell catalysts such as Pt. This has prompted the development of intermetallic catalysts which are less susceptible to CO poisoning than Pt. PtBi is suggested to be a suitable alternative demonstrating high activity (due to electronic effects) and low CO adsorption energies (increased Pt-Pt distance compared to pure Pt).[13] Similar results were also observed for Pt-Zn and Pt-Pb intermetallics.[14,15].

Selective Alkyne Semi-hydrogenation:

Selective semi-hydrogenation of alkyne in an alkene rich stream is a commercially important and well-studied system. Alkynes are typically present in trace amounts in alkene feeds destined for polymerization [16]. However, alkynes are poisonous to the polymerization catalyst and must be reduced to ppm level. Ideally, only the alkyne should be selectively semi-hydrogenated to decrease its concentration and enhances the alkene feed stream. However, typical hydrogenation catalysts (Pd or Ni) either lead to total hydrogenation of all unsaturated C-C bonds to (low value) alkane (Pd) or forms oligomers and green oil (Ni).

The geometric (and also the electronic) effects of alloying are seen to impart suitable catalytic properties for this reaction to a large number of intermetallic

compounds. In this case, the primary design concept is limiting Pd cluster size to just a few atoms as alkyne semi-hydrogenation requires fewer number of Pd atoms. [17,18] It is important to note that reducing the number of Pd atoms per active site increases the selectivity. Identifying the best catalyst is essentially an optimization challenge, balancing the gain in selectivity with the loss in activity [19].

Of all alkyne semi-hydrogenation reactions, acetylene semi-hydrogenation is considered to be the most challenging (in terms of selectivity) because of the small molecular size and very strong interaction of reaction intermediates with transition metal surfaces (particularly Pd).[20] Several intermetallics such as Pd-In,[21] Pd-Zn [22] and Pd-Ga [23-25] have shown high selectivity for this reaction.

The considerable effort is made for replacing Pd with cheaper base metals. Spanjers et al [26] studied the Ni-Zn phase diagram and found that only the γ -brass phase has a sufficiently high selectivity, almost 3 times higher than any other Ni-Zn alloy. This was attributed to the high degree of site isolation of Ni in Zn due to the unique crystal structure of this phase. In fact, it was concluded that the γ -brass phase had effectively single atom Ni sites [27] which led to high ethylene selectivity by minimizing oligomerization. Liu et al. [28] has demonstrated high acetylene semi-hydrogenation selectivity on Ni₃Ga and Ni₃Sn₂. Another highly selective Al-Fe catalyst having a unit cell of more than 100 atoms has been reported by Armbruster and co-workers.[29] It was found that neither of the pure components under experimental conditions was able to catalyze the reaction. The catalytic activity was therefore attributed to the small but apparently significant change in DOS due to alloying. Further, reduction of Fe-Fe coordination was also hypothesized to be an important factor for reducing oligomerization.

Intermetallic compounds have been found to be effective for semi-hydrogenation of higher molecular weight alkynes as well. For example, Ni-Ga intermetallics were found to be selective for phenylacetylene semi-hydrogenation [30, 28] while Pd₃Pb is selective for hydrogenating functionalized alkynes (aldehyde, ketone, carboxylic acid and ester) to (E)- alkenes.[31].

Steam Reforming of Methanol:

Steam reforming of methanol is gaining importance in the field of fuel cell development because methanol can act as a relatively safe, high yield and easy to

handle liquid source of hydrogen. However, parallel CO formation pathways must be suppressed to ensure the success of any methanol-based hydrogen storage approach. Pure Pd and Pt are exclusively selective to CO and is therefore not suitable. On the other hand, near-surface intermetallics such as Pd-Zn, Pd-Ga and Pd-In which are generated *in situ* from Pd/MO_x materials under reactive or pre-treatment conditions are found to be highly selective towards the desired products (CO₂+H₂). The high selectivity is attributed to the different preferred configurations of formaldehyde on intermetallic versus pure metal surfaces possibly due to differences in electronic structure [32]. Of these PdZn is perhaps the most widely studied; Armbruster et al. has published a detailed review of this chemistry on PdZn catalysts.[33] As pointed out, the near-surface composition plays a huge role in the selectivity of PdZn catalysts for this chemistry. Rameshan et al. reported that if the intermetallic existed to a depth of at least 5 layers below the surface (including the top exposed surface) the catalyst is selective towards CO₂ but if there is only a surface monolayer of the intermetallic on a Pd substrate then the pathway for CO production is favoured [34] Further, as previously mentioned, the thickness (number of layers from the surface) of PdZn near-surface intermetallic is a function of temperature and becomes effectively a monolayer (on a Pd substrate) above 623K thereby reversing the CO/CO₂ selectivity.

Low Temperature Electrocatalytic Oxygen Reduction:

The electrocatalytic reduction of oxygen is the typical cathode half reaction for low temperature fuel cells. The preferred pure metal catalyst for this reaction is Pt. However, the high cost of Pt is detrimental to the commercialization of this technology and there is considerable attention on increasing the intrinsic activity through alloying with base metals and introducing beneficial active site ensemble effects [35-37]. The key descriptor for activity is the adsorption energy of oxygenated species (most importantly OH) on the catalyst surface. Reduction in the OH bond strength is correlated with catalyst activity.[38] Alloying of Pt with suitable transition metals (Fe[39-41], Cr[42, 43], Co[44], Ni[45]) leads to a Pt d-band downshift which weakens this surface-OH interaction, thus increasing activity.[46] Further, it is seen that the specific activity of intermetallic Pt-M phases are always higher than alloys of similar composition.[47] The reason may be that the disorder in random alloys results in a fraction of the active sites to have the desired ensemble morphology whereas in the ordered intermetallics the desired ensemble morphology is assured in the entire catalyst.

Other examples:

Several other chemistries have also been successfully tested on different intermetallic materials. For example, Ni-Ga intermetallics are reported to be highly active and selective catalysts for CO₂ reduction to methanol [48] and even to alkanes and alkenes.[40] Pt- Ge, Al-Cu and Pd-Zn intermetallic catalysts were found to be selective for butadiene semi-hydrogenation.[50, 51] Pd-Zr and Co-Hf intermetallic compounds are seen to be more active for dry reforming of methane compared to the constituent pure metals.[52, 53] Takeshita et al. has reported a number of transition metal-rare earth metal intermetallics to be highly active for ammonia synthesis.[54] Pd-Zn catalysts have been found to be effective for a variety of reactions including partial methanol oxidation, methanol dehydrogenation and ester hydrogenation [55-57].

Synthesis of Intermetallic Compounds

The synthesis of metallic catalysts either by wet or dry methods are well known in literature, but however the synthesis of intermetallics has not received that much attention. Even if a method is available, it is only applicable to a set of elements and not generally applicable for any set of other elements. Conventionally, high temperature solid state diffusion methodology is employed and this method often results in thermodynamically stable phases with high purity. Heating and cooling cycles have to be carefully chosen for phase purity of intermetallics. It should be noted that because of high temperature treatments the resulting samples will have low surface area and thus find applications in limited catalytic activity.

Miura et al. [58] adapted the high temperature diffusion method to synthesize supported Pt-Zn NPs. A Pt/Vulcan material and a lump of Zn (mole ratio 1:1) physically separated in a tube furnace were heated to 500°C for 8 h under a flow of nitrogen. The entire amount of Zn was consumed and PtZn intermetallic NPs were synthesized with particle size less than 15 nm. This approach is limited since it could not be extended to metals such as Bi, Pb or Tl because of their lower vapor pressure (even at temperatures approaching 800°C). Shao et al. [59] mixed together stoichiometric amount of Ni and Mg NPs formed by arc melting and heated to 623 K under hydrogen atmosphere for 2 h leading to the formation of Mg₂NiH₄ which can be dehydrogenated to phase pure Mg₂Ni ($d = 30\text{-}50$ nm) by evacuation at 623 K for 45 min.

Li et al. [60] used *in situ* reduction of layered double hydroxide precursors and found that the starting composition as well as the reduction temperature had an effect on the synthesized Ni- Ga intermetallic phase and particle size. Zhou et al.

synthesized a PdZn intermetallic by calcining and reducing a Pd/ZnO material.[61] A similar method was also used in synthesizing NiZn/ZnO NPs.[62] Onda et al. [63] used chemical vapor deposition of a Sn complex on Ni/SiO₂ to prepare a number of phase-pure Ni-Sn supported catalysts. Milanova et al. used a template approach to synthesize Cu-Sn and Ni-Sn NPs using a porous C-foam support.[64] Solvothermal techniques have been successfully applied by Sarkar et al. [65] to synthesize Pd₂Ga. Other possible techniques include electro-deposition [66] and mechanical attrition methods (reviewed in detail by Koch and Whittenberger [67]). Several techniques have also been applied to access metastable ordered intermetallic structures (which are not accessible through high temperature bulk synthesis) but phase-purity is often an issue due to the presence of residual pure metals or oxides [68-70].

Researchers have tried to adopt established wet chemical methods for the synthesis of monometallic NP to intermetallics. Cable and Schaak synthesized a number of M-Zn intermetallics through a solution synthesis method starting with a zero-valent organometallic Zn source.[71] Notable amongst these is the Cu₅Zn₈ γ -brass phase because accessing this phase in NP dimensions are challenging owing to its large and complex but highly symmetric crystal structure. Cable and Schaak developed a modified polyol method for the synthesis of M- Sn and Pt-M' intermetallics with sizes ranging from 10-100 nm.[72] Other similar solution based techniques are also reported in literature [73-76]. Brian et al [77] synthesized ternary intermetallic Au-Cu-Sn and Au-Ni-Sn phases through polyol method. A major drawback of many of these techniques is that there is no rational guideline as to which starting composition is required to access which intermetallic phase. Further, in many solution-based synthesis of intermetallics[71, 72], rigorous particle size control has also proven to be elusive. Zn is known to form a large number of catalytically relevant intermetallic compounds [78]. However, a potential drawback of Zn containing intermetallics is the ubiquitous presence of ZnO (observed by Schaak,[71]) which may significantly affect catalytic properties.[15] Barkholtz et al [79] circumvented this issue by using LiOH (at 200 0C), a reducing agent, as the synthetic medium to synthesize PdZn. In recent times significant effort has been focused on synthesizing hybrid intermetallics- pure metal/alloy catalysts with specific core-shell architecture via various de-alloying techniques. Examples are available in literature where either the core or the shell or even both may be intermetallics [80-84]. These materials are of particular importance for catalyzing electrochemical half reactions commonly utilized in fuel cells.

In general, simply ensuring stoichiometric addition of different metal precursors is neither a sufficient nor a necessary condition for intermetallic NP synthesis. Proper characterization is essential to ascertain that the correct phase is indeed formed and preclude the existence of mixed phases, undesired oxides or core-shell structures.

Concluding Remarks

Intermetallics, by virtue of their unique properties (compared to pure metals) may be effectively employed to perform a large number of chemical transformations [85-86] while providing added opportunities for optimizing activity and selectivity through manipulation of active site nuclearity and electronic structure. In this context it is worth mentioning that catalytic studies on ternary (or higher) intermetallic phases are rarely reported as of yet even though polymetallic catalysts (typically involving doping of small amounts of one or more metal as modifier) have been reported in literature [87-89]. This paper has highlighted the challenges of reliably synthesizing phase-pure intermetallic NPs. It is expected that synthesizing ternary phases or intermetallics with catalytically enhanced special nano-porous structures will be even more challenging. However, such efforts have already gained considerable focus in the last few years [90-93] and with the development of appropriate synthetic methods, we can potentially access an unlimited number of well-defined unique active site morphologies which may cater to any number of practically important reactions and be individually tailored for optimal performance for any type of chemistry.

Apart from better control over synthesis of intermetallics (particularly in NP form) the other significant improvement desirable in this field is to develop more sensitive and advanced methods for identifying the true surface morphology of intermetallics under reactive conditions. At present most catalytic properties of intermetallics are interpreted on the basis of bulk structure but as highlighted in this review it may prove to be a gross misinterpretation/simplification due to surface segregation effects.

Overall, it is apparent intermetallics offer several advantages over pure metals and even alloys for catalysis and will continue to gain traction in the catalysis community as we head towards a greener future where high selectivity would become indispensable to meet ever stricter waste (by-product) disposal and raw material procurement (such as mining of crude oil) laws. Further it may be hoped that development in the areas mentioned above will not only increase our ability to synthesize optimized catalysts but also improve our understanding of the fundamental surface phenomena which effects such increased activity and

selectivity, ultimately leading to enrichment of the entire field of catalysis in general.

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