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Mg-hydrides as Solid Fuels for Hydrogen Storage: Article review

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Abstract: Storage of hydrogen is one of the key challenges in developing hydrogen economy. Storage of hydrogen is a serious problem. Due to high inflammability, adequate safety measures should be taken during the storage of H2 fuel. In this review, we will focus on (i) hydrogen storage strategies to overcome the key barriers of high desorption temperature and low kinetics ii) hydrogen storage technologies for synthesis of adsorbent materials capable of adsorbing large amounts of hydrogen and which have proven useful both on gravimetric and volumetric basis, keeping in mind their advantages and disadvantages while they tend to store hydrogen both in the atomic and molecular form and iii) Solid fuels hydrogen storage materials specifically metal hydrides and complex hydrides. Highlighted of Mg hydrides, Mg complex hydrides, Mg based catalysts, and Nano-structured Mg complex hydrides in the past and present.

Keywords: hydrogen storage, hydrides, Mg complex hydrides, Mg nano structured, kinetics, thermodynamics.

1 Introduction

With the rapid population growth and economic development, fossil fuel reserves are largely depleted and the environmental pollution is further aggravated. Exploring sustainable clean energy sources and environmental technology to satisfy the world's growing demand are emerging as hot research fields and one of the foremost challenges for this century [1]**.** Among renewable energy resources, hydrogen as the new energy carrier is an alternative to fossil fuels. Specially, it is potential for implementation in a carbon-free emission cycle and high efficiency when combined with oxygen in the electrochemical reaction of a fuel cell to produce electricity. However, a main obstacle impeding anticipated future hydrogen economy is the lack of safe, efficient and economical on-board hydrogen storage. In response to this challenge, the U.S. Department of Energy (DOE) [2], has set technical targets for new hydrogen storage technologies to meet the light duty vehicle system. These include the gravimetric and volumetric densities, ease of charge and discharge, system and fuel costs [2-4]**.** Some of the key targets, which were revised in 2007, 2010, 2020 and ultimate DO targets are summarized in Table 1. Unfortunately, none of the current hydrogen storage technologies can fulfill these benchmarks. Therefore, developing reliable media and technologies to efficiently storage hydrogen in high density has been the focus of research efforts for several decades.

Table 1: Revised DOE hydrogen storage target.

Storage System Target	Gravimetric Density kg/kg	Volumetric Density kWh/Lsystem ($kg\ H_2/L$ system)	Cost \$/kWh (\$/kg H_2)	References
2007	1.5 (0.045)	1.2 (0.036)	-	Satyapal et al., 2007
2010	- (0.045)	- (0.028)	- -	U.S. DOE's 2010

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2020	1.5 (0.045)	1.0 (0.030)	\$10 (\$333)	U.S. DOE's 2020
Ultimate	2.2 (0.065)	1.7 (0.050)	\$8 (\$266)	

Research on hydrogen storage is being done on a larger scale in order to develop safe, reliable, compact and cost-effective materials which can be used for fuel cell technology [5]. Like any other product, hydrogen must be packaged, transported, stored and transferred, to bring it from production to final use. The main technological problem of a viable hydrogen economy is its storage and so far, finding a cost-effective method of storing hydrogen remains an indomitable challenge. Hydrogen must be made more energy dense to be useful for transportation. However, the solutions to the hydrogen storage problem are surfacing at a fast pace , scientists are researching innovative ways to store hydrogen [6-9]. In this review, we will focus on (i) hydrogen storage strategies ii) hydrogen storage technologies iii) Solid fuels hydrogen storage materials specifically hydrides complex hydrides, Mg-based catalysts and Nano-structured Mg complex hydrides, which directs researchers to design the ideal materials for hydrogen storage.

2 Hydrogen Storage Strategies

Hydrogen storage strategies can be basically classified into two categories: physical and chemical routes. Physisorption as the alternative way in physical hydrogen storage routes, adsorbs hydrogen in highly porous solid state adsorbents such as metal organic frameworks (MOFs) and nano-porous carbon. MOF exhibits large molecular hydrogen uptake capacity. It is remarkable because at 77 K (-196.15 ^{O}C) and 1.0 atm, it absorb hydrogen at a density near of liquid hydrogen 20K (-253.15^{O}C and 1 atm) when considering hydrogen density in the pores. More details about carbon/MOFs have been summarized in previous review articles [10-14]. However, significant hydrogen adsorptive storage capacities in physisorption need to be reached at liquid-nitrogen temperatures 77 K (-196.15 ^{O}C) and pressures of several MPa. This is attributed to weak binding energy between molecular hydrogen and the surface of sorbents in the range of 2–5 kJ mol $^{-1}$ H_2 [15] . Generally, the hydrogen storage properties of physisorption appear to be limited by specific surface area, pore structures and pore size distributions, surface functionality and the bulk density of the adsorbents [16]. Hydrides of some metals and non-metals form a different class of materials for hydrogen storage characterized by their ability to store larger amounts of H_2 through the formation of chemical bonds (chemical route). For instance, metal hydrides for hydrogen storage starts with dissociation of hydrogen molecules, migration and chemical bonding of the hydrogen atoms by integration in the lattice of metals with a high binding energy (450 kJ mol^{-1} H_2), therefore storage capacities and the operating temperatures are elevated. However, the main shortcoming in chemisorption is usually requiring high temperatures to absorb/release the hydrogen due to high binding energy [17-19]. Fig. 1 shows the range of binding energies targeted by [5], suggesting that the ideal materials for hydrogen storage would achieve a compromise between physisorption and chemisorption within the range of 10–60 kJ mol^{-1} H_2, which is strong enough to hold H_2 but weak enough to allow for quick desorption. In contrast, metal complex hydrides contains a high density of hydrogen and some of metal hydrides possess good reversibility such as MgH_2, however, they are generally plagued with the issues of unfavorable thermodynamics and kinetics which are critically reviewed by [20,21].

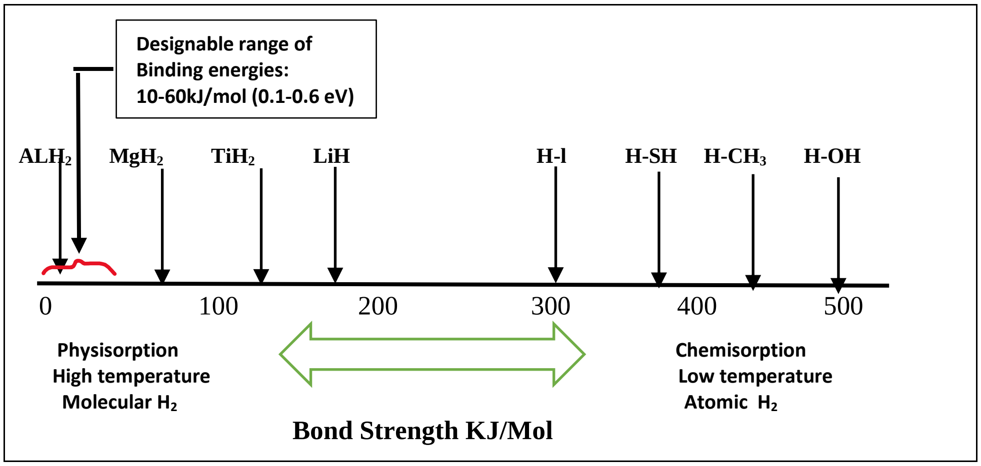

Fig. 1: Targeted range of bond strengths that allowhydrogen release around room temperature.

Ki Chul Kim, 2018 [22] review a 3 primary strategies, namely, introduction of appropriate dopants, particle size control, and design of novel reactant mixtures based on high-throughput screening methods, briefly described the aim of evaluating the potential of metal hydrides for hydrogen storage applications. The review suggests that successful development of promising hydrogen storage systems will depend on collaborative introduction of these 3 primary design strategies through the combined utilization of experimental and computational techniques to overcome the major challenges associated with the reaction thermodynamics of metal hydrides.

3 Hydrogen Storage technologies

Hydrogen storage is clearly one of the key challenges in developing hydrogen economy. Hydrogen can be stored as (a) pressurized gas, (ii) cryogenic liquid and (iii) solid fuel as chemical or physical combination with materials, such as metal hydrides, complex hydrides and carbon materials. Each of these options possesses attractive attributes for hydrogen storage. The traditional hydrogen storage facilities are complicated because of its low boiling point 77 k (-196.15 ^{O}C) and low density in the gaseous state (0.08988 g/l) at 1 atm. Available technologies permit directly to store hydrogen by modifying its physical state in gaseous or liquid form in pressurized or in cryogenic tanks. Currently, gaseous hydrogen compression and hydrogen liquefaction are the most mature technologies. However, they are still associated with drawbacks such as manufacturing cylinders capable of withstanding ultra-high pressure (up to 70 MPa) with light weight, energy consuming process for gaseous hydrogen compression and liquefaction, permeation and safety issues. Fig. 2 presents H_2 gravimetric capacity as a function of hydrogen release temperature for many of the unique hydrogen storage materials investigated by fuel cell technology office (FCTO) with the ultimate targets for gravimetric capacity of 7.5 wt% and min/max operating temperatures of 40^{O}C (-233.15 K) - 85^{O}C (188.15 k) [23]. These hydrides basically are consisting of chemically decomposable hydrides ($NaBH_4$ and NH_3BH_3), metal complex hydrides (aluminates [AlH_4], amides [NH_2] , and borohydrides [BH_4]) and metal hydrides (AlH_3 and MgH_2). In most cases, although chemically decomposable hydrides have the merits on ambient temperature of H_2 generated through chemical reaction such as reacting with water, the critical problem of these materials is not on-board hydrogen regeneration which lowers its market potential as hydrogen storage option.

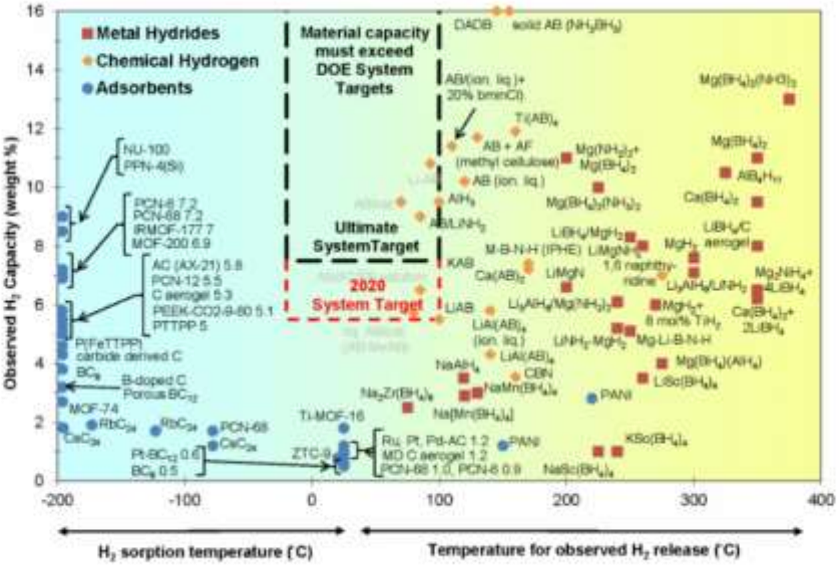

Fig. 2:H_2 gravimetric capacity as a function of hydrogen release temperature for many of the unique hydrogen storage materials.

3.1 Compressed storage hydrogen

Gas compression is known as the most time and energy efficient method which is able to provide an easy to use source for consumers. As hydrogen has a lower specific gravity than other fuel gases, it takes more energy to compress hydrogen for given mass and compression ratio [24]. The volumetric storage density of hydrogen at 25^{o} C is 0.0807 P kg m^{-3}, based on thermodynamics. where at P = 350 bars, the volumetric density is 28 H_2 kg m^{-3} in a vehicle, that can travel 500 to 700 km before refilling, the high-pressure storage vessel should be sized to 0.18 m^3[25]. The efficiency of energy storage by compressed hydrogen gas is about 94%. This efficiency can compare with the efficiency of battery storage around 75% . It is noted that increasing the hydrogen storage pressure increases the volumetric storage density, but the overall energy efficiency will decrease. Steel vessels are commonly used for high-pressure gas compression storage with operating pressure as high as 700 bars [26]. However, for hydrogen storage, steel is not a desirable material. It is because the diffusion of hydrogen into steel causes hydrogen embrittlement failure, especially when the vessels undergo frequent charge and discharge. In the case of rupture, steel projectiles may cause serious injuries. Furthermore, the gravimetric storage density, defined as the ratio of the mass of stored gas to the mass of vessel, is low, normally in an order of 0.01 H_2-kg/kg. The hydrogen embrittlement problem can be resolved by using vessels made of composite materials comprised of polyethylene, or carbon fiber and epoxy resin with thin aluminum liner [27]. The main advantages of compressed gas storage are reliability, indefinite storage time, easy to use, affordable cost and efficiency, as well as environmental benefits. Its main disadvantage is the low storage density which depends on the storage pressure and the potential for developing leaks. Hence, many professionals anticipate that hydrogen storage in high pressure cylinders is very unlikely to be a popular method in future. In addition high-pressure storage results in higher capital and operating costs. The overall storage cost is projected to be 1.50–4.20 US$/G and more than 30 US$/ G for tube storage at storage period of 1 day. Capital costs for pressure vessel storage are typically 3000–5000 US$/ G of hydrogen storage capacity [28,29]. Fig.3 shows the difference in storage cost estimates between industry and literature for gaseous storage systems. Also Brian et.al., [30] reported that the cost for the distributed production scenario is between $2.30/kg and $3.20/kg, with a projected cost of $2.70/kg of H_2. For high-pressure tube trailers, the panel found costs between $1.00/kg and $1.20/kg, with a projected cost of approximately $1.10/kg H_2.

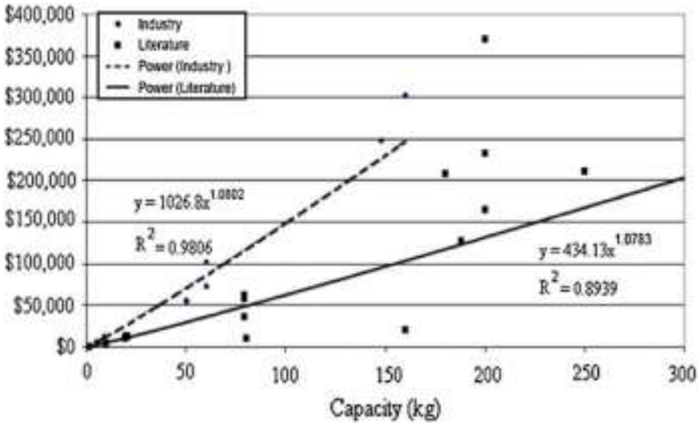

Fig.3: Summary of gaseous hydrogen storage costs.

3.2 Liquid storage hydrogen

Liquid hydrogen, is noncorrosive and colorless at 20 K (-253.15). Liquid hydrogen tanks can store 0.070 kg l^{-1} of liquid hydrogen compared to 0.030 kg l^{-1} as in case of compressed gas tanks. Hydrogen gas can be liquefied and stored in a thermally insulated vessel. Liquid hydrogen has higher volumetric storage density (20 to 50 H_2-kg/m^3) as well as gravimetric storage density (8 to 25 H_2-kg/kg) than storage in compressed hydrogen [27]. Hydrogen gas is compressed and cooled below the inversion temperature of 202 K (-71.15^{O}C). Subsequent expansion causes the formation of cryogenic hydrogen liquid at boiling point of 20 K (-253^o C). The energy storage density has been estimated to be 5 MJ/liter **[**31**]**. With a calorific value of 120 MJ/ H_2-kg, the volumetric storage density of hydrogen liquefaction is about 40 H_2-kg/m^3. The energy required to liquefy hydrogen for storage in an ideal Linde thermodynamic cycle has been calculated to be 11.88 MJ/H_2-kg [25] about 64% higher than the energy required for high-pressure hydrogen gas compression. Taking into account the caloric value of hydrogen of 120 MJ/H_2-kg, the energy efficiency of hydrogen liquefaction storage is 91%. Amos et al., [32] reported that the energy consumption would be 10 kWh/H_2-kg (36 MJ/ H_2-kg), equivalent to an energy efficiency of 77% for hydrogen storage. It is possible to increase this efficiency by modification of the thermodynamics of the Linde cycle with multiple heat exchangers, compressors, and expansion valves. However, the equipment cost and corresponding maintenance cost will increase accordingly. The main advantage of storage of liquefied hydrogen is its high density in low pressure. These features enable compact and light weight storage and efficient delivery options. The disadvantages of liquid hydrogen is that it requires the addition of a refrigeration unit to maintain a cryogenic state, thus adding weight and energy costs, and a resultant 40% loss in energy content. The liquefying process of hydrogen adds an excess 30% to the production power demand. Furthermore, utilizing gas liquefiers add more sophistication to the production system. As a result, liquid hydrogen costs 4–5 times more than the compressed gas state product. Nowadays research is centered around the development of composite tank materials which would result in lighter and stronger tanks. Although the technology appears to be very promising as it is gravimetrically and volumetrically efficient, additional research needs to be carried out to overcome problems dealing with the uptake and release of hydrogen, high hydrogen liquefaction rate that causes large energy loss, hydrogen boil-off and tank cost. Hydrogen liquefaction storage is less environmental than high-pressure hydrogen gas compression because of lower energy efficiency. From the life cycle point of view, low energy efficiency means high pollutant emission. In general, hydrogen liquefaction storage is more hazardous than high-pressure hydrogen gas compression storage as: (1) Unlike hydrogen gas, liquid hydrogen is heavier than air. Therefore, in case of leakage, liquid hydrogen flows downwards and accumulates before it vaporizes; (2) Boil-off hydrogen vapor must be vented to a safe location clear from any source of ignition; (3) The safety valve and vent of a storage vessel may be clogged by ice due to the cooling of moist air. The subsequent pressure build-up may cause the vessel to rupture; (4) Liquid hydrogen is subject to contamination of air condensed onto equipment during repeated charging and discharging. The mixture can then be easily ignited. It is important to prevent air condensation or oxygen enrichment by proper insulation and sealing. (5) Air leaking into liquid hydrogen can lead to fire or explosion. The pressure of the storage vessel must be maintained above the atmospheric pressure to prevent air from entering the vessel [15,33]. Amos et al., [32] estimated the capital cost per unit of liquid hydrogen production rate to be US$44,100/kg/hour. For example, a hydrogen liquefaction storage system of 300- kg/hour capacity, that can instantaneously charge 5 kg of liquid hydrogen in one minute, will cost about US$13 million. The operating cost, including the energy for compressor and cooling liquid nitrogen, is about US$0.5/kg.

3.3 Solid fuels hydrogen storage materials

Adsorbing hydrogen on a solid adsorbent at moderate pressures and ambient temperatures is another potential method for hydrogen storage. The method is safer and requires less expensive storage equipment than the high-pressure compression and cryogenic systems [9]. An optimum hydrogen-storage material is required to have high hydrogen capacity per unit mass and unit volume which determines the amount of available energy, low dissociation temperature, moderate dissociation pressure, low heat of formation in order to minimize the energy necessary for hydrogen release, low heat dissipation during the exothermic hydride formation, reversibility, limited energy loss during charge and discharge of hydrogen, fast kinetics, high stability against O_2 and moisture for long cycle life, cyclability, low cost of recycling and charging infrastructures, provide reactivity (high safety) and high hydrogen storage densities. Hydrogen can be stored using the process of chemical storage or by physisorption. Chemical storage uses technologies in which hydrogen is generated through a chemical reaction. The materials which store hydrogen through chemical storage are metal hydrides and complex hydrides. The main difference between them is the transition of metals to ionic or covalent compounds for the complex hydrides upon absorbing hydrogen. The capture and release of hydrogen on materials involves molecular adsorption, diffusion, chemical bonding and Van der Waals attraction and dissociation. Hydrogen can also be adsorbed in molecular/ionic form on suitable surfaces using pressure, temperature and electrochemical potential to control its surface structure and bonding strength. Synthesis of adsorbent solid materials capable of adsorbing large amounts of hydrogen at such conditions is, however, the main issue that still needs to be addressed, in order to commercialize hydrogen storage systems.

There are four types of hydrides: 1) metallic or interstitial hydrides such as $LaNi_5H_6$, MgH_2, and $NaAlH_4$. Due to small size dihydrogen in these hydride, hydrogen occupies interstices in the metal lattice producing distribution without any charge in its type, so these are known as interstitial hydrides, 2) saline (ionic) compounds such as alkali and alkaline earth metals. They are crystalline, nonvolatile and non-conducting solid state and have high melting and boiling points, 3) covalent of molecular hydride such as HF, CH_4,NH_3,H_2O. They consist of discrete covalent molecules which are held together by weak Vander Waal's forces of attraction, they have low melting and boiling point and volatile, 4) dimeric (polymeric) hydride which identified on the basis of structure such as borane. Hydrogen storage in metal hydrides depends on different parameters and consists of several mechanistic steps. Metals hydrides differ in the ability to dissociate hydrogen, this being dependent on surface structure, morphology and purity. Table 2 presents the comparison between the three systems of H_2 storage.

Table 2: Comparison between three principal approaches used for storing hydrogen.[25]

Storage approach	Volumetric hydrogen Capacity, (kgH_2m^{-3}	Storage capacity, kg l^{-1}	Disadvantages
Gaseous storage method (compressed H2 gas	40 -60	0.07	- Safety problem - High cost of pressurization

under 80 MPa (800 bar) pressure			- Large pressure drop during use - Hydrogen embrittlement of storage tanks
Liquid storage method at cryogenic tank at −225°C	~71	0.03	- Since it is open, large thermal losses are expected - Safety problem - High cost of liquefaction
Solid-state method via metal hydrides	80-160	-	None of the above

3.3.1 Metal hydrides

Some metals are able to build a chemical bond with hydrogen as per their inter atomic lattice. In this method, hydrogen is bonded to the metal in reduced temperatures and releases the gas by getting heated. An advantage of this method is the ability of bonding at normal or low pressures and releasing at high pressure conditions. The most novel method of this sort is called the “chemical hydride slurry approach as reported by Andrew et al., 2015. In this method, the reaction between hydrogen and a chemical hydride/organic slurry is used in order to store hydrogen. The high purity hydrogen can be extracted at the point of use from the media by their action between the slurry and water. The hydride/organic slurry usually have a fluid-like nature which brings unique opportunities of storage, transportation and pumping. Improvements in energy transmission of hydrogen, stabilizing the stored fuel at normal temperature and pressure, high volumetric energy content and very low harmful emissions could be named as the advantages of this method..

Metal hydrides such as magnesium hydride (MgH$_{2)}$ and aluminum hydride (AlH$_3$), are famous for their unique ability to absorb hydrogen and release it later, either at room temperature or through heating of the tank. The main disadvantages of MgH$_2$ as a hydrogen store is the high temperature of hydrogen discharge, slow desorption kinetics and a high reactivity toward air and oxygen, slow dehydrogenation kinetics and relatively high desorption temperatures due to the highly stable Mg−H bond. Thermodynamic properties of the magnesium hydride system have been investigated by Soloveichika et al., [34] . The results showed high operating temperature which is too high for practical on-board applications and high thermodynamic stability of MgH$_2$ results in a relatively high desorption enthalpy, which corresponds to an unfavorable desorption temperature of 300^{O}C at 1bar H$_2$ pressure [35,36]. Kinetic parameters of the process of thermal decomposition of the MgH$_2$ hydride obtained by the method of the mechano activation of magnesium in a hydrogen atmosphere and of the commercial AlH$_3$ hydride have been studied upon the rapid heating in the range of temperatures of 150-510 ^{O}C at hydrogen pressures of 0-2 atm. Terent’eva et al., [37] reported that the activation energies of the hydrogen desorption are 135 kJ/mol for MgH$_2$ and 107 kJ/mol for AlH$_3$.

The resistance of metal hydrides to impurities is one of the critical issues for on-board applications in order to maintain performance over the lifetime of the material. The effects of N$_2$, O$_2$, CO$_2$ and CO on a pure magnesium powder have been studied [38]. Both O$_2$ and N$_2$ slowed the rate of hydrogen absorption, while CO and CO$_2$ entirely prevented the uptake of hydrogen [39].

For stationary applications, a major imediment for practical use of MgH$_2$ for hydrogen storage related to fuel cell technology is that its equilibrium temperature at 1 bar hydrogen pressure and 561.15 K (288 ^{O}C), which is much higher than the fuel cell operation temperature 358.15 K (85^{O}C). This is attributed to the fact that magnesium has very strong affinity to hydrogen and the decomposition enthalpy of MgH$_2$ is 75 kJ/mol H$_2$, rendering the material thermodynamically and too stable within the temperature range that is considered. In addition to the thermodynamic issues, the kinetics of dehydrogenation of MgH$_2$ is also slow at moderate temperatures. MgH$_2$ must be heated to 300-400 ^{O}C to achieve an adequate rate of dehydrogenation and hydrogenation, if no additives are used [40].

A series of comprehensive hydride databases reported have been constructed [41] and made freely available on the Internet (URL http://hydpark.ca.sandia.gov). They include extensive listings of alloys reported to hydride, detailed engineering properties on selected hydrogen-storage elements and alloys and a hydride-applications database.

3.3.2 Complex hydrides

Complex hydrides are metal salts, typically containing more than one metal or metalloid, where the anion contains the hydride. They typically have higher hydrogen gravimetric storage capacities and volumetric densities than simple hydrides. Complex hydrides occupy the chemical formula $A_xMe_yH_z$. The A elements are mainly elements of the first and second groups of the periodic table, and the Me part is occupied either by aluminum or boron. Light metals such as Li, Be, Na, Mg, B and Al, form a large variety of metal–hydrogen compounds. They are especially interesting due to their light weight and the number of hydrogen atoms per metal atom, which is in many cases at the order of H/M = 2. Heavier ones may enter the multiple component system only as a low abundant additive, most likely for alteration of properties or as a catalyst [42.] The complex hydrides that contain Al and B (boron) present very attractive hydrogen storage properties for mobile and portable applications, especially if they are combined with a low-atomic-weight cation such as Li, Be, Na, or Mg [43].

Complex hydrides are very interesting and promising materials for hydrogen storage applications. They are costlier, but they are capable to store H_2 in a smaller space while retaining their energy effectiveness. When pressure of the gas is increased, energy density by volume gets improved. Although the technology is simple, the process is volumetrically and gravimetrically inefficient and undergoes desorption at higher temperatures 600 K (326.85 ^{O}C).

3.3.3 Magnesium complex hydride

A critical factor for hydrogen absorption by metals is the metal surface, which activates dissociation of hydrogen molecules and allows easy diffusion of hydrogen into the bulk. As the reaction progresses, hydrogen diffusion takes place and the hydride layer grows, producing a nearly impermeable layer (Reule et al., 2000), diffusion through this hydride layer becomes the rate-limiting step in the hydride formation process (Friedlmeier, 1997). In addition to formation of a compact hydride layer, exposure to oxygen also lowers absorption rates due to the formation of a highly stable oxide layer [44-46].

Magnesium based metal hydride are considered attractive candidates as rechargeable hydrogen storage materials because of their high hydrogen capacities (theoretically up to 7.6 wt. %), good-quality functional properties such as heat resistance, vibration absorbing, reversibility, recyclability and low costs [47]. Firstly introduced the concept of “reactive hydride composite” combining MgH_2 and borohydride ($LiBH_4$) through the reaction of $2LiBH_4+MgH_2 \leftrightarrow 2LiH+MgB_2+4H_2$ (ΔH¼ 46 kJ mol^{-1} H_2), in this system the chemical reaction between the two hydrides can simultaneously lower the overall reaction enthalpy and still remain the high gravimetric hydrogen storage capacity (10.5 wt%). However, although from a thermodynamic point of view such hydrides are optimized, they still suffer from slow ionic mobility and thus poor kinetics. Andreasen et al., have reviewed the kinetics in terms of apparent activation energies and apparent pre factors of Mg-based hydrides[48]. It was suggested that variations in apparent activation energies correlate with the presence of MgO surface layer inhibiting diffusion of hydrogen. Thus, oxidized samples show large apparent activation energies and well activated samples show smaller activation energies.

Many efforts has focused on Mg-based hydrides in recent years to reduce the desorption temperature and to fasten the re/dehydrogenation reactions. These can be accomplished to some extent by changing the microstructure of the hydride by 1) alloying either by doping with transition metal elements to improve surface properties or by ball-milling (mechanical alloying) with elements which reduce the stability of the hydrides 2) using proper catalysts to improve the absorption/desorption kinetics [49] and 3) producing novel nanostructured composite which have the advantage of combining alloy engineering and nano structuring to change the thermodynamics of Mg/MgH_2 to some extent [50].

3.3.3.1 Alloy and alloy doping

Mixing Mg with Ti leads to an alloy with markedly faster hydrogenation kinetics as compared to that of pure Mg, and the resulting hydrides are too stable for hydrogen storage applications as reported by Süleyman et al.; [51]. Moreover, Mg-Ti alloys are thermodynamically unstable with respect to decomposition into the elements. Süleyman et al., [51] used first-principles density functional theory calculations that adding Al or Si to Mg-Ti to make the alloys more stable and their hydrides less stable. They found that controlling the structure of Mg-Ti-X (X = Al or Si) alloys by growing multilayers of Mg and TiX allows for tuning the hydrogenation energy and improves the alloys as hydrogen storage materials. It is remarkable that theoretical investigation has indicated that alloying with Ti–Al/Si can remarkably destabilize the magnesium hydride phase, lowering the hydrogenation energies to a range of 39–48 kJ mol^{-1} H_2, which is suitable for most commercial applications. More importantly, this calculation correlates well with experimental results of the sputtered Mg–Al-Ti multiplayers, in which nanometric Mg or Mg–Al–Ti layers are confined by 2 nm thick AlTi layers, attain a hydrogen capacity of 5.1 wt% without significant degradation over 200 cycles at 200^{O}C . Also it is reported that catalysts doping has been regarded as one of the most feasible means to improve the de-/rehydrogenation kinetics of MgH_2 because it can effectively relieve the de-/rehydrogenation energy barrier of MgH_2 systems. Hanada et al., [52] proved that the smaller particle size of metallic element doped, the better dehydrogenation property exhibits on MgH_2.

Hydrogen absorption/desorption properties of studied Mg-based alloy hydrides are summarized in Table 3 as reported by Sakintunaa et al.; [9] .

Table 3 : Hydrogen absorption/desorption properties of Mg-based alloy hydrides [9]

Mol %	Method	Temperature (^oC)	pressure	Tdes:	Cycling stability	Max with of H_2
MgH_2-5 mol% Fe_2O_3	BM	T_{abs}:300	P_{abs}:2-15	Tdes:20	No data	1.37
30wt%Mg-mNi$_{5-x}$ (CoAlMn)$_x$	BM	T_{abs}:15	P_{abs}: 6	T_{abs}:83	No data	2.30
Mg-5wt%Fe-Ti$_{l.2}$	BM	T_{abs} and T_{abs}: 400	P_{abs}:30	T_{abs}: No data	9 cycle: stable after forth cycle	2.70
MgH_2-5mol V_2O_5	BM	T_{abs} 250	P_{abs}: 15	T_{abs}:1.6	No data	3.20
90Mg-10Al	BM	T_{abs} and T_{abs}: 400	P_{abs}:15 P_{abs}:12	T_{abs}:27-19 T_{abs}:0.5-5.8	No data	3.30
Mg-50wt% ZrFe$_{1.4}$ Ce$_{0.6}$	BM	T_{abs} 250-350 T_{abs} 300-350	P_{abs} :20 P_{abs} :1	T_{abs} 1 T_{abs} 5	2 cyc: not stable	3.40
Mg-10 wt% CeO_2	BM	T_{abs} and T_{abs}: 300	P_{abs}:11 P_{abs}:0.5	T_{abs} 60 T_{abs} 60	5 cyc: not stable	3.43
Mg-20 wt% Mn(la, Nd, Ce)	BM (pellet form)	T_{abs} 300 T_{abs} 480	P_{abs} :10 P_{abs} :1	T_{abs}:10 T_{abs} :5	No data	3.50
Mg-40 wt% ZrFe$_{14}$ Cr$_{06}$	BM	T_{abs} 270-280	P_{abs} :1	T_{abs}:15	2 cyc: not stable	3.60
La2Mg$_{17}$-40 wt% LaNi$_5$	BM	T_{abs} and T_{abs}: 250-303	P_{abs} and P_{ab}:4-7	T_{abs} :0.45 T_{abs} :4	20 cyc: stable	3.70
$La_{15}Ni_{15}Mg_{17}$	Hydriding combustion synthesis	T_{abs} and T_{abs}: 250-400	P_{abs} :2.21-11.34	T_{abs}:15	Not stable	4.03
Mg-50 wt% LaNi$_5$	BM BM	T_{abs} 250-300 T_{abs} 200	P_{abs}:1.62-15.48 P_{abs} and P_{abs}:10-15	T_{abs}:5 T_{abs} :333	Not stable	4.10
MgH_2- 2LiNH$_2$	BM	T_{abs} 250-300 T_{abs} 200	P_{abs} : 50 P_{abs} :10	T_{abs} :60	4 cyc: stable after 2nd cycle	4.30
Mg_2 C_oH_5	Mixing	T_{abs} 450-550	P_{abs}:17-25	No data	1000 cyc: stable	4.48
MgH_2-5 mol% Al_2O_3	BM	T_{abs} 300	P_{abs}: 15	T_{abs} :67	No data	4.49
1.1MgH_2-2LiNH$_2$	BM	T_{abs} 200	P_{abs} : 30	T_{abs} :30	9 cyc: stable	4.50
Mg-20wt% TiO_2	BM	T_{abs} 350 T_{abs} 330-350	P_{abs} :20 ba P_{abs} : 1	T_{abs} :2 T_{abs} : 10	No data	4.70
Mg- 30 wt% MmNi$_{4\cdot6}$Fe$_{0.4}$	BM (hexane medium)	T_{abs} 300-550	P_{abs} :2	T_{abs}: 30	No data	5.00
Mg_2-5 wt%V	BM	T_{abs}:300	P_{abs}: 1-3	T_{abs}:2	2000 cyc: stable	5.00
Mg-Fe-Mg2 FeH6	Mixing	T_{abs} 473-552	Pabs:77-85	T_{abs} :10 T_{abs} :90	600 cyc: stable	5.00
MgH2-Mg2FeH6	Mixing	T_{abs} 350-525	Pabs:3.6-93.7	T_{abs} :90-1440	No data	5.00
MgH2-5at%Ti	BM	T_{abs} 200	Pabs: 10	T_{abs} :3.33	No data	5.00
MgH_2-5at%Ni	BM	T_{abs} 4:300 T_{abs} 200 T_{abs} 300	P_{abs}:0.15 P_{abs}:10 P_{abs}: 0.15	T_{abs}:0.83 T_{abs}:5 T_{abs}:16.7	No data	5.00
Mg-30wt%LaNi$_{2.28}$	BM	T_{abs} 280	P_{abs}:30	T_{abs}: 1.6	3cyc: stable	5.54
MgH_2-5at%V	BM	T_{abs} 200 T_{abs} 300	P_{abs}:0.15 P_{abs}: 10	T_{abs}:333 T_{abs}:1.66	No data	
Mg10wt% Fe2O3	BM	T_{abs} 320	Pabs:12	T_{abs}: 60	No data	5.60
Mg10wt%CFMmNi5	Mixing And encapsulation	T_{abs}:500	$P_{abs\&}$: P_{abs} 3-10	T_{abs}:40	No data	5.60
Mg-10wt%Al_2O_3	BM	T_{abs}:300	P_{abs}: 11 P_{abs}:0.5	T_{abs}: 60 T_{abs}s: 60	5cyc: stable	5.66

3.3.3.2 Mechanical Ball milling alloy

The ball-milling creating fresh surfaces during processing is an economic process that is widely applied to metal hydrides to achieve good surface properties [53, 21] The main effects of ball-milling are increasing of surface area, formation of micro/nanostructures and creation of defects on the surface and in the interior of the material. The induced lattice defects may aid the diffusion of hydrogen in materials by providing many sites with low activation energy of diffusion. Guoxian et al., reported that the induced micro strain assists diffusion by reducing the hysteresis of hydrogen absorption and desorption [54]. The increased surface contact with catalyst during ball-milling leads to fast kinetics of hydrogen transformations. Huot et al., [55] investigated the structural difference between milled and un-milled MgH_2. Faster hydrogen desorption kinetics, reduction in activation energy and enhanced kinetics observed for the milled MgH_2 compared to the un-milled one. The activation energies for desorption were measured as 156 kJ/mol and 120 kJ/mol for the milled and un-milled powders, respectively. The oxide particles may operate as a milling ball during high-energy ball-milling that creates many defects in the Mg powder. Jung et al., [56] reported that defects provide hydrogen an easy path to Mg . Zaluska et al., [46] has been found that ball-milling of Mg_2NiH_4 substantially decreases the desorption temperature. Depending on the ball-milling conditions, the shift of the onset of desorption temperature can be as large as 100 ^{O}C for MgH_2 and 40 ^{O}C for Mg_2NiH_4.

3.3.4 Mg based catalyst

Catalysis is one of the critical factors in the improvement of hydrogen sorption kinetics in metal hydride systems [46]. Metal based catalyst indicated that whether mixed as additives with small quantities or doped as alloying components, can promote improved energetic of H_2 sorption in Mg [49] Adding catalysts contributes to lower hydrogenation activation energy in two ways: reducing crystalline size of milled MgH_2 powder, as well as facilitating the hydrogen diffusion in Mg/MgH_2.

Metal based catalysts comprised of (i) transition metals (e.g. Pd, Fe, V, Ni, Ti, Mn, Co, Cu) (ii) transition metal oxides (e.g. Nb_2O_5, Sc_2O_3, TiO_2, V_2O_5, Cr_2O_3, Mn_2O_3, Fe_3O_4, CuO, Al_2O_3) , (iii) transition metal halides (e.g. Cl, F) and (iv) transition metal alloys (e.g. $LaNi_5$, FeTi (Mn), Mg_2Ni, and Mg_3La). Such metal based catalysts enable fast and effective dissociation of hydrogen molecules for absorption or Mg–H bond destabilization for desorption, respectively, which result in enhanced kinetics of hydrogenation or lower desorption temperatures in Mg/MgH_2 system. Effective catalysts, even added in small amounts enhance the formation of a hydride in reasonable extent.

Jianfeng etal., investigate the isothermal hydrogenation kinetics for a number of un-catalyzed and catalyzed MgH_2 samples prepared by high-energy ball milling [50] . The effects of processing parameters on the hydrogenation kinetics of magnesium hydrides were studied. Different kinetic models were employed to further understand the mechanism of hydrogenation. The best kinetic model to describe the hydrogenation behavior of the ball-milled Mg/MgH_2 in this work was found to be the JMA (Johnson-Mehl-Arrami) model. In addition, hydrogen diffusion was found to be a controlling step when the kinetic rates are slow.

There is intensive research about finding a proper catalyst to enhance the hydrating properties. Oelerich et al., investigated different amounts of oxides for catalysis but they found that only 0.2 mol% of the catalyst is sufficient to provide fast sorption kinetics [57]. It was reported that the rate of absorption is controlled by: the rate of hydrogen dissociation at the surface, the capability of hydrogen to penetrate from the surface which is typically covered by an oxide layer into metal, the rate of hydrogen diffusion into the bulk metal and through the hydride already formed. The poor kinetics of MgH_2 are greatly improved by addition of different oxide catalysts that enhance hydrating properties at relatively low temperature, such as V_2O_5 and Cr_2O_3 **.** It was also proposed that Cr_2O_3 yields fast hydrogen absorption, whereas V_2O_5 and Fe_3O_4 cause the most rapid desorption of hydrogen [56-59]. The addition of TiO_2 also resulted in a markedly improved hydrogenation performance of Mg, rapid kinetics, low working temperature and excellent oxidation resistance [58]. In addition to catalyst type, the amount of catalysts used has a significant effect on hydrogen absorption behavior. Palladium (Pd) is a good catalyst for hydrogen dissociation reaction. The reactivity of palladium after exposure to oxygen is recovered during exposure to hydrogen because of the easy decomposition of palladium oxide. However, high cost of palladium is the main disadvantage for the industrial applications [59] Hydrogen molecules have a strong affinity for nickel (Ni) and readily dissociate and adsorb onto surface-layer nickel clusters [60, 61]. Through the addition of 1% of nickel to magnesium, Holtz et al., found a 50% increase in hydrogen capacity, a decrease in the temperature for the onset of hydrogenation from 275 to 175 ◦C, and a lowering of the dehydrogenation onset temperature from 350 to 275 ^{O}C [62]. Also Pd, Ni and Ge can be used for the catalysis of hydrogenation kinetics. The presence of Ge decreases the hydride decomposition temperature in a range from 50 to 150 ^{O}C, depending on the catalyst amount. But the catalytic effect of Ge disappears after few hydrogen absorption/desorption cycles [63]. Vanadium (V) also acts as a catalyst for the dissociation of hydrogen molecules. It was also reported that using V as a catalyst, hydrogen capacity can be increased up to 5.8 wt% while the thermodynamic parameters of MgH_2 were not altered [64]. Titanium and vanadium block the oxidation of the alloy surface, and therefore, increase the discharge capacity over multiple cycles [65.66]. The catalytic role of V_2O_5 in the recycling of hydrogen in magnesium hydride was investigated. They find that the Mg–H bond length becomes elongated when MgH_2 clusters are positioned on single, two, and three coordinated oxygen sites (O_1, O_2, and O_3) on the V_2O_5 surface. Molecular hydrogen is predicted to spontaneously form at the hole site on the V_2O_5 surface. Additionally, the activation barrier for the dissociation of hydrogen on V-doped Mg surface is 0.20 eV, which is only 1/5 of that on pure Mg surface. The results indicate that oxygen sites on the V_2O_5 surface and the V dopant in Mg may be important facilitators for dehydrogenation and re-hydrogenation, respectively. This results can aid in the rational design and development of Mg-based hydrogen storage materials. Satish et.al., investigated the effect of TiH_2 templated over graphene (TiH_2@Gr) on the hydrogen sorption characteristics of MgH_2/Mg [67]. The catalytic effect of TiH_2@Gr on MgH_2 is found to be better than Ti@Gr and TiO_2@Gr. The onset desorption temperature for MgH_2–TiH_2@Gr is ~204 °C, which is 31 °C and 36 °C lower than MgH_2–Ti@Gr, MgH_2–TiO_2@Gr respectively.

3.3.5 Mg Nano-structured complex hydrides

In the past decade, the rapid development of nano-engineering brought the new hope for these metal complex hydrides as the new generation of solid-state hydrogen storage materials. Andreas et al.; summarize the progress to date in the area of nanostructured metal hydrides and intends to understand and explain the innovative concepts and strategies developed over the past decade to tune the thermodynamics and kinetics of hydrogen storage reactions [68] . Research on nano-structure hydrogen storage materials has clearly demonstrated that reduced size, low dimensionality and low coordination can significantly lead to very different properties from the bulk counter parts, which were summarized in recent review articles because the physics and chemistry of matter at the nanoscale can be fundamentally altered [33,46,69,70] Considerable research has focused on the role that nanostructures which can play in the search for “ideal” hydrogen storage materials [48,70, 71,72]

Usually, nanoscale catalysts are more effective in improving the hydrogen storage performance of MgH_2 than conventional catalysts because of the more active catalytic sites generated by the intimate contacts between nano catalysts and MgH_2. A special emphasis is placed on nano magnesium hydrides composites, and highlights the strategy of combining nanosizing and interfacial effect which would be the potential research direction in future prospect. Peng et al., reported that Mg nanostructures have enhanced the great potential of bulk Mg in the area of energy storage and conversion due to their lightweight, abundant, and high-energy density properties [71]. They highlight the recent developments in the synthesis of Mg nanostructures and their application in two specific areas: high-energy batteries and hydrogen storage which will benefit further developments of Mg nanostructures. Shang et al., reported that considerable efforts have been made to improve the kinetics of Mg-based alloys at ambient temperatures by means of microstructure manipulation, catalysis, nano scaling and employment of composites [43]. Reducing Mg particles to nano scale and doping with various catalysts are considered as efficient approaches for improving the hydrogen storage properties. It has been established that doping Ni or Mg_2Ni into nano-Mg/MgH_2 through physical routes remarkably improves the hydrogen sorption kinetics. In addition the hydrating properties are enhanced by catalysis through nanoparticles of Pd located on magnesium surface [46] Catalytic effect on Mg–50 wt% $LaNi_5$ nanocomposite is also reported by Liang et al., [64] Recently, more examples have been investigated and confirmed that the nanostructure alloys and nanocomposites can integrate different components to gain multiple functionality, including Mg-Ti-Al/Si thin film, MgH_2–Nb_2O_5/V_2O_5 nanocomposites, Mg–TiH_2 nanocomposites and so on [65, 66, 72,73] has been coprecipitated a Mg–Ni nanocomposite from a tetrahydrofuran (THF) solution containing anhydrous magnesium chloride ($MgCl_2$), nickel chloride ($NiCl_2$), and lithium naphthalide (LiNp) as the reducing agent. Transmission electron microscopy observations reveal that Ni nanoparticles are distributed homogeneously on the surface of those larger Mg particles with sizes ranging from 10 to 20 nm in the nanocomposite.

A series of MgH_2-based composites were prepared by adding a small amount (1 mol%) of nanoparticle of Fe or Co, Ni or Cu metals into MgH_2 through ball milling for 2 h under argon atmosphere [73]. All catalyzed MgH_2 materials showed much better dehydrogenation properties, and the best performance was achieved by Ni nano catalyzed MgH_2 composite comparing with that of the Ni micro doping, which indicates that the smaller particle as a catalytic metal leads to better H-storage kinetics. Moreover, the 2 mol% Ni nano-doped MgH_2 composites prepared by soft ; (200 rpm, milling time of 15 min) showed the most superior hydrogen storage properties: about 6.5 wt% hydrogen desorbed within nearly 4 hours at 163^{O}C. On the other hand, some debatable catalytic mechanisms still exist in nanocomposites such as MgH_2–metal oxides systems. For instance, the proposed superior catalytic effect of Nb_2O_5 in comparison to pure Nb is still a matter of discussion. Another good example is MgH_2/Mg_2NiH_4 nanocomposite material. It is known that alloyed Mg_2NiH_4 lowers the hydrogen absorption temperature to about 200

^{O}C due to reducing the large reaction enthalpy, however, at the expense of the theoretical hydrogen storage capacity drop to 3.6 wt%. The nanocomposite combines some of the advantage of the high hydrogen capacity of magnesium with the lower temperature of operation of Mg_2Ni and in consequence can operate at a temperature as low as 220 ^{O}C with fast kinetics and with total hydrogen capacity of above 5 wt% [73,74]. Although Mg_2NiH_4 has been experimentally found that $LaNi_5$ can also store hydrogen but the storage capacity is below 2 wt%. A catalyzed MgH_2 based nanocomposites is chemically destabilizing MgH_2 with the addition of high hydrogen content metal complex materials such as borohydrides [75] , alanates, and amides. Zaluski et al., reported that the presence of Pd as a catalyst in nanocrystalline Mg_2Ni, $LaNi_5$ and FeTi systems, enhance the absorption rates even at lower temperatures and maintain less sensitivity to air exposures [46]. Xiubo et al**.,** reported that the Mg-5.0 wt%Ni-2.3 wt%V nanocomposite has been produced through reducing $NiCl_2$ with the Mg-V nanoparticles (NPs) prepared by hydrogen plasma metal reaction (HPMR) approach [76]. They show synergistic catalytic effects on the hydrogen storage properties of Mg-Ni-V nanocomposite. The nanocomposite can absorb 4.6 wt% H_2 within 30 min at 473 K (199.85^{O}C) and desorb 5.2 wt% H_2 within 10 min at 623 K (349.85^{O}C). The activation energies of hydrogenation/dehydrogenation processes are decreased to 52.8 and 85.1 kJ mol^{-1} H_2, lower than those of the Mg-5.4 wt% Ni nanocomposite of 63.2 and 89.3 kJ mol^{-1} H_2. The enhanced hydrogen storage performances of the Mg-Ni-V nanocomposite are mainly attributed to the synergistic catalytic effects of the Mg_2Ni and V catalysts, and the nano size effect of Mg NPs on the decrease of the hydrogen diffusion distance. Zaluska et al., developed a new type of catalytic compounds [77]. These catalytic complexes demonstrated remarkable enhancement in sodium alanates and magnesium, as well as in hydrogen generation through hydrolysis. A nanocrystalline Mg-1.9wt%TiO-1wt%Ni alloy shows good absorption kinetics at room temperature [64]. The Ti decreases the kinetic barriers of absorption while the Ni protects the alloy from deactivation due to oxide layer formation. The effect of Nb_2O_5 concentration on the kinetics of magnesium hydrogen sorption reaction at 300 ^{O}C is studied. Fastest kinetics are obtained using 0.5 mol% Nb_2O_5 with a 7.0 wt% of hydrogen capacity (Barkhordarian et al. 2004). In the search for efficient and inexpensive catalysts for hydrogen sorption reactions, Shao et al., 2011, prepared nanocrystalline Ti-catalyzed MgH_2 by a homogeneously catalyzed synthesis method. Ti-catalyzed MgH_2 compared with a commercial MgH_2 sample. The catalyzed MgH_2 nanocrystalline sample consists of two MgH_2 phases-a tetrahedral β- MgH_2 phase and an orthorhombic high-pressure modification γ- MgH_2. Transmission electron microscopy was used for the observation of the morphology of the samples and to confirm the nanostructure. BET proved surface area of 108 m^2 g^{-1} of the nanostructured material. This sample exhibits a hydrogen desorption temperature more than 130 °C lower compared to commercial MgH_2. After desorption, the catalyzed nanocrystalline sample absorbs hydrogen 40 times faster than commercial MgH_2 at 300 °C. Both the Ti catalyst and the nanocrystalline structure with correspondingly high surface area are thought to play important roles in the improvement of hydrogen storage properties. The desorption enthalpy and entropy values of the catalyzed MgH_2 nanocrystalline sample are 77.7 kJ mol^{-1}H_2 and 138.3 kJ mol^{-1}H_2, respectively. Thermodynamic properties do not change with the nanostructure.

3.4 Cyclic Stability

Cyclic stability is one of the major criteria for applicability of metal/metal hydride systems for reversible hydrogen storage. Depending on the nature of the additives, cycling temperatures and starting microstructures, various structures and intermediate phases can be obtained. There are few publications regarding high number of cyclic tests. **Song et al.,** synthesized magnesium hydrides with additives of Cr_2O_3, Al_2O_3 and CeO_2. All the samples absorb and desorb less hydrogen at the fifth cycle than at the first cycle due to the agglomeration of the particles during hydrogenation/dehydrogenation cycling. Metals such as Ce, La, Nd and Pr, are used to increase the cyclic stability [58,78] In addition, Li et al., reported formation phase changes, segregation and disintegration of La2Mg17 + 40 wt% LaNi5 during cycling at temperatures up to 350 ^{O}C [79]. It was also reported that hydrogen capacity of La0.5Ni1.5Mg17 decreases with cycling. They indicated that they are almost stable even after 800 cycles with small fluctuations in the hydrogen capacity. The cyclic stability of MgH_2–5 wt%V is studied by Dehouche et al**.,** up to 2000 cycles. They concluded that there is no change in isotherms and no disintegration of the materials even when hydrogen content reached 5 wt% [80]. Also the cyclic stability of MgH_2 + 0.2 mol% Cr_2O_3 is previously examined at 1000 cycles. Dehouche et al. reported that although desorption time is increased, an increase of H_2 storage capacity is reached to 8% between the first and the 500 or 1000 cycle due to structural relaxations and crystallite growth [59]. Friedlmeier et al. 1995, observed a decrease in the kinetics of hydrogen absorption after 4300 cycles, but no loss in the hydrogen capacity of Mg at 2% Ni alloy. However, to achieve the same storage capacity, the system temperature had to be increased. Nevertheless, Dehouche et al., showed 15% decrease in hydrogen capacity after 2100 cycles with a starting material of nanocrystalline Mg_2Ni. This was attributed to the formation of the non-hydride forming $MgNi_2$ phase, during the cycling process. The performance of MgH_2.V.Ti was evaluated by Dehouche et al.,[80] after 1000 cycles under a H_2 atmosphere containing 101 ppm moisture. Hydrogen-storage capacity increased 5% but desorption properties deteriorated due to surface modification of the particles. Cyclic stability of the kinetics of catalyzed MgH_2 was systematically investigated [81]. Three systems including MgH_2–TiH_2, MgH_2–$TiMn_2$, and MgH_2–VTiCr were prepared by high energy ball milling. Results show that the kinetics of high-temperature (300°C) hydrogenation and dehydrogenation maintained a good stability during 100 hydrogen cycles. However, when testing the hydrogenation kinetics at the low-temperature range from 25 to 150°C (298.15- 423.15 K), a severe degradation was observed after hydrogen cycles. Among the three materials, the MgH_2–VTiCr system shows better cyclic performance. The degradation of low-temperature kinetics can be mainly related to the hydrogenation–dehydrogenation cycling reactions.

3.5 Conclusion and recommendation

The review focuses on various hydrogen storing technologies that can be employed for creating an economic source of hydrogen such as compressed H_2 storage, liquid hydrogen storage and solid fuels hydrogen storage. Mg hydride, complex Mg hydride, Mg-based catalyst and Mg based nano-catalyst were studied from the point of view of their ability to absorb hydrogen and release it later and, their hydrogenation and dehydrogenation kinetics and effect of adding oxide catalyst and nano oxide catalyst in improving properties of Mg-hydrides. It can be concluded from the present review that: 1) MgH_2 is famous for its unique ability to absorb hydrogen and release it later, either at room temperature or through heating of the tank. The main disadvantages of MgH_2 as a hydrogen store is the high temperature of hydrogen discharge, slow desorption kinetics and a high reactivity toward air and oxygen, relatively high desorption temperatures due to the highly stable Mg−H bond., 2) Mg complex hydride have higher hydrogen gravimetric storage capacities and volumetric densities than simple hydrides, 3)Mg based catalyst whether catalysts mixed as additives with small quantities or doped as alloying components, can promote improved energetic of H_2 sorption kinetics and enhance hydrating properties at relatively low temperature, 4) nanoscale catalysts proved improving the hydrogen storage performance of MgH_2 than conventional catalysts because of the more active catalytic sites generated by the intimate contacts between nano catalysts and MgH_2 and 5) Nano-structured Mg complex hydrides enhance the absorption rates even at lower temperatures and proved faster kinetics than MgH_2 Reviewing of cyclic stability also included as it is one of the major criteria for applicability of metal/metal hydride systems for reversible hydrogen storage. As the present review proved promising results for using nano scale catalyst which improve hydrogen storing, faster kinetics and lower decomposition temperature, but it is recommended to further researches work are needed to produce an economic nano catalyst to be applied in transportation and stationary applications. In addition cyclic stability needs more study as there are few publications regarding high number of cyclic tests.

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