Review article

Nanomaterials in the advancement of hydrogen energy storage

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A B S T R A C T

The hydrogen economy is the key solution to secure a long-term energy future. Hydrogen production, storage, transportation, and its usage completes the unit of an economic system. These areas have been the topics of discussion for the past few decades. However, its storage methods have conflicted for on-board hydrogen applications. In this review, the promising systems based on solid-state hydrogen storage are discussed. It works generally on the principles of chemisorption and physisorption. The usage of hydrogen packing material in the system enhances volumetric and gravimetric densities of the system and helps in improving ambient conditions and system kinetics. Numerous aspects like pore size, surface area ligand functionalization and pore volume of the materials are intensively discussed. This review also examines the newly developed research based on MOF (Metal-Organic Frameworks). These hybrid clusters are employed for nano-confinement of hydrogen at elevated temperatures. A combination of the various methodologies may give another course to a wide scope in the area of energy storage materials later in the future.

1. Introduction

In the past few years, fossil fuel utilization, especially oil and gas has been in high demand and it affects the area of the interest of current researchers. The release of breathtaking toxins from burning of fuel includes oxides of nitrogen (NO_x), oxides of Sulphur (SO_x) [1, 2], and other fine particles which cannot be separated by the process of filtration. Dioxins produced during combustion are known as carcinogens. Similarly, fossil fuels also produce immense quality of 'greenhouse gases' mostly carbon dioxide (CO_2) and all other environmentally harmful by-products [3, 4]. These challenges increased the concern of technologists, scientists, economists, and policy-makers to develop and generate other alternative energy sources. To overcome all these drawbacks, future energy sources needs to conquer the criteria of releasing environment-friendly by-products, renewability, and availability [1, 4]. Hydrogen is a clean and sustainable energy source, which turns it to be the best substitute for fossil fuels. Hydrogen is an achromatic, tasteless and non-poisonous molecule, which is a non-combustible source that resists the release of greenhouse gases and air pollutants. Hydrogen has an exceptionally high gravimetric energy density of (20 KJ g^{-1}), which is almost thrice to the energy density of gasoline and seven times to the

energy density of other fossil fuels [4]. However, it is not easy to use this economical clean fuel because once the production is completed, it becomes very difficult to store the hydrogen fuel for transportation and utilization [5, 6]. The main concern regarding the hydrogen economy is its low volumetric energy. These days, most of the transportation sectors are dependent upon refined petroleum fuels. But with time, petroleum fuels are seemingly becoming unaffordable and unavailable [7, 8]. To replace this traditional fuel, hydrogen plays an ideal role. However, before engaging it as a transportation fuel, it is essential to develop a high-density storage channel [7, 9].

Presently, several approaches (as presented in Fig. 1) are available for hydrogen storage [1, 4, 10], such as the high-weight tanks, which have high storage capacity (350 bars to 700 bars). Even though such pressure, the energy density is still lower than the customary sources of the energy system. The storage tanks ought to be comprised of solid and light weight material that can hold high-pressure conditions. The cryogenic liquefaction of atomic hydrogen has been one of the future strategies to store hydrogen fuel for the vehicle industry. Yet the fundamental concern is that the liquefaction of hydrogen happens at a low temperature of 20 °C. Therefore, if the storage container cannot have good strength, the ambient heat flow will go through the tank and initi-
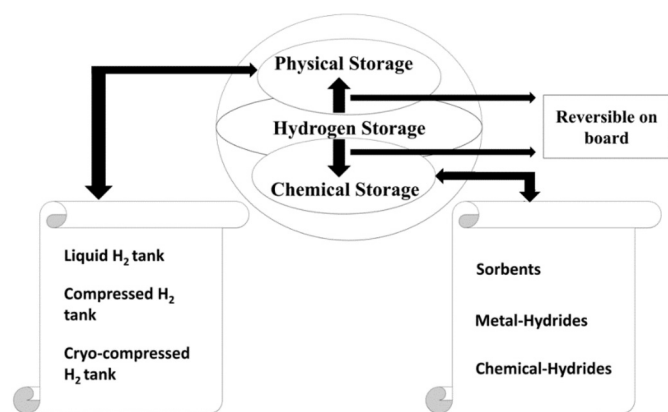
Fig. 1. Schematic illustration of literature for hydrogen storage techniques.

ate the dehumidification of the hydrogen which will further increase the internal pressure of the tank, and finally, it will become one of the main reason for fuel loss (i.e. boil-off). According to the principle of hydrogen adsorption in solid metals (for an instance Li, Mg, or Al) by dissociation [1, 4], the chemical storage of solid compound is more feasible and safe as compared to the phase conversion of the material (e.g., lique-faction). This method is capable of restoring hydrogen on large-scale at ambient temperature and pressure conditions. The general structural energy of a material depends on its specific gravity. However, due to the higher endothermic enthalpy of desorption of hydrogen, this technique requires excessively high temperature to desorb hydrogen from its parent material. This reduces the energy efficiency of the material. Chemical hydrogen storage method signifies the trapping of hydrogen at relatively low pressures and releasing it at higher temperatures by co-valent bonding in either solid or liquid form. However, there are a lot of potential benefits of chemical storage, but there are still some problems that need to be resolved. The general issues include the structural and thermal instability of the material towards consistent temperature and pressure. To overcome these issues, we need to use highly porous adsorbents, such as zeolites [11], and porous polymers [12]. On the other hand, the efficiency of adsorbents used for physisorption solemnly depends on the specific surface area (SSA) and void characteristics (size and shape) [13]. The carbonaceous substances are one of the best highly porous adsorbents with characteristics like high SSA, high chemical and thermal stability, excellent kinetics, and lightweight. Moreover, it can be easily synthesized from a variety of organic compounds [5, 14, 15].
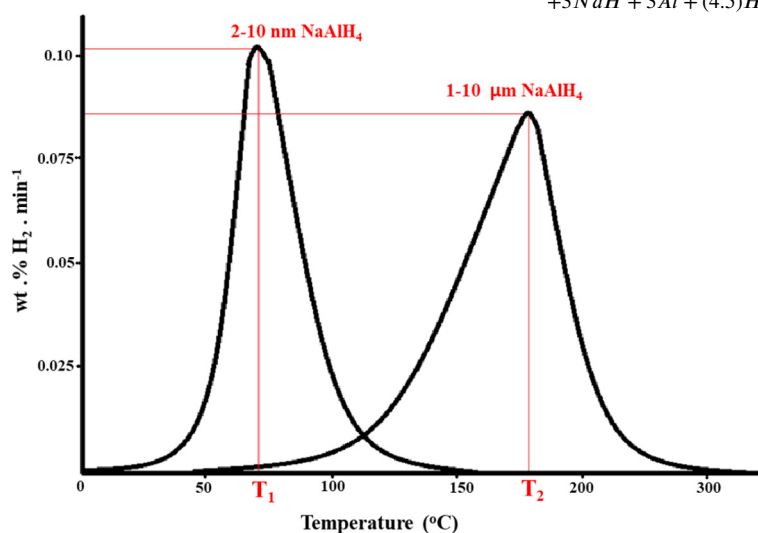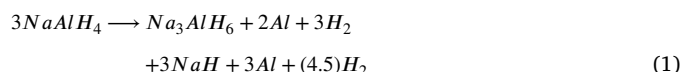
Finally, before start using hydrogen fuel, it is very important to do a brief investigation about its storage methods. This paper is mainly focused on the techniques to store hydrogen fuel safely for a long period. The theme of this study is to explain all the viable developments which have been conducted in the previous studies and to discuss its kinetic and cyclic stabilities.
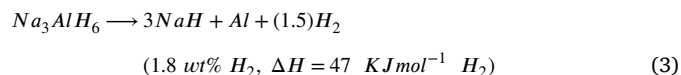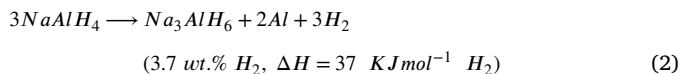
2. Developments

The industrial revolution, environment aspects, and energy problems have activated the ever-increasing concern to exploit renewable clean energy in the current situation. Hydrogen fuel has been considered as a new energy currency for the past few years. High gravimetric energy density, renewable affordability, and environmental benefits of hydrogen enhanced its credibility. As a vital application of hydrogen energy, hydrogen fuel cells are capable of converting chemical energy into electric energy with high efficiency, which can be used in all transportation applications. However, to store this novel fuel we required very high-quality and stable supply pressure containers. The aim of this paper is to analyze few recent developments in the field of hydrogen fuel storage. We covered all the aspects of the developed systems and their catalytic doping properties to store the highest volumetric density fuel safely.

2.1. Sodium alanate system

Bogdanovich and Schwickardi [16] proposed sodium alanate framework ($NaAlH_4$ and Na_3AlH_6) for on-board storage of hydrogen fuel. These when activated with Ti, the material immediately acts as a reversible hydrogen storage system at moderate conditions for powering PEM (polymer electrolyte energy) unit [17, 18, 19]. Baldé et al. [20] investigated Ti-doped $NiAlH_4$ isotherm as shown in Fig. 2 with the heating ramp of $5\,^{\circ}C\ min^{-1}$. The curve clearly shows that nano-meter sized particles between the range of 2-10 nm are desorbed easily between the temperature range of 50-100 °C. Whereas the reported particles of size between 1-10 micro-meter desorbs hydrogen at a moderately higher the temperature of around 160 °C. Because of its ideal execution potential, it is commonly used as the basis of an investigation in hydrogen storage materials. The rate of absorption and desorption is increased when the system is doped at $TiCl_3$. The response is shown in the following reaction:

$$3NaAlH_4 \longrightarrow Na_3AlH_6 + 2Al + 3H_2$$
$$+3NaH + 3Al + (4.5)H_2 \tag{1}$$

Fig. 2. Temperature desorption profile of hydrogen for $NaAlH_4$/CNF samples in Ar atmosphere [20]. *Reprinted with permission from J. Am. Chem. Soc. 130 (2008) 6761-5. Copyright (2008) American Chemical Society.*

In 1985, Bureau et al. [21] determined the crystal structure of $NaAlH_4$ through single-crystal X-ray diffraction. The compound when doped with certain catalysts, can discharge and take hydrogen reversibly as per the following reactions.
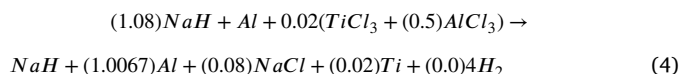
$$3 NaAlH_4 \longrightarrow Na_3AlH_6 + 2Al + 3H_2$$

$$(3.7\ wt.\%\ H_2,\ \Delta H = 37\ KJ mol^{-1}\ H_2) \tag{2}$$

$$Na_3AlH_6 \longrightarrow 3 NaH + Al + (1.5)H_2$$

$$(1.8\ wt\%\ H_2,\ \Delta H = 47\ KJ mol^{-1}\ H_2) \tag{3}$$

In reaction (2), $NaAlH_4$ releases around 3·7 wt% H_2 at 190 °C and the reaction (3) does the same at 225 °C with 1·8 wt% on heating. Likewise, dehydrogenation of NaH develops only at excess temperature of 400 °C. This is because temperature for decay is different for various application. Hence, this is not satisfactory for fuel-cell controlled automobiles [22].

The presumed equilibrium for first and the second decomposition curves are not stable under 100 °C (for instance 0·1 MPa at around 30 °C for first decomposition step and almost similar at 100 °C for second decomposition step). It is not suitable to apply on PEM control systems where different heat collectors will be used to descent hydrogen release [23]. Various doping methods of $NaAlH_4$ are available for improving the fundamental properties of the compound. Among all these, high-energy ball milling is widely preferred due to the following reasons:

1. High surface area.
2. Generation properties of nanostructures.
3. Responsible for creating lattice imperfections on the surface and at the inner of complex hydride.

The improvement in surface area contact with the catalyst during high ball-milling degenerates the energy of separation and recombination of hydrogen. Sodium alanate material used was manufactured on mechanical scale-based milling equipment, enhanced towards fast kinetics using titanium-based economical catalysts [17, 19]. The whole process was carried out in purified Ar (argon) atmosphere. Before synthesis, the NaH and Al were pre-mixed in the molar extent of 1·08 to 1 according to the reaction (4) [18].

$$(1.08) NaH + Al + 0.02(TiCl_3 + (0.5)AlCl_3) \rightarrow$$

$$NaH + (1.0067)Al + (0.08)NaCl + (0.02)Ti + (0.0)4H_2 \tag{4}$$

To escape through the aggregation of mass, wet milling using cyclohexane was used. The resulting stage was followed by the evacuation of milling to dry sections. To monitor the effect of carbon on the hydrogenation reaction, some part of the material was prepared in analogous with an extra 5 wt% of carbon after ball milling as shown in Table 1. This mixture was mixed for an extra 30 minutes. Ball milling makes the surface defects in an economical process and can broadly be connected to achieve great properties of complex metal hydrides [24, 25].

The time for the reaction of high ball-milling is much shorter when contrasted with the direct synthesis of $NaAlH_4$ in the organic solvent. Also, the response temperature is low and material which is to be prepared have progressively reactive properties during hydrogen uptake and discharge reactions [26, 27, 28]. Sodium alanate ($NaAlH_4$) is a highly perceived hydrogen storage material that forms Na_3AlH_6 and Al with the arrival of hydrogen in gas structure.

The response rates are irrationally moderate for fuel cell applications except if it is doped with transition metals (especially Ti). Through wide hypotheses, it has been presumed that the flux of point defects conveys the extended scope of metal transference going with the absorption reaction. The Al-H framework is much porous and the tweaks in reaction interface results in the development of the Al phase.

Table 1. Initial sodium alanate material balance in the dissolved state after milling [24]. *(Adapted with permission from Cornelis P. Baleé et al., J. Am. Chem. Soc. 130 (2008) 6761–6765. Copyright (2008) American Chemical Society)*.

Compound	Molar mass (g-mol^{-1})	Amount (mol)	Mass (g)	Mass fraction
Al	26.98	1	26.98	0.453
NaH	24.00	1	24.00	0.402
Inerts:				
Al (excess)	26.98	0.0067	0.18	0.003
NaCl	58.44	0.08	4.68	0.078
Ti	47.88	0.02	0.96	0.016
C (5 wt %)	12.01	0.237	2.85	0.048
Total Inerts	-	-	8.66	0.145
Total Inerts	-	-	**59.64**	**1.000**

2.1.1. Catalyst-doped $NaAlH_4$

As the foremost method to be considered for the storage of hydrogen, properties of catalyst and the doping technique can strongly impact the kinetic and thermodynamic execution of $NaAlH_4$ systems. Catalysis is the major factor that governs the sorption and desorption kinetics of the system of complex metal hydrides that leads to effective separation and recombination of H_2 molecules [29]. A wide number of catalysts have been tested for hydrogenation and dehydrogenation of $NaAlH_4$. Ti-doped $NaAlH_4$ came out to be important progress for reversible $NaAlH_4$ and was seen as a potential system for onboard hydrogen storage. However, the capacity quickly decreased from 4·2 wt% to 3·1 wt% after 31 cycles. It also displays inadequate dehydrogenation kinetics for practical H_2 storage applications. Later on, efforts were made for catalytic enhancement of $NaAlH_4$ on the mechanical mixing of Ti-dopant [30]. The kinetic and cyclic properties were claimed to be much closer to the demands of the system [30, 31]. Bogdanovich et al. [32] found an outstanding result of colloids-doped $NaAlH_4$ in 2003. These reported the sensitivity of hydrogenation and stability properties of the system towards the particle size of dopants. The storage capacity remained above 4·5 wt% H_2 even after 25 cycles. But at the same time, hydrogenation rate decreased immensely. Though the cost of synthesis and preparation time of colloid-Ti was too high, the method was no longer considered for the doping. Fan et al. [33] investigated energy and hydrogen desorption thermodynamics of $CeAl_4$-doped $NaAlH_4$ and found the separation level for second-step desorption to be 0.096 MPa at 120 °C. More recently synthesized TiB_2 and TiN catalysts for the synthesis of sodium-alanate through mechanical milling reported remarkably mild recharging conditions of 90 °C at 4 MPa H_2 pressure. The results were similar for high-pressure hydrogen (50 bar H_2), suggesting good reversibility of TiN-doped $NaAlH_4$ [34]. Furthermore, several other compounds like Hf, Cr, Sc, Nb, Zr, Fe, La, and V-based catalysts also improved $NaAlH_4$ performances [35, 36, 37]. These findings enhanced the H_2 storage properties of sodium-alanate and further widens up the path for developing high-performance catalysts. The noted problem of $NaAlH_4$ is that the raw materials NaH/Al or commercial samples are not pure, which degrades the capacities of hydrogen storage systems. This could be overcome by recrystallization of raw materials. Moreover, dopant is also responsible for the reduction of reversible storage capacity. This is because of the increase in overall sample weight and it may react with sodium alanate to decrease its amount in the system. Subsequently after dehydrogenation, the agglomeration of lighter particles brings about the development of heavier particles which may be used for reduction in limiting further cycles.

Even though the significant augmentation in kinetic and thermodynamic properties, a sequence of scientific and technological concerns of the system still needs to be focused on. The properties that should be enhanced can be summarized as:

1. The cyclic steadiness of $NaAlH_4$ system is not fully explained for PEM fuel cells. Working on important points such as linking chemical and physical paths is required. Also, an operational nanoscale hydride storage material still needs to be engineered.

2. The storage capacity of the system is low and needs to be improved through light-weight complex hydrides [29, 30]. Interestingly, two different multi-functioning hydrides doped into nonporous framework materials can be promising agents [22].

3. Kinetic properties of $NaAlH_4$ are not preferred to use in combination with PEM fuel cells. These may achieve the goal by modifying the catalytic properties and changing the doping methodology. Collective use of catalyzed and nano-confined samples are the potential candidates for application in fuel cell.

4. A comprehensive exploration of the fundamental mechanism for uptake and release of hydrogen around $NaAlH_4$ system is yet required.

2.2. Lithium amide - magnesium hydride

The limit of hydrogen in interstitial hydrides of many alloys is confined to 1·7 wt% [38]. This estimation is lower than the preferred value utilized for vehicular applications. However, magnesium hydride is a special case because of its ability to approach nearer to practically 8·2 wt% [39]. Chen et al. [40] in 2002 synthesized another system of lithium nitride (Li_3N) which uptakes 11·5 wt% H_2 reversibly in comparison to $NaAlH_4$ system with 5·6 wt% H_2 storage. Hydrogenation of Li is a two-step reaction as shown below:

$$Step\ 1: Li_3N + H_2 \rightarrow Li_2NH + LiH$$

$$Step\ 2: Li_2NH + H_2 \rightarrow LiNH_2 + LiH$$
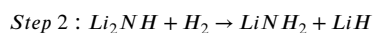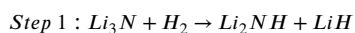
5·74 wt% H_2 and 11·5 wt% H_2 is consumed by Li_3N for the initial step and overall reaction respectively. The pressure for hydrogen corresponding to the first reaction is 0·01 bar at 255 °C. The findings by Chen et al. [40] confirm the high relative pressure of 1 bar at a moderately high temperature of 285 °C for imide hydrogenation. Storage material with such property should be destabilized before applying it to the practical purpose of vehicular transport. In the first-ever study by Weifang Luo et al. [41] in 2002, two samples were used for examination. The first sample was employed for investigating hydrogen sorption characteristics of the reaction ($LiNH_2$ + LiH) to validate the results of Chen et al. [40]. Likewise, second sample was used for the investigation of newly synthesized material.

$$Sample\ 1: LiNH_2 + LiH$$

$$Sample\ 2: LiNH_2 + MgH_2$$

Central compounds like lithium amide and lithium hydride were utilized without pretreatment. These were blended in the molar ratio of $LiNH_2$:LiH = 1:1·1 for the first and $LiNH_2$:MgH_2 = 2:1·1 for the subsequent sample. To avoid decomposition of amide over the range of the reaction, 10% excess of lithium hydride and magnesium hydride was incorporated. Glove box with argon climate was utilized for sample transportation followed by ball milling with SPEX 8000-high industrial facility. Desorbed gas was assessed by mass spectroscopy to recognize any NH_3 from the self-deterioration of amide in both of the samples. Hydrogen uptake in the precedents was assessed as the wt% of the whole model weight.

$$2LiNH_2 + MgH_2 \leftrightarrow Li_2Mg(NH)_2 + 2H_2 \tag{5}$$
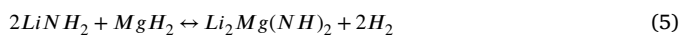
According to the condition depicted in reaction (5), the theoretical limit of system is 5·35 wt% for the second sample whereas the experimental limit is around 4·5 wt%. Such a difference in values may result from segregate surfaces of two strong reactants. Desorption kinetics can likewise be enhanced by better sample blending. It was additionally inferred that the plateau pressure of 3 bar at 100 °C would justify the essential weight extend for transportation applications. In the examination coordinated from the findings of Chen et al. [40], the calculated reaction enthalpy came close to the proposed value. Replacing LiH by less stable hydride,

for instance, MgH_2 in lithium amide/hydride storage system reduces its stability. Even after continuous cycles, there is no degradation of hydrogen storage limits. This innovative storage material can absorb hydrogen reversibly at a pressure of 32 bar at 200 °C and is useful for powering hydrogen based fuel cells.

2.3. Metal-based borohydrides

Light alkaline-earth and alkaline metals based borohydrides like $LiBH_4$ and $Mg(BH_4)_2$, are potential candidates for H_2 storage materials. These presents high conceptual hydrogen storage capacities [42, 43]. The most common decomposition routes are shown in reactions (6) and (7) [44, 45]. These pathways lead to high gravimetric densities of the system.

$$LiBH_4 \rightarrow LiH + B + (1.5)H_2 \quad 13:9\ \ wt\% \tag{6}$$

$$Mg(BH_4)_2 \rightarrow MgB_2 + 4H_2 \quad 14:9\ \ wt\% \tag{7}$$
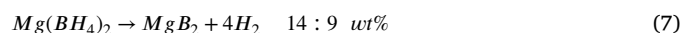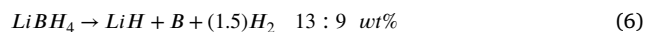
The above mentioned routes are the only options having various hydrogen exchange limitations in kinetic and thermodynamics properties obstructing the reversible dehydrogenation reaction. To minimize these limitations, it is proposed to proceed with a scaffolding of these hydrides in nanoporous structures [46]. The chemical steadiness of dehydrogenation stage will eliminate the dehydrogenation enthalpy and hence thermodynamic processing of storage materials can be controlled [47]. Li et al. [48] investigated that $M(BH_4)_n$ (metal-borohydrides) having excessively high H_2 densities are potential hydrides for hydrogen storage. However, the high temperature of reaction and slow kinetics of the system lessens its prospective for practical applications. The thermodynamic properties of metal borohydrides are estimated from the electronegativity of metal. The intermediate compound formed may continue with high temperature and moderate kinetics, whose development is prevented by the combination of $M(BH_4)_n$ with other metal hydrides. This changes the path of reaction and improves H_2 storage properties in prospects of both kinetically and thermodynamically.

However, none of the present materials satisfies on-board hydrogen storage requirements, and hence continuous attempts are demanded to discover the novel material. Constructive designs to reach a fast reaction kinetics is a practical direction to research the field of on-board hydrogen storage in metal borohydrides.

2.3.1. Sodium borohydride

Catalytic hydrogenation from $NaBH_4$ in the liquid phase: $NaBH_4$ is among the most focused chemical hydrides due to its outstanding high hydrogen capacity (10·8 wt% theoretically) [49], the operating conditions, and its control over hydrogen generation rate [50]. Hydrogen storage in $NaBH_4$ is unconfined through hydrolysis or thermolysis. However, only hydrolysis (directed in the aqueous phase at lesser temperatures) is used in practical applications because the majority of hydrogen is generated from water in this technique, ensuring high volumetric density outputs of the system [51]. Besides this, the generated hydrogen is highly pure and undergoes humidification to facilitate its use in fuel cells. The hydrolysis of $NaBH_4$ occurs at room temperature and releases a theoretical value of 10·8 wt% through the following reaction:

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \tag{8}$$

Reaction (8) represents that the 4 moles of hydrogen are released, which generally require more water in real conditions due to less solubility of borate byproducts and $NaBH_4$ in water. By using excess water, the storage capacity of hydrogen is hindered [52]. Moreover, $NaBH_4$ proceeds self-hydrolysis (i.e. without catalyst) with thermodynamically favored exothermic reaction. The initial hydrolysis of the components makes the intermediates basic and thus gets reduced at higher pH. This inhibits the production rate of hydrogen. To overcome this, stabilizers in the form of bases are employed to avoid premature reaction. In addition

to this, acids in the form of catalysts are used to enhance the kinetics of $NaBH_4$ hydrolysis [49, 50]. Moreover, studies have also shown metal-catalysts as potential candidates for hydrolysis reaction [51]. In early 1950s, acid-catalyzed hydrolysis was reported by Finholt et al. [50] at ambient conditions which released 90% of the stoichiometric quantity of hydrogen. However, the method employs excessive amounts of acids, resulting in heavy and bulkiness of the reaction. The use of acid-catalyst for hydrolysis of $NaBH_4$ was not initiated due to difficulty in monitoring the reaction. Yet Prosini and Gilson [53] designed a hydrogen generator on the concept of "hydrogen in demand" using sodium borohydride in acid accelerators. Subramanian and Murugesan [54] further used dense $NaBH_4$ and acidic water to generate hydrogen for transportation applications. The various acids used in tests were: organic acids; CH_3COOH, H_2CO_2, and mineral acids: H_3PO_4, HCl, HNO_3, H_2SO_4. The results of mineral acids suggested that increasing the concentration of the acid will enhance the production rate of hydrogen. Whereas, in the case of organic acids, high clusters are needed to produce hydrogen on a similar scale of mineral acids [51, 54]. The catalyst efficiencies of heterogeneous catalyst clusters with metals and alloys were reported [55, 56]. Initially, metal salts like $RhCl_3$, $IrCl_4$, $RuCl_3$, etc. were investigated in the hydrolysis of $NaBH_4$ through RuC_3, $RhCl_3$, and H_2PtCl_6 [50, 57]. These attempts were reported as the most active ones which gets reduced to its elementary state with the progress of reaction. The study by Amendola et al. [58, 59] suggested that ruthenium metal doped on anionic surface performs efficiently than cationic resins. Further, the observations were made about the lessening of water molecules for hydrolysis due to high concentrations of hydroxyl ions from NaOH. Kojima et al. [60] gave the first-ever claims about several oxides ($LiCoO_2$, Co_3O_4, Ti_2O_3, TiO_2, TiO, $LiNiO_3$, CoO, SiO_2, $LiMn_2O_4$, and NiO) supported by transition metals. 1·5 wt% of $Pt/LiCoO_2$ catalyst gave the highest performance of more than 200 $L(H_2)$ min^{-1} g^{-1} (Pt) which is almost tenfold the rate showed by catalyst Ru as claimed by Amendola et al. [58, 59]. A combined alloy of both Ru and Pt as reported by Rangel et al. [61] when investigated, the efficiency of $Pt-Ru/LiCoO_2$ came out almost two times that of single Pt-based and Ru-based catalysts. Overall, noble metals confirmed elevated activity than the non-noble metals [51].

Additionally, the production of hydrogen from $NaBH_4$ in solvents (like alcohols) was also investigated [61]. When compared to ethanol, methanol showed more reactivity towards $NaBH_4$. Reaction (9) depicts the reactivity of methanol towards sodium borohydride [62, 63].

$$NaBH_4 + 4CH_3OH \rightarrow NaB(OCH_3)_4 + 4H_2 \tag{9}$$
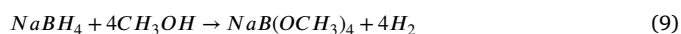
Hannauer et al. [62] experimented with hydrogen production in CH_3OH and its mixtures ($NaBH_4/H_2O$ in molar ratios of 2 and 10) and the best system came out to be with the molar ratio 10. Demirci and team performed metal-catalyzed methanolysis with Ru/TiO_2 and Co/TiO_2 as a catalyst and the second catalyst processed higher catalytic performance. H_2 production rates were increased from 144 to 644 $L(H_2)$ min^{-1} g^{-1} (Co) as the uptake of Co on TiO_2 was reduced from 20 wt% to 1 wt% [62].

$NaBH_4$ regeneration process: A cost-effective and environment friendly process of recycling spent fuel to $NaBH_4$ is required to use it as an effective hydrogen fuel. In the hydrolysis of $NaBH_4$, BH_4^- gets transformed into $B(OH)_4^-$ [64, 65] with $B(OH)_3$ as a principal by-product in aqueous solution at pH < 9, while $B(OH)_4^-$ forms at pH > 9 [62]. The compounds when dried at < 110 °C, $NaBO_2·4H_2O$ and $NaBO_2·2H_2O$ [66] were the only compounds that remained in the system. Traces of $Na_2B_4O_7·5H_2O$ were also reported [66] along with the washed components. The borate components are thermodynamically stable [49] and hence need greater energies to redevelop the initial material. This demerit came out as a major concern regarding the development of stable paths to synthesis of $NaBH_4$ from $NaBO_2$ [51]. The general recycling cycle includes the splitting of borates from unreacted $NaBH_4$ and drying it roughly at 300 °C to get anhydrous $NaBO_2$ [67, 68]. Few $NaBH_4$ production paths reported in the literature are:
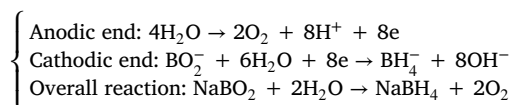
- In the Bayer process for $NaBH_4$ preparation [69], the reaction between SiO_2 (silica), Na (metallic sodium), $Na_2B_4O_7$ (borax) and H_2 (hydrogen) is carried out at considerable higher temperatures. Further, the process is modified to utilize economical metal as a reducing agent like Mg (magnesium) [51, 70] or its hydride (MgH_2) [71, 72] (as shown in reaction (10)) in place of Na.

$$NaBO_2 + 2MgH_2 \rightarrow NaBH_4 + 2MgO \tag{10}$$
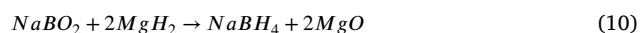
However, fast kinetics through reducing metals cannot be achieved due to weak phenomenon of mass transfer over the solid particles. Also, the high pressure of H_2 results in increased temperature of decomposition of MgH_2. Thus demanding extra high-temperature conditions to reach the desired product. This finding contradicted the theoretical conditions which included the room temperature as per standard Gibbs free energy i.e. ΔG_o = -269.7 kJ mol^{-1} [51]. Since the modified Bayer process demands special reaction conditions and few hazardous materials, hence the bulky production could be at high-risk to obtain the reasonable yield [73].

- A set of thermal synthetic processes [51] was proposed by Millenium Cell Inc. which were equipped to prepare for certain adjustments that will improve gas emissions, energy efficiencies, and cost of a response with boron compounds [73]. Apart from this, formaldehyde is utilized for carbon-based reductions [74].
- A single step thermal reduction of $NaBH_4$ with the help of reducing agents (carbon, methane, or hydrogen) wasn't thermodynamically stable under rational conditions [75, 76].
- Cooper et al. [74] gave the first-ever electrolytic process. The reaction was carried in caustic solution of $NaBO_2$ as depicted below:

$$\begin{cases} \text{Anodic end: } 4H_2O \rightarrow 2O_2 + 8H^+ + 8e \\ \text{Cathodic end: } BO_2^- + 6H_2O + 8e \rightarrow BH_4^- + 8OH^- \\ \text{Overall reaction: } NaBO_2 + 2H_2O \rightarrow NaBH_4 + 2O_2 \end{cases}$$

Small amounts of $NaBH_4$ was obtained in final product. Also, Na-B-O-H in the liquid state was recommended by Davis and Calabretta for electrolysis of BO_2^- to BH_4^- [77]. In the present scenario, none of the above mentioned methods promises the economical production $NaBH_4$. However, the path to achieve the lowest of all costs still lies in the electrochemical processes and hence demands intensive research.

2.4. Metal-organic framework (MOF)

Metal-Organic frameworks are in huge interests since 2003 when Yaghi and group [78] gave the first historically speaking determinations of hydrogen adsorption on MOF. A constraint of 4.5 wt% at 77 K at a pressure under 1 atm, and 1.0 wt% at room temperature with 20 bar pressure of the material $Zn_4O(bdc)$ (bdc implies 1,4-benzene dicarboxylate) (furthermore insinuated as MOF-5 and IRMOF-1) is being observed. MOFs always remained exceptional substitutes for zeolites and activated carbons, which are additionally the representations of physisorption-based materials.

Most of MOF clusters are in loose powdered form and can be hard to install into significant devices [79, 80]. Small packing densities will affect the volume capacities of MOFs while installing them in the tank through pipe structures. Furthermore, the powder MOF may lead to contamination of fittings during running cycles. Moreover, loosely packed powders can easily be spread into the atmosphere, affecting the process of shaping [81]. Efforts have been made by the University of Michigan [82], BASF [83], and Ford [84] to accomplish higher volume densities at moderate conditions. These MOFs are mainly megalith, beds, or pellets with higher bulk densities [85]. Various manufacturing paths are available [86, 87, 88] for MOF processing, the selection of

which depends upon the textural properties of the porous MOF compounds.

Porosity and surface area are two basics for estimating the storage capacity of MOF for hydrogen fuel. These materials are produced from coordination bonding between multi-dentate ligands and little metal-containing groups. Solvent species from synthesis occupy pores and channels, which results in the breakdown of structure [89]. Factors of present interest, which would update the frameworks for promising hydrogen storage systems at ambient conditions includes SSA, pore-volume, pore size, and developing hydrogen binding sites with higher energies.

Improving moisture tolerance is another major strategy to commercialize MOF materials. Investigations by Dingemans et al. and team member Yang et al. [90] found that MOF-5 attached to hydrophobic methyl shows stability for five days. Further, Yang et al. [91] synthesized a hybrid cluster of acid-based MWCNTs to improve stability whereas Yoo et al. [92] suggested adding surfactants in the drying process. These surfactants are consumed on MOF-5 prompting its hydrophobic surface, this builds the strength to face the moisture. Another major study includes the fabrication of MOF-5 with Ni as a dopant [93]. The fabrication was carried out through the solvothermal crystallization to enhance the hydro-stability. UiO-66 (Zr-based MOF) [94], KHUST-1 (Cu-based MOF) [95], and MIL-101 (Cr-based MOF) [96] are few compounds with excellent thermal, pressure and moisture stabilities and these are considered among the top options for system upgradation.

However, verification of their hydro-stability characterization has to be done for the long run.

Micropores with extensive volume and reasonable diameter can accomplish effective adsorption of hydrogen on materials [97, 98, 99]. In the underlying phases of study, the research is majorly focused in the synthesis of porous frameworks, which after a short time can be loaded up with hydrogen. This incorporates "MIL", characterization of MOFs as portrayed by Latroche et al. [100] with pore sizes of the range higher than 25 Å and "IRMOF" arrangement given by Rowsell et al. [98] with non-interpenetrated networks. Such MOFs as given in Table 2 have a pore volume greater than 1.5 cm^3g^{-1} and are likely to hold hydrogen at high pressure. The cutoff points are 6·01 wt% in MIL-101 and 6·7 wt% in IRMOF-20 at 77 K [89]. Despite this, still the 80% volume of the material is empty space as shown by Langmuir interpretation in Fig. 3.

The accompanying case reveals that molecules with pores size 4·5-5·0 Å store more hydrogen than comparatively larger ones. This estimation of pore sizes is analogous to kinetic diameter for H_2 of the range 2·8 Å. Pores size of this range permit reaction of H_2 with different parts of compounds. Furthermore, curvature of pores played an important factor as a dynamic factors but was probably difficult to claim it experimentally [104]. This is due to the immediate after effect of various techniques used in the assessment of pore sizes. Dublin-Astakhov examination on the Horvath-Kawazoe model of gas sorption data is effective among the most used methods to report pore size but is restricted to the adsorption data and gas used. The recently reported MOF sys-

Table 2. Surface area, porosity, and hydrogen adsorption data for selected MOFs [99]. (Adapted with permission from Thomas et al., Dal. Trans. (2009) 1487–1505. Copyright (2009) Royal Society of Chemistry).

Material	Pore vol./cm^3g^{-1}	SA/m^2g^{-1}	H_2 uptake at 77 K, 1 atm wt%	Max. H_2 uptake (wt%)		ΔH_{ads}/KJ mol^{-1}
				77 K	298 K	
IRMOF-6, $Zn_4O(cbbdc)_3$ [100, 101]	1.14	3263	1.48		4.9, 32 bar	
IRMOF-18, $Zn_4O(tmbdc)_3$ [98]		1501	0.89			
MIL-53(Al), Al(OH)(bdc) [99, 100]	0.59	1590	2.1	16 bar	3.8, 16 bar	
MIL-53(Cr), Cr(OH)(bdc) [99, 100]	0.56	1500	1.8		3.1, 15 bar	
MIL-101, $Cr_3OF(bdc)$ [100]	1.9	5500	2.5	0.43, 40 bar	6.1, 40 bar	10
IRMOF-9, $Zn_4O(bpdc)_3$ [101]	0.90	2613	1.17			
IRMOF-2, $Zn_4O(bbdc)_2$ [102]	0.88	2544	1.12			
IRMOF-3, $Zn_4O(abdc)_3$ [101]	1.07	3062	1.42			
IRMOF-13, $Zn_4O(pydc)_4$ [101]	0.73	2100	1.73			
IRMOF-8, $Zn_4O(ndc)_3$ [101, 102]		1818	1.50	0.4, 30 bar	3.6, 10 bar	6.1
IRMOF-20, $Zn_4O(ttdc)_3$ [101, 102]	1.53	4590	1.35		6.7, 70 bar	
IRMOF-11, $Zn_4O(hpdc)_3$ [101, 102]		2340	1.9		3.5, 34 bar	9.0

Abbreviations: bdc = 1,4-benzenedicarboxylate, bbdc = 2-bromo-1,4-benzenedicarboxylate, abdc = 2-amino-1,4-benzenedicarboxylate, cbbdc = 1,2-cyclobutane-3,6-benzenedicarboxylate, ndc = 2,6-naphthalenedicarboxylate, bpdc = 4,4-biphenyldicarboxylate, hpdc = 4,5,9,10-tetrahydropyrene-2,7-dicarboxylate, pydc = pyrene-2,7-dicarboxylate, tmbdc = 2,3,5,6-tetramethylbenzene-1,4,-dicarboxylate, ttde = thieno-[3,2b]thiophene-2,5-dicarboxylate.
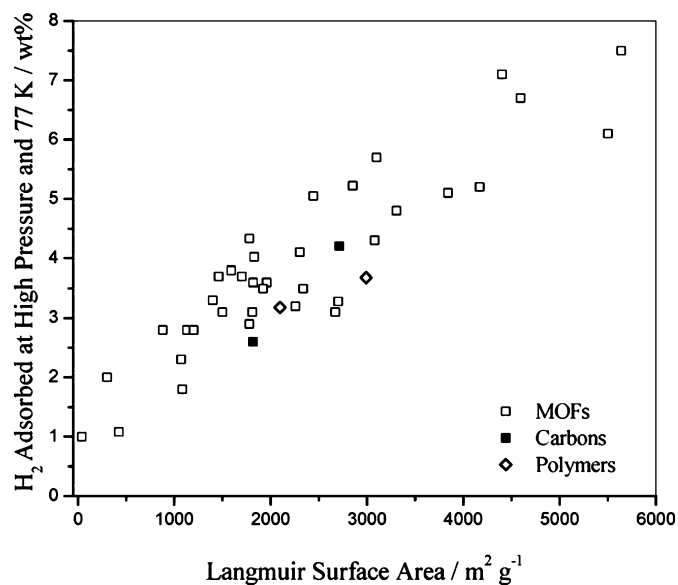
Fig. 3. Relation between surface area and saturation hydrogen uptake at 77 K (Langmuir isotherm, N₂, surface graph) [103]. (Reprinted with permission from Thomas et al., Dal. Trans. (2009) 1487–1505. Copyright (2009) Royal Society of Chemistry).

tem, $Cu_3(tatb)_2$ (tatb = triazine-4,4',4"-s-triazine-2,4,6-triyltribenzoate or PCN-6) incorporates a paddle-wheel of copper-carboxylate associated with trigonal triazine-based ligand. Interestingly, MOF experienced 41% development in surface area, 29% addition in gravimetric hydrogen uptake, and 133% enhancement in volumetric hydrogen uptake with this kind of material [105]. Two Grand Canonical Monte Carlo studies on the IRMOF series indicate that small pore size and multiplicity of the system permits di-hydrogen molecule to interact with a central portion of multiple ligands [105, 106]. Both the studies settle to the statement that overall pore volume becomes furthermore significant at higher pressures. The overall result of interpenetration increases the net interaction energy, ΔH_{ads}, and is redirected to increase in hydrogen uptake at 77 K and 1 atm.

Mesopores of few MOFs are excessively large in order to uptake H₂ efficiently. In such cases, the fabrication of composites by monitoring its pore magnitude is one of the ways to attain greater H₂ capacity [107]. Besides this, a combination of two similar MOFs, or MOFs of different components has presented a good optimization of surface configuration and pore geometry [81, 108, 109]. The volumetric density of provided MOF can be enhanced by modeling powdered MOF material to a definite structure to obtain correct ratios between pore volumes, density, and secondary surface area [110]. Modeling methods like template method, uniaxial pressing, and powder extrusion were employed to synthesize fine surface MOF particles into contrasting compacted structures to boost up their H₂ storage capacities [111, 112]. The most favorable approach to store H₂ in MOF is based upon the spillover mechanism. Boudart et al. [113] discovered the term 'spillover' in the year 1969 to explain the movement of hydrogen atoms from the parent metal to a region with lesser activation energy. Hence to complete the desorption cycle, the adsorbed H₂ migrates in a reverse manner from parent surface to the metal surface. Adsorption at room temperature is a sign of stronger bonding between the host material and the hydrogen atom. Spillover mechanism exhibits the property to function at room temperature and not at 77 K, which is regarded as the principle temperature needed for adsorption of H₂ into porous sorbents without spillover. Although Prins et al. [114] stated that spillover does not take place in all conditions. And Talyzin and Luzan [115] conveyed no H₂ stock enrichment through spillover. Also the Pt/C-doped MOF developed by Campesi et al. [116] did not report any spillover and claimed it to be below the limits of detection.

The tremendous enthusiasm to improve non-petroleum alternative hydrogen power devices demands a dense storage system. MOF is considered as an ideal model with high porosity, surface area, and low thickness. These are continuous crystalline connecting metal particles through different natural linkers. Some encouraging models are stated in Table 2. Such MOFs having uncovered metal destinations prone to water present in air decrease the H₂ uptake gradually with time. Some MOFs reduce readily because of their unsteadiness towards acids and bases. This classification may incorporate MOFs arranged from carboxylic acids. Another stability source is metal particle facing the amalgamation of MOF which is still under the process of development. It is recently reported that the synthesis of MOFs from ligands with hydrophobic functional groups can develop a water-stable MOF structure [117]. Table 2 may also be read by differentiating the connections between the heat of adsorption and the hydrogen uptake in free pore void volume. The geometric harmonization between the natural linkers and the sides of metals lead to very arranged and sometimes permeable materials [118, 103]. This empowers the material to have explicit pore diameters, substance functionalities, and topologies. It is required to know the dependence of material properties on adsorption to plan the engineering of the system. This strategy remains prominent because of less energy consumption and to desorb artificially bonded hydrogen.

2.5. Carbon nanotubes

Adsorption of hydrogen in carbon-based materials happens close to carbon surface because of *Van der Waals* forces applied by C-particles onto the atoms of hydrogen. The absorbed gas signifies the gas volume which could possibly be fed to the provided volume in correspondence to the total gas occupying the same volume in the absence of adsorption at identical pressure and temperature conditions [119, 120]. At steady temperature, the total absorbed gas is proportional to the pressure and is unconfined with decreasing pressure. This shows the reversibility of the system with respect to pressure [121].

Nanostructured materials are of huge interests due to their features like adsorption on the surface, short sub-atomic adsorption and desorption time, solid-state storage, high gravimetric and volumetric densities, and the grain boundaries. The thermodynamic and kinetic stabilities of hydrogen adsorption and desorption on parent material are not quite the same as that of chemical and metal hydrides. These are influenced by decreasing diffusion length and increasing the diffusion rate. The possibility of hydrogen adsorption on nanomaterial follows equilibrium-based figures, which are the function of pressure and temperature [122]. Simonya et al. [118] performed different assessments with carbon nanotubes as an effective hydrogen-storage material in the year 2002. In any case, the greater part of them did not reach the standards of the Department of Energy (DOE) of 6 wt% for applications in the transport. In the principal working, sending point charges on the surface of a material can enhance the storage limit and expand the binding capacity of hydrogen. Charge-induced dipole plays another important role in settling hydrogen particles. One among these is a Silicon-Carbon Nanotubes blended in 2001 [123] with point charges on material's surface to affirm their candidature for effective hydrogen storage substitute [124]. Fig. 4 demonstrates SiC-NT with Si and C particle substituted with point charges. More than half of the charge is consistently exchanged from Si to C [125]. Researchers from Germany have adequately structured 3D carbon nanotube lattices to uptake and release hydrogen at higher efficiencies and have shown good results to maintain the ecological hydrogen economy. Stefano Leoni's group at the Technical University of Dresden are utilizing a computer-based system to enterprize the structure of 3D carbon nanotube which could store more hydrogen at room temperatures as compared to some other carbon-based material.

In the same way, the sorption of MgH_2 (magnesium hydride) is recently investigated with a synergistic approach of doping Fe and Ti nanoparticle. The hydrogen storage properties are improved as
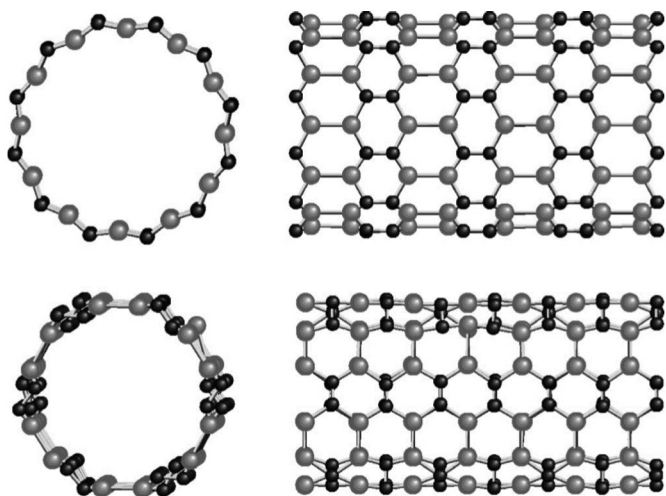
Fig. 4. Single-wall Silicon Carbon nanotubes. The top panel represents zigzag configuration and bottom panel represents armchair configuration [125]. Menon, Madhu, et al., Phys. Rev. B, 69 (2004) 115322. Copyright 2004 American Physical Society.

Fig. 6. Room temperature H_2 sorption kinetics of polyaniline nanospheres [130]. (Adapted from Niemann et al., Nanosc. Tech. (2008) 950967 under CCA license.)

the diffusion occurs in host lattice of MgH_2 [126]. The intention of CNT/nanocatalyst for both $NaAlH_4$ and MgH_2 is to power-up the system and enhance its reversible hydrogen storage properties. Mechanical milling helps to pulverize the particles of MgH_2 into nanocrystalline or micro phases and hence lowers desorption activation energy. Hydrogen sorption for nanocatalyst doped MgH_2 is mechanically milled and the agglomeration of MgH_2 is shown in Fig. 5 along with their activation energies. This also displays MgH_2 nanocluster model and nanocatalyst distribution over active sites for efficient hydrogen storage onboard. The resulting material will be non-toxic, lightweight, and shoddy to make, and henceforth it would be ideal for applications at large scales. Aristizabal et al. [128] investigated that nanotube material supports 5·5 wt% hydrogen uptake at room temperature which is apparently an ideal chance to meet US DOE's goals of 6 wt% limit including total weight after gas adsorption. Hydrogen storage capacities can be helped by adding metals to carbon structures like B, Ca, K, Li, Ag, Ni, Pd, Fe, Pt, Ru, Ti,
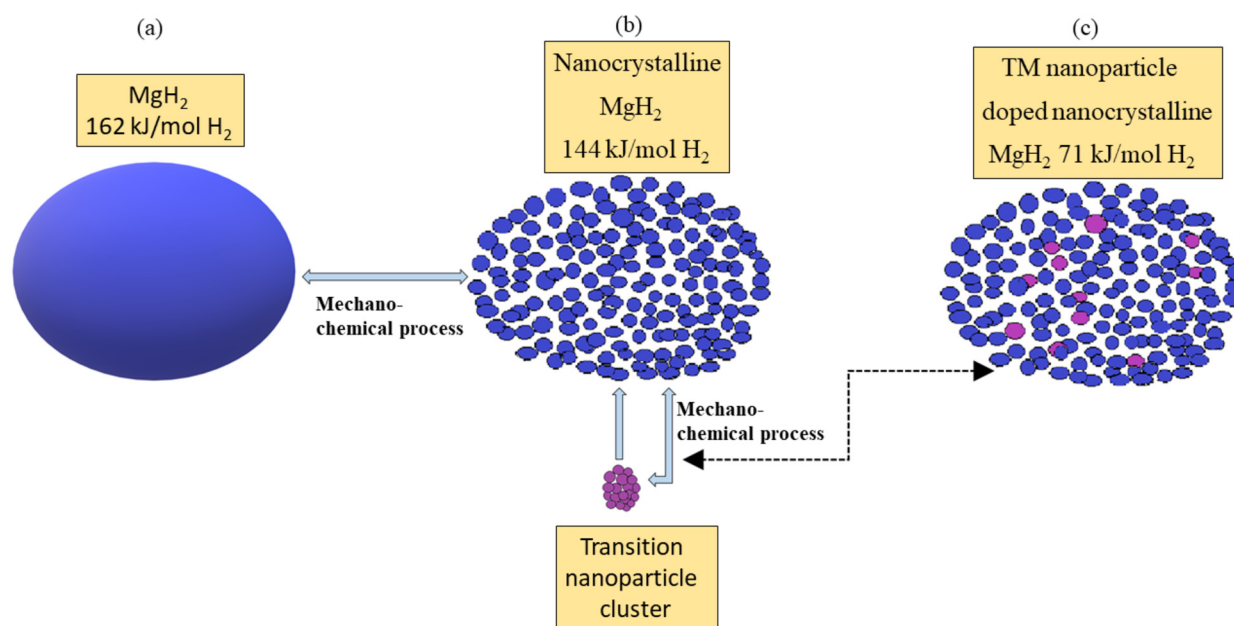
TiO_2 [124, 125, 126]. Freshly synthesized CNT was found to uptake 0·1 wt% of H_2 at 573 K and ambient pressures [117]. In addition to this, oxidation is the pathway to identify defects and doping with the Pd-Ni catalyst which upgrades the hydrogen storage up to 6·6 wt% at 610 K and ambient pressure. Another study reveals that 6-8 wt% H_2 adsorption could be reached through polyaniline nanocomposite, but the experimental capacity reported is 1·4-1·7 wt% [125, 129]. Polyaniline is chosen as a nanocomposite matrix material due to its inexpensiveness and easiness to polymerize. It can be seen from Fig. 6 that the release and uptake of hydrogen of 4·0 wt% happen in the initial stages. Also, the kinetics and storage intake gets reduced with repeated cycles. Normal examinations and hypotheses have built a trust factor on carbon nanotubes doped with suitable material as the potential material for hydrogen storage system [131]. Various investigations of dimensions of doped CNT at various response conditions have proposed a few negative outlines of the H-system, which should be addressed in nearly future. For implementing carbon nanotubes in practical purposes, its large-scale manufacturing and applications are of yet far to go. The key

Fig. 5. Theoretical model of MgH_2 agglomeration (a) plain, (b) nanocrystalline, and (c) nanocatalysed-doped material [127]. (Reprinted with permission from Brian D. Adams et al., Materials Today, 14 (2011) 282–2899. Copyright (2011) Elsevier.)
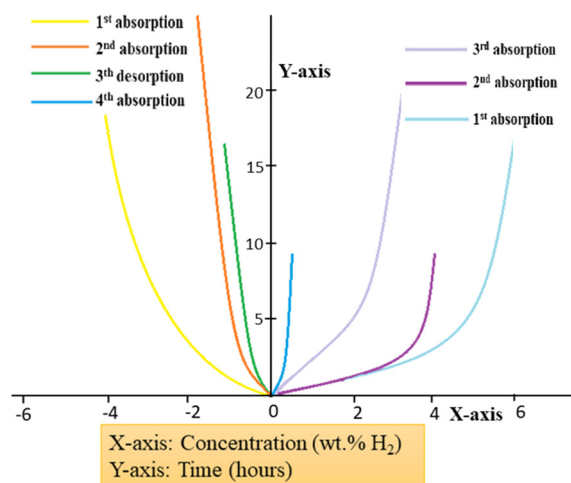
focuses for further studies and trials on these materials can be considered as:

1. Low cost for mass production of CNTs with organized microstructures.
2. Operation of metal-doped CNT for increasing hydrogen storage capacities, energy, and volumetric density.
3. Explanation of adsorption and desorption kinetics [127].
4. Monitoring of operational temperature and pressure conditions.
5. Designing and its improvements for hydrogen storage systems in running vehicles.

2.6. Conclusions and future outlook

With developing concerns about atmospheric changes and consumption of non-sustainable power sources, a visualized hydrogen economy stays a feasible option in contrast to other energy sources. In this review, different solid-state H_2 storage materials have been investigated. To accomplish the H_2 economy, its storage remains the interest, as traditional storage frameworks may not be effective and safe for several onboard applications.

To diminish the concern of the future fuel, the hydrogen has to be used in the right direction and efficient storage systems need to be developed or previously developed systems are required to be modified to tackle the depleting fossil fuel concern.

The article discusses numerous nanomaterials and their substitutes as the potential systems. The performance of these depends upon the properties and operating conditions of the system. Chemical storage systems including complex and metal hydrides are promising but exhibit poor reversibility and cost-viability. Physical adsorption based on carbonaceous materials and different permeable materials with the high surface area has expanded multiple research fields due to its simple reversibility and efficient kinetics. However, low operating temperature is ideal for porous material hydrogen uptake. To improve the system performance, a metal-based catalysts may be induced into the adsorbent surface to enhance the hydrogen spillover effect and ion-ion interactions. Furthermore, volumetric and gravimetric techniques may be used to test the hydrogen sorption capabilities of the system. Both the techniques follow different mechanisms but the results are the same.

Difficulties of the solid-state hydrogen storage systems should be progressively researched to meet on-board targets given by the United States Department of Energy. It is anticipated that new methodologies must develop for solid-state H_2 storage to add to the effective activity of hydrogen vision.

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Author contribution statement

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