METAL HYDRIDES AND METAL-ORGANIC FRAMEWORKS FOR HYDROGEN STORAGE IN AUTOMOTIVE APPLICATIONS: A REVIEW

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Abstract: *Hydrogen is an attractive automotive fuel because it is carbon-free, abundantly available from water, and has an exceptional mass-energy density. Hydrogen storage has become a trendy topic in recent years with its ability to design low-cost, lightweight materials that can reversibly and rapidly store hydrogen near ambient conditions. Various materials-based systems, such as metal hydrides and metal-organic frameworks (MOFs), have been introduced. This paper discusses and compares each material in terms of hydrogen storage capacity, kinetics, and viability. Different types of metal hydrides, such as magnesium hydrides, complex hydrides, and intermetallic-compounds hydrides, are considered. Furthermore, promising MOFs materials such as zinc- and copper-based MOFs are mentioned. The paper also compares the materials in terms of storage cost, which is rarely discussed in the literature. Results show that metal hydrides require severe pressures and temperatures to achieve optimum storage capacity, which is difficult to obtain and maintain. On the other hand, MOFs have some advantages, such as high surface area, high pore volume, as well as rich open metal sites. However, these properties being offered via MOFs have a limitation of low hydrogen uptake at ambient temperatures for hydrogen storage. This limitation is overcome by designing MOFs with unsaturated open metal sites. Future research is needed to optimize metal hydrides and MOFs to perform better under normal operating conditions to meet the recommendations of the United States Department of Energy.*
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1. Introduction

As the effects of climate change become more pressing, nations worldwide are adopting approaches to mitigate global warming and reduce their global carbon footprint. One of the most promising approaches is the adoption of renewable energy sources such as wind power, solar panels, and hydroelectric power [1]. These sources not only provide clean energy, but they also offer an opportunity to get freed from the fossil fuels that have been established as the major contributors to global warming and climate change. While these renewable sources of energy are promising for addressing global climate issues, they also have a number of drawbacks. The generation of energy from these sources highly depends on the climatic conditions, hence, fluctuations and intermittency make it difficult to evaluate their power- generating capacity, which leads to an imbalance between power generation and load demand [2]. These energy sources are also, most of the time, located far away from the energy demand, making it difficult to transport energy.

To address these challenges, energy storage has been cited as the most promising alternative. Hydrogen has been remarkably studied recently as a versatile energy carrier for both stationary and mobile applications. As such, hydrogen storage has been shown to be a promising approach to moving energy from centralized to distributed generation, thus

improving access to energy in remote areas and improving energy security, reliability, and overall performance. While hydrogen storage is a promising approach, achieving optimum storage capacity remains a major challenge in developing a hydrogen economy. This has evoked the development of different storage options such as pressurized hydrogen gas, cryogenic liquid, and combination with different metals to produce metal hydrides to improve storage capacity [3].

The developed countries intend to reduce the emissions and start to use green energies that are powered by hydrogen, but there are some challenges arising from the performance, safety, and cost when storing hydrogen. Current materials suffer from low hydrogen uptake at ambient temperature, slow kinetics, and expensive storage costs. Hydrogen is extremely flammable and requires restricted safety measurements. Thus, the United States Department of Energy (U.S. DOE) specifies the system requirements for hydrogen storage as shown in Table 1. The utilization of data will serve as a guiding factor in the identification of metal hydrides that closely matched with the optimal recommendations as well as in assessing potential areas for enhancement [1].

This review focuses on metal hydrides and MOFs as potential hydrogen storage options, discussing the chemistry behind their working principles, challenges, and different techniques used to enhance their storage capacity. Three types of metal hydrides are considered, such as magnesium hydrides, complex hydrides, and intermetallic compounds hydrides. Different types of MOFs, such as zinc- and copper-based MOFs, are included. Each material is assessed in terms of the operating conditions and hydrogen storage capacity. Usually, metal hydrides and MOFs are discussed individually in the literature; however, this paper combines the two categories for better understanding and evaluation. The paper also discusses the storage cost of the materials, which is rarely mentioned in the literature.

Table 1. United States Department of Energy recommendations for hydrogen storage [4].

Storage parameter	unit	2020	2025	ultimate
Material-based gravimetric capacity	[kWh/kg]	1.5	1.8	2.2
Storage system cost (fuel cost)	[$/kWh net]	10	9	8
	[$/kg H2]	333	300	266
Operating ambient temperature	[°C]	-40/60 (sun)	-40/60 (sun)	-40/60 (sun)
Min/max delivery temperature	[°C]	-40/85	-40/85	-40/85
Cycle life (1/4 tank to full)	[cycles]	1500	1500	1500
Min. delivery pressure from tank	[bar]	5	5	5
Max. delivery pressure from tank	[bar]	12	12	12
Charging/Discharging rates	[min]	3-5	3-5	3-5
Fuel purity (H$_2$ from storage)	[%H$_2$]	99.97 dry basis	99.97 dry basis	99.97 dry basis

2. Metal hydride

Metal hydrides are compounds of hydrogen and metals. They have been considered a potential option for hydrogen storage due to their high gravimetric and volumetric hydrogen storage capacities, as well as their relatively low cost and ease of handling compared to other hydrogen storage methods [1]. Metal hydrides are formed when hydrogen reacts with different metal elements to form hydrogen-metal compounds—hydrogen

hydrides [5]. The bond between hydrogen and metals is dependent on whether the reacting elements share or completely transfer their electrons. The resulting compound can exist either as a solid, liquid or gas. Solid metal hydrides are formed through chemical reactions and act as physical storage. Metal hydrides can also be formed from alloys of different metals to form a solid-state storage under moderate pressure and temperature. As mentioned above, high volumetric and gravimetric capability gives metal hydrides the capacity to pack more hydrogen atoms in a metal of the same volume as liquid hydrogen. Abe et al. noted that this is possible because when hydrogen gas is brought into contact with metal, it forms hydrogen molecules as it gets adsorbed on the surface of the metal [1]. If sufficient energy is added to the compound, the hydrogen molecules dissociate into atoms and diffuse further into the interstitial sites of the metal crystal to form a solid solution. This can continue until the metal becomes saturated with hydrogen atoms, allowing the metal to carry higher amounts of hydrogen atoms.

2.1.   Type of Metal Hydrides

Metal hydrides are broadly categorized into two groups based on the temperature of hydrogen absorption and desorption [6]. According to this categorization, there are low-temperature and high-temperature hydrides. Low-temperature metal hydrides are formed from the covalent bonding between the hydrogen atoms and metal atoms. They are characterized by high molecular weight, low hydrogen equilibrium pressure, and fast kinematics. Low-temperature hydrides are mostly solid solution or intermetallic alloy hydrides that operate at moderate ambient temperatures. Low-temperature hydrides are further categorized according to stoichiometry, and they include AB_5–type (e.g. $LaNi_5$), AB_2– type (e.g. $TieZr$ alloys), A_2B-type (e.g. Sb_2Ti, Sn_2Co) and AB-type (e.g. $TieFe$ alloys), where

A represents elements with high affinity for hydrogen typically rare-earth, and B represents elements with low hydrogen affinity. High-temperature metal hydrides, on the other hand, are formed from ionic bonds and, hence, are high-temperature hydrides. They are characterized by low molecular weight and higher hydrogen atom storage capacity compared to low-temperature metal hydrides.

Mainly there are three types of metal hydrides: magnesium hydrides, complex hydrides, and intermetallic compounds hydrides. Mg-based metal hydrides have magnesium as the core of the compound, which can be modified with additives and catalysts to increase its properties. For example, MgH_2, MgH_2-5mol% V_2O_5, and MgH_2-5at% Ni. Complex hydrides combine light metals or metalloids and usually include bromides, amides, borohydrides, and alanates [7]. For instance, $NaAlH_4$, $NaBH_4$, and $LiNH_2$. Intermetallic compounds combine two or more metals that act as a medium for storing hydrogen. For illustration, AB_5–type ($LaNi_5$), AB_2– type ($TieZr$ alloys), A_2B-type (Sb_2Ti, Sn_2Co) and AB-type ($TieFe$ alloys). Choosing the ideal metal hydride must be done in parallel with the recommendations given in Table 1. The advantages and disadvantages of each metal hydride are shown in Table 2 and followed by examples in Table 3.

Table 3 compares some types of metal hydrides with the activation temperature, pressure, kinetics, and weight capacity. Although the magnesium-based metal hydride has a higher temperature absorption and desorption, it has lower pressure, lower kinetics, and a higher weight capacity than the other metal hydrides, which means there are some obstacles to achieving the U.S. DOE recommendation. In the following section, magnesium-based hydrides and methods to improve the performance will discussed.

Table 2. Advantages and disadvantages of metal hydride compounds

	Mg-based Metal Hydrides	Complex Hydrides	Intermetallic Compounds
Advantages	• Highest energy density • High H_2 capacity • Low cost	• High H_2 capacity	• Light molar mass

Disadvantages	• High-temperature discharge • Slow desorption rate	• Hazardous • 2-step reactions • High-temperature reaction • Unstable	• Low-H_2 capacity • Low-life cycle • Weight penalty

Table 3. Comparison between different metal hydrides for hydrogen storage [3].

Material	Type	Temperature (°C)	Pressure (bar)	Kinetics (min)	Max gravimetric capacity of H_2 wt%	Ref.
Mg-10wt% Al2O3 (mg-based)	Ball milling	Abs: 300 Des: 300	Abs: 11 Des: 0.5	Abs:60 Des:60	5.66	[8]
MgH_2-5wt%V (mg-based)	Magnesium-based	200 (Abs.) 300 (Des.)	10 (Abs.) 0.15 (Des.)	4.2 (Abs.) 33 (Des.)	5.8	[9]
Li_3N (complex)	mixing	Abs: 50 Des:240-270	Abs:0.5 Des:1	Abs:20	6	[10]
$LiNH_2$-LiH-1mol% (Complex)	Complex Hydride	150-250 (Des.)	30 (Abs.)	30 (Abs.)	5	[11]
$La_{1.8}Ca_{0.2}Mg_{14}N_{13}$ (intermetallic)	Ball milling	Abs:27-327 Des:27-327	Abs:40 Des:1	Abs: 15 Des 10	5	[12]
FeTi (intermetallic)	Intermetallic compounds	25 (Abs.)	100 (Abs.)	N/A	1.92	[13]

Abs: Absorption rate; Des: Desorption rate

Magnesium hydrides have been the center of focus over the past several years regarding hydrogen storage. Recent studies are beginning to shed light on the potential of magnesium hydrides to address some of the major challenges faced by other metal hydrides regarding hydrogen storage. Ma et al. noticed that magnesium-based hydrides have been shown to exhibit several advantages as compared to other metal hydrides [14]. Some of the advantages associated with magnesium hydrides include low cost, higher storage capacity, and improved kinetic performance. In addition, magnesium-based hydrides have demonstrated good-quality functional properties such as heat resistance, recyclability, vibration absorption, and reversibility, making them more attractive for recent research and development. This section discusses magnesium-based hydrides, highlighting how different catalysts affect the properties of magnesium-based hydrides.

Add that the magnesium-based hydrides have been studied since the 1960s. The studies focused on different aspects of Mg-based hydrides regarding their storage capacity and improving their effectiveness [15]. The main areas of focus on Mg-based hydrides in reviews have been on Mg-Ni-based storage alloys, catalyst-enhanced Mg-based hydrides, the interrelation between the composition of Mg-based hydrides, and optimization of the MgH_2 through catalyst additives [15]. Consequently, several achievements have been made to improve the storage capacity of Mg-based hydrides through a variety of synthesis methods, like using catalysts, nanoadditives, and mechanical techniques.

Mg-based hydrides can be synthesized through a direct reaction between hydrogen and metal or through a chemical approach, which involves a reaction of Mg-organic compounds.

Mg-based hydrides synthesized from chemical reactions are more reactive compared to those synthesized from the direct reaction of Mg and hydrogen. Mg-based hydrides that have been evaluated during hydrogen storage research include Mg_2NiH_4, Mg_2FeH_6, and others. Given the high temperature required to achieve the absorption of hydrogens in the Mg-based alloys, different catalysts are used, resulting in different Mg-based hydride compounds depending on the type of catalyst used. Some of these catalysts exhibit better catalytic properties that improve the dehydrogenation of the Mg-based hydrides. Some of the catalysts that have been used to improve Mg-based hydride dehydrogenation include Ni, Ti, and V. For example, Table 4 compares the activation energy dissociation for different catalysts. Although there are many factors that participate in selecting the best catalyst, like selectivity, cost, and availability, the activation energy is a major factor of consideration [16].

Table 4. Dissociation energy in comparison to magnesium with different doping [16]

Metal	Dissociation energy (eV)
Pure Mg	0.87, 0.40, 0.50, 1.15, 1.05, 0.95, 1.00
Ti-doped Mg	Null
Ni-doped Mg	0.06
V-doped Mg	Null
Cu-doped Mg	0.56
Pd-doped Mg	0.39
Fe-doped Mg	0.03
Ag-doped Mg	1.18

2.2. Enhancement of metal hydrides

2.2.1. Additives

Additives can help enhance hydrogen storage by scaling the surface area and shortening the diffusion path for hydrogen desorption and absorption, resulting in higher capacity, lower activation energy, and lower desorption and absorption times [17]. Additives are introduced while reducing the metal hydride particles by using mechanical or chemical techniques, like ball milling. Additives can be in the form of metals or non-metals (carbon materials).

Metals are common catalysts that improve the metal hydride property, where they can be cheap, environment-friendly, high-active catalyst, and prevent undesired byproducts (MgO). Metals only need a small amount of doping to have a large impact on the metal hydride. Besides, selected metals do not react while mixing with the magnesium-based metal; however, they react well after dehydration. For example, El-Eskandarany et al. introduced Ni particles to MgH_2 and found that Ni improved reversibility and stability after 100 cycles [18]. Also, Fe particles had the same impact on reversibility and kinetics [17].

A review by Yartys et al. demonstrated that graphene, a two-dimensional carbon, is a good catalyst that improves the dehydrogenation of the Mg-based hydrides [15]. The most effective additives are carbon-based materials like graphene, carbon nanotubes, and carbon fiber. It is found that the graphene sheet (GNS) has a significantly higher enhancement than the rest of the additives. This shows that the production of Mg particles can be increased by up to 5.7 wt% when graphene is used as a catalyst. By further incorporating Ni into the Mg/GNS composite, the hydrogen storage capacity of the composite is significantly improved, demonstrating an improved catalytic property. Liu et al. compared the performance of Ni-catalyzed MgH_2 and MgH_2-5wt.%GNS at 300°C. The objective of the experiment was to assess the amount of hydrogen desorbed over time. The findings of the study indicate that an increase in the milling duration of metal hydrides leads to improved performance, The findings of the study indicate that an increase in the milling duration of metal hydrides leads to improved performance, likely due to the corresponding increase in surface area. It was

found that MgH$_2$-5 wt.% GNS performed better than MgH$_2$; while it took 120 min for MgH$_2$-20h to reach 2%wt. capacity, it only took 20 min for MgH$_2$-5wt.% GNS-20h to reach 5%wt.

capacity. Table 5 shows a comparison between different additives for improving the performance of magnesium hydrides.

Table 5. Comparison between different additives for magnesium-based hydrides

Additive	Doping Amount	Size (nm)	Temp. (°C)	Isothermal Hydrogen	H$_2$ (wt%)	Ea (kJ/mol)	Ref.
Nickel (Ni)	4 mol%	50	143 (Abs.)	325°C 0.02 bar 11 min	7	81.5	[19]
Iron (Fe)	5 wt%	25	150 (Abs.)	20°C 1.5 MPa 60 min	5.5	74	[20]
Niobium (Nb)	7.5 wt%	12	N/A	200°C 40 bar 10 min	4	86.4	[21]
Graphene particles	40 wt%	N/A	340 (Abs.)	340°C 20 min	4	80.8	[22]
Graphene nanosheets	5 wt%	N/A	300 (Abs.)	300°C 1 min	6.6	64.7	[23]

2.2.2. Particle size

One of the ways to modify the properties of the metal hydrides is the nanosizing of the particles. It can improve the surface area and porosity of the metal, improving the time reaction, lowering the reaction energy, and increasing the capacity of the hydrogen storage. Because strong chemical bonds occur between the hydrogen and the metals, it will need higher energy to release the hydrogen; however, reducing the particle size will help reduce the energy taken to roughly 30% for MgH$_2$ due to increasing the porosity size and shortening the path of absorption and desorption, which will allow fast diffusion to the metal. Although increasing the porosity and surface area will decrease the weight capacity, it will open new sights for hydrogen bonds with lower energy use [24]. There are many techniques to reduce the particle size and enhance the properties of the metal hydride; however, four commonly used techniques will be discussed: ball milling, rod milling, cold roll, and high-pressure torsion (HPT). The ball milling technique involves grinding metal hydride powders in a ball mill, which uses a rotating cylinder filled with balls to crush the powders. This technique can be used to create smaller and more homogenous particle sizes, which can improve the hydrogen

storage properties of the metal hydride [25]. The rod milling technique grind metal hydride using a rod instead of a ball. The method uses a rotating cylinder filled with rods to crush the powders. The fraction between the rods is between 35 and 40%, and the difference between rod and ball milling is that the rods do not collide with each other, rather than crush the particle with the walls until it becomes fine enough to pass through the rods [26]. A study by El-Eskandarany et al. showed that LaNi$_3$ amorphous alloy nanopowders have been found to improve the performance and hydrogen storage properties of MgH$_2$ when used as a catalytic additive [27]. The addition of LaNi$_3$ nanopowders to MgH$_2$ increases the rate of the hydrogen desorption and absorption reactions, reducing the activation energy required for these processes, which is reduced to 73.26 kJ/mol. Also, it leads to faster hydrogen uptake and release, resulting in 8 mins at 200°C and 2 mins at 225°C, and higher hydrogen storage capacity to ~6wt% at 200°C. Besides, the use of LaNi$_3$ nanopowders can also improve the thermal stability of MgH$_2$, making it less likely to degrade at high temperatures [27].

The cold roll technique involves passing metal hydride powders through a set of rollers,

which compress and shape the powders. This technique can also be used to create smaller and more homogenous particle sizes and improve hydrogen storage properties. The Zhang et al. experiments revealed that the deformation in the material occurred which increased the kinetic of particles during adsorption and desorption processes; however, it only lasted a few cycles [28]. A review of a comparison made between cold rolling and ball milling techniques concluded that the cold-roll samples sustained the weight percentage, while the mall-milled samples decreased slightly [29]. However, both mechanical techniques improve the kinetics.

High-pressure torsion (HPT) is a technique used to obtain nanostructured metal using high pressure and rotation torsional straining on a thin disk in between. Strozi et al. reviewed the effect of HPT and concluded that it still has room to improve due to its positive effect only on the first hydrogenation cycle [30]. On the other hand, Gunderov et al. study concludes that HPT raises the sample's microhardness, which results in yield stress and β-state strength improvement [31].

A study was made to compare the three techniques for forming nanopowders. The plot shows that ball milling can reduce particle size the most, where it reaches 0.01 μm. Although cold rolling has the least particle reduction, it has other disadvantages, like deforming the shape of the crystal.

3.   Metal-Organic Frameworks (MOFs)

The idea of linking two various or identical metals via ligands has been an illusion since the founding of reticular chemistry. The story began in the mid-60s when Tomic successfully prepared thermally stable polymers with different ligands that linked selected metal ions such as Zn, Li, and Al onto 1D building blocks [32]. Three decades later, in 1990, Hoskins and Robson proposed scaffolding-like materials that consisted of polymeric frameworks of 3D-linked molecular rods [33]. In 1995, the first metal-organic framework (MOF) was discovered by Omar Yaghi and his co- worker. The first MOF ever synthesized was synthesized via hydrothermal technique, forming a crystalline, porous framework [34]. Since that year, MOFs have attracted a vast number of researchers due to their high porosity, crystallinity, large surface area, and tunable structure, where these exceptional properties could be utilized for numerous areas such as gas separation and storage, purifications, and catalysis. As of 2022, more than 100,000 MOFs with various structures are reported and registered on the CSD database [35].

Porous materials proved to be highly attractive to both academia and industry due to their unforeseen properties, which assist in many areas, such as gas storage and separation, drug delivery, and catalysis. Zeolites, covalent-organic frameworks (COFs), and metal-organic frameworks (MOFs) are all instances of porous materials. There are three types of porous materials classified by the size of their pores. Materials with a pore size of less than 2 nm are called microporous materials, while materials with pore sizes ranging from 2 to 50 nm are mesopore materials. Macroporous materials have a pore size larger than 50 nm. These porous materials' properties are highly influenced by the pore's size [36].

MOFs, or porous coordination polymers (PCP), are porous and crystalline materials that can be synthesized via linking metal ions along with organic ligands such as tri-carboxylic acids, pyridyl groups, and imidazoles. MOF's network structure is either formed in two dimensions or three dimensions [37].

One of the significant factors that inluence the overall quality and properties of porous products is material synthesis. Crystallinity, surface area, pore size, and chemical and thermal stability of MOFs are all controlled through various parameters during synthesis or post-synthesis. Particularly, synthesizing MOFs could be carried out via many routes, such as solvothermal, microwave, electrochemical, mechanochemical, and sonochemical synthesis.

The solvothermal synthesis method of MOFs is widely utilized, where it could be performed at room temperature or with the existence of heat in a solvent such as dimethylformamide (DMF) [38]. In the following section, various types of MOFs will be discussed.

3.1.1. Type of MOFs

Different types of MOFs show reasonable hydrogen adsorption. The selection of the most applicable MOFs is very significant for optimum hydrogen storage. Choosing an adequate metal ion and organic linker is extremely important to obtain acceptable product performance. The first consideration in this case is the metal ion used or the secondary building units (SBU). Copper (II) nitrate ($Cu(NO_3)_2(H_2O)_n$) SBU is a promising candidate for hydrogen storage. It is the existence of a di-copper paddlewheel SBU in a twisted boracite network with a tight cavity that generates a stronger binding affinity for hydrogen [39].

A study conducted by Long and Kaye on utilizing the six dehydrated Prussian blue analogs $M_3[Co(CN)_6]_2$ (M = Mn, Fe, Co, Ni, Cu, and Zn) to examine their porosity and hydrogen storage properties [40]. Prussian blue analogs possess purely inorganic face-centered cubic framework structures where each node is occupied by metal ions that are bridged by CN^- ions to form a three- dimensional network [41]. It revealed that the Cu compound has the highest hydrogen uptake (1.8 wt%) at -196°C and 1.2 bar in comparison with other materials assessed. In addition to the Ni compound, Cu one has the highest heat of adsorption (6.5 kJ/mol) with H_2 adsorbed at 1.4 wt%. These results confirm the high binding energy of copper to hydrogen, which is required for enhancing the MOFs-H_2 interactions. These properties have made Cu-MOFs an excellent candidate for hydrogen storage.

A vast number of MOFs are designed and prepared with various structures, metal ions, and organic linkers. Of them, each one is designed with regard to desirable properties to meet specifications for numerous applications. In terms of hydrogen storage, several MOFs are being utilized and characterized under different conditions to reach their optimum characteristics. For instance, MOF-5-based Zn shows outstanding hydrogen uptake (11.5 wt%) at 170 bar and -196□C. However, these conditions are not applicable due to the high cost of operating. Moreover, at room temperature, hydrogen uptake drops from 11.5 wt% to 0.2 wt% at 67 bars. A target of 4.5 wt% set by US DOE to operate at ambient conditions could be achieved through enhancing many factors such as Brunauer, Emmett and Teller (BET) surface area and isosteric heat of adsorption Q_{st}. Table 6 depicts numerous MOFs based on various metals with their hydrogen uptake, Q_{st}, BET area, and PV at different conditions. Cu-MOFs display significant hydrogen uptake and stand as a promising candidate for hydrogen storage.

Table 6. Surface area (BET), pore volume (PV), and hydrogen storage properties under specific conditions for metal–organic frameworks.

MOF Type	Hydrogen uptake			Q_{st} (kJ/mol)	BET Area (m^2/g)	PV (cm^3/g)	Ref.
	P (bar)	T (°C)	wt%				
MOF-5 based Zn	1	-196	1.32	4.8	3362	-	[42]
	50	-196	4.7	3.8	2296	-	[42]
	170	-196	11.5	-	-	-	[42]
	60	-73	0.9	-	-	-	[42]
	48	25	1.65	-	-	-	[42]
	60	25	0.45	-	-	-	[42]
	67	25	0.2	-	-	-	[42]
HKUST-1 based Cu	1	-196	2.18	6.1	1239	0.62	[43]
	1	-196	2.48	6.8	1507	0.75	[43]
	50	-196	3.6	4.5	1154	-	[43]
	65	25	0.35	4.5	-	-	[43]
TUDMOF-2 based Mg	1	-196	0.78	-	-	-	[44]
	1.12	-196	0.46	9.5	190	-	[45]

MOF-74	1	-196	1.75	8.3	783	0.39	[46]
based Zn	26.1	-196	2.21	-	950	-	[47]
	30	-196	2.8	8.8	870	-	[48]
ZIF-8 based	1	-196	1.27	-	1630	0.64	[49]
Zn	30	-196	3.3	-	-	-	[50]
	55	-196	3.01	-	-	-	[49]
	60	298	0.13	-	-	-	[50]
PCN12 based	1	-196	2.55	7	1931	0.91	[43]
Cu	45	-196	5.23	-	-	-	[43]
	3.5	-243	7.89	-	-	-	[43]
NU-100 based	1	-196	1.82	6.1	6143	2.82	[42]
Cu	56	-196	9.95	-	-	-	[42]
	70	-196	16.4	-	-	-	[42]
Cu-BTT	1.2	-196	2.42	10	1710	-	[51]
MOF-177	1	-196	1.23	-	4526	-	[52]
based zinc	66	-196	7.1	-	4750	1.69	[53]
CUK-2	1	-196	0.66	-	420	0.17	[54]
	10	25	0.03	-	1595	0.77	[55]
NOTT-401	1	-196	2.31	6.65	1514	0.66	[56]
	1	-196	0.9	-	297	-	[57]
SNU-6	1	-196	1.68	7.74	2590	1.05	[58]
Zn-MOF-205	80	-196	7	-	4460	1.05	[59]

3.2. Optimization of MOFs

3.2.1.1. Surface Area and Porosity

A study was conducted by Srivastava et al. to assess the impact of copper-based MOFs with various organic linkers on the surface area, pores size, isosteric heat of adsorption, and total uptake of hydrogen. All MOFs studied consist of the same secondary building unit (SBU), which is $Cu(NO_3)_2(H_2O)n$ connected through different organic linkers forming MOF-199, PCN-20, MOF- 399, and PCN-6' [60]. The organic linkers differ in length, determined by the number of aromatic benzene rings; the longest organic linker is H3BBC, forming MOF-399, while the shortest is H3BTC, belonging to MOF-199. The other two organic linkers used are H3TATB and H3TTCA, forming PCN-6' and PCN-20, respectively. The research shows that as the length of the organic linker increases, both the pore volume and surface area increase, as illustrated in Table 7. The latter also provides simulated data of excess hydrogen uptake by weight percent for various MOFs at -196°C and 25°C. The simulation was performed using Grand Conical Monte Carlo (GCMC) for the prediction of adsorption isotherms through replicating experimental data. Due to the high porosity and surface area, MOF-399 depicts the highest hydrogen uptake at -196°C (8.6 wt%) among all the MOFs. PCN-6' shows the optimum hydrogen uptake at ambient temperature (1.03 wt%), while it performed well with hydrogen uptake (8.5 wt%) at -196°C due to its high density and low pore volume. A significant variation is observed in adsorption capacity at 25°C for all MOFs due to increased gas kinetics, caused by the more dispersity of hydrogen molecules, hence there is reduce in adsorption capacity at ambeint temperature. As a whole, PCN-6' is the best hydrogen storage material due to its high adsorption capacity at both temperatures. Hence, MOFs containing smaller pore sizes and large surface areas show higher hydrogen-MOF interactions and increased hydrogen adsorption capacities [60].

Table 7. Surface area (BET), pore volume (PV), and hydrogen storage uptake at different temperatures for various Cu-MOFs.

MOFs	PV (cm^3/g)	BET Area (m^2/g)	Simulated Excess Hydrogen Uptake wt% at 50 bars		Ref.
			-196°C	25°C	
MOF-399	7.55	7157	8.6	0.34	[60]
PCN-20	1.59	3525	6.8	0.52	[60]
PCN-6'	1.045	2869	8.5	1.03	[60]
MOF-199	0.404	1132	4.3	0.34	[60]

3.2.2. Isosteric heat of adsorption

The isosteric heat of adsorption is evaluated by the interaction strength between hydrogen and MOFs (adsorbate and adsorbent). The isosteric heat of adsorption is strongly affected by the pore volume of the adsorbent. In our case, various MOFs are evaluated based on their isosteric heat of adsorption, as shown in Table 8 [60]. MOF-199 has the highest isosteric heat of adsorption at 7.5 and 8 (kJ/mol) at -196 and 25°C, respectively, due to its low pore volume, while MOF-399, with the highest pore volume, has the lowest isosteric heat of adsorption at 3.5 (kJ/mol) at -196 and 25°C. All data are taken under 1 bar pressure. This confirms that for increasing the isosteric heat of adsorption, which plays a vital role in interactions among hydrogen and MOFs, the pore volume needs to be reduced while increasing surface area is preferable for enhancing the hydrogen adsorption capacities.

Table 8. Surface area (BET), pore volume (PV), and isosteric heat of adsorption for various Cu-MOFs.

MOFs	PV (cm^3/g)	BET Area (m^2/g)	Isosteric heat of adsorption (kJ/mol) at 1 bar		Reference
			-196°C	25°C	
MOF-399	7.55	7157	3.5	3.5	[60]
PCN-20	1.59	3525	6	5.5	[60]
PCN-6'	1.045	2869	4.5	4	[60]
MOF-199	0.404	1132	7.5	8	[60]

Many techniques are suggested to raise the isosteric heat of adsorption of MOF materials to meet the theoretical calculations required of adsorbent materials at ambient conditions (15–20 kJ/mol). In this regard, most MOFs materials show an average enthalpy of adsorption to H$_2$ of 5 kJ/mol due to weak physisorption. The open metal sites (OMS) method for MOF materials has been introduced recently to enhance the isosteric heat of adsorption. The OMS method is performed by installing unsaturated metal centers cooperatively [50]. The benefit of OMS in MOF frameworks is to polarize hydrogen, which has been proven that exposed metal sites in MOFs have the ability to have stronger polarization of H$_2$ than regular frameworks for physisorption, resulting in better interaction between metal ions and H$_2$.

Enhancing the interaction among metal ions and H$_2$ is indicated by the increase in the isosteric heat of adsorption. Few MOFs with OMS have exceeded the suggested enthalpy of adsorption at ambient conditions, as illustrated in Table 9. When the ionic radius of the metal ion drops, the metal ion has a higher charge density. The higher charge density of the exposed metal cations on the framework surface facilitates inducing a dipole moment in H$_2$, thus leading to stronger binding. Consequently, a stronger polarizing ability results in enhanced interaction between metal and dihydrogen molecules. It is obviously seen that Cu-based MOFs with open sites show the highest isosteric heat of adsorption (32 kJ/mol), which is very exceptional in comparison with other MOFs due

to the Jahn-Teller effect originating from their d^9 electronic configuration [50]. Other MOFs with OMS are showing good heat of adsorption due to the successful OMS technique utilized and its positive impact on the frameworks.

Table 9. Porous MOFs with open metal sites (OMS) and heat of adsorption (Q_{st}).

MOFs	OMS	M-D$_2$(Centroid) distance (Å)	Q_{st} (kJ/mol)	Ref.
Cu(I)-MFU-4l	Cu(I)	1.6	32	[61]
V$_2$Cl$_2$.8(btdd)	V(II)	1.966(8)	20.9	[49]
Fe-BTT	Fe(II)	2.17(5)	11.9	[50]
Co2(*m*-dobdc)	Co(II)	2.23(5)	11.5	[62]
Ni-MOF-74	Ni(II)	2.201(1)	11.9	[62]
Mn-BTT	Mn(II)	2.27	10.1	[62]
Mg-MOF-74	Mg(II)	2.45(4)	10.3	[63]
MIL-101	Cr(III)	-	10	[64]
Zn-MOF-74	Zn(II)	-	8.3	[65]
socMOF	Ln(III)	-	6.5	[66]

3.2.3.   Spillover Technique

Spillover phenomena are known for the hydrogenation of catalysts. It is utilized to dissociate the chemisorption of hydrogen (H_2) on the metal, hence the migration of the hydrogen atoms (H) onto the surface of the support. The enhancement of hydrogen storage capacity in MOFs could be achieved via numerous factors such as porosity, surface area, and so forth. Another dominant factor for hydrogen storage by MOFs is the isosteric heat of adsorption, which increases with the addition of palladium and platinum to the MOFs, where they act as spillover receptors [67].

The mechanism of spillover could be illustrated by an example of hydrogen spillover adsorbing on porous carbon materials (PCM), resulting in improved hydrogen adsorption interaction. The mechanism of spillover in PCM is traced by the steps as follows: a) chemisorption on the surface; b) dissociation of hydrogen on the metal catalyst; c) migration of hydrogen from the metal catalyst to the PCM surface; and d) diffusion and desorption at the substrate surface [69]. Many considerations on spillover mechanisms should be highlighted. The first is hydrogen chemisorption, which should be overcome during the spillover of hydrogen via the nucleation phase, where the chemisorption of hydrogen on the catalyst requires 0.8–1.8 eV of energy. Secondly, the adsorption of hydrogen needs a vast adsorption capacity in the catalyst. Next, for the migration of hydrogen atoms to the substrate, 2.45–3.2 eV of barrier energy must be overcome, which could be mitigated by hole doping. Finally, the difficulty of hydrogen atom diffusion in the substrate is caused by the high strength of the C-H bond [67].

3.2.1.   MOFs outpace over other candidates

A crucial benefit of MOFs is to provide a high surface area and pore volume, leading to the highest achievable H_2 uptake. These high surface area and pore volume characteristics are rarely found in other competing materials, such as metal hydrides whose surface area could not exceed 10 m^2/g in best scenarios, while MOFs materials have recorded higher than 7000 m^2/g and 5 cm^3/g as a surface area and pore volume, respectively. For instance, according to Table 10, NU-100 based copper shows a gravimetric weight of around 16.4 wt% at -196°C/70 bar with a surface area of 6140 m^2/g while MgH$_2$/Ni/GNS material has recorded a 6.6 wt% at high temperature of 300°C [70]. It is obvious that metal hydrides have limitations, such as high temperatures and fast reactions with moisture. Also, the need for heavy tanks for storing hydrogen in metal hydride materials is limiting its applications. Another advantage on MOFs side as a better selection for hydrogen storage is the feature of unsaturated open metal sites. This advantageous property will increase the binding affinities between hydrogen and

framework. In addition, the spillover technique is well-proven to increase hydrogen uptake in MOFs materials. This technique increases the

3.2.2. MOFs applicability at ambient temperatures

Numerous efforts have been made to achieve an acceptable hydrogen storage uptake at ambient conditions in the last decade. Farha *et al.* [71] have been successful in obtaining tremendous progress for hydrogen storage uptake by designing new MOFs operating under practical conditions (233 K/100 bar to 296 K/5 bar). NU-2100 is one of the promising MOFs for hydrogen storage capacity due to its high volumetric uptake, 10.4 g/L at ambient temperature and resistance to moisture. The NU-2100 was initially introduced and known as Cu^I-MFU-4*l* with open Cu sites, which it was shown a strong π-interaction of hydrogen with copper sites and has a high isosteric heat of adsorption (32 kJ/mol) [64,74,75]. However, Cu

isosteric heat of adsorption, allowing higher interaction of hydrogen.

(I) centers in Cu^I-MFU- 4*l* are swiftly oxidized to Cu(II) upon air exposure due to air sensitivity. Addressing this defect led to the design of air-stable MOFs called NU-2100. This NU-2100 is based on Cu(I)-MOF with a very high isosteric heat of adsorption (32 ± 2 kJ/mol), indicating strong interactions of the MOF with hydrogen. The key solution beyond the enhancement of H$_2$-MOF interaction is through designing MOFs with unsaturated open metal sites that act as strong Lewis acids, allowing strong interactions with guest molecules such as hydrogen, revealing high isosteric heat of adsorption [74-76]. Table 10 generally compares metal hydrides and MOFs for hydrogen storage in terms of performance, capacity, and cost.

Table 10. Advantages and limitations of metal-organic frameworks (MOFs) and metal hydrides for hydrogen storage [70,71,77].

Property	Metal-Organic Frameworks (MOFs)	Metal Hydrides
Advantages	• High crystallinity • Tunable structure • High surface area and pore volume • Rich open metal sites • Designability	• Low-energy activation • High H$_2$ uptake • Materials availability • Room of improvements
Disadvantages	• Low H$_2$ uptake • Processability	• High-temperature discharge • Slow kinetics • Low cyclability • High cost of materials

Selected Materials Performance (Gravimetric & Volumetric capacities)	• NU-100-Cu
	  -196°C/70bar
	  16.4 wt%
	
	• NU-2100-Cu
	  -40.15 °C /100 bar to 22.8 °C /5 bar
	  10.4 g/L
	
	• Ni$_2$(m-dobdc)
	  25°C/100bar
	  1.9 wt%, 11.9 g/L
		• MgH$_2$/Ni/GNS 5%
		  300°C
		  6.6 wt%
		
		• MgH$_2$-Fe 5%
		  20°C/15bar
		  5.5 wt%

4. Conclusions and Recommendations

While metal hydrides provide a promising approach to hydrogen storage and solve some of the existing problems regarding fossil fuels and environmental issues, their adoption is

obstructed by several factors. One of the major challenges encountered in adopting metal hydrides is sluggish hydrogenation and dehydrogenation kinetics and thermodynamic

stability [25]. Metal hydrides require severe pressures and temperatures to achieve optimum storage capacity, which is difficult to achieve and maintain. Consequently, this makes it difficult to achieve performance targets for hydrogen storage in metal hydrides. Another challenge is the limited capacity of metal hydrides to store hydrogen [78]. While metal hydrides can store large amounts of hydrogen, the storage capacity is still much lower with regard to the cost-benefit approach. This limits the practical application of metal hydrides in large-scale hydrogen storage projects, especially during their transportation. In addition to the aforementioned challenges, metal hydrides also face cost and durability issues. The high cost of metal hydrides is a major barrier to their commercialization, and the high cost of raw materials and manufacturing processes makes them uncompetitive with other hydrogen storage methods. While significant effort has been made to achieve the optimum hydrogen storage capacity of metal hydrides and address the arising challenges, there is still no specific approach to meet all the practical, technological, and financial applications of metal hydrides [78]. Recent developments in material science made it possible to develop various approaches to address the above challenges. When it comes to the material design, it was established that transition metal catalysts and carbon additives are thus used to improve the hydrogenation kinetics of metal hydrides. Nanoconfinement techniques are also being implemented to enhance thermodynamic stabilization and improve reaction enthalpy.

On the other hand, metal-organic frameworks (MOFs) are specified as one of the competitive candidates for hydrogen storage, offering exceptional properties in terms of crystallinity and tunability of structures. In addition, MOFs have some advantages over other candidates for hydrogen storage capacity, such as high surface area, high pore volume, and rich open metal sites. However, these properties offered via MOFs have a limitation of low hydrogen uptake at ambient temperature for hydrogen storage. This drawback is overcome by introducing unsaturated open metal sites when designing MOFs to comply with the US DOE recommendations for optimum characteristics of hydrogen storage capacity. Also, processing MOF materials on a large scale is considered another challenge, especially when considering a cost-effective shift from laboratory scale to industrial scale.

In conclusion, the results presented in this research provide a distinct advantage to MOFs when compared to other selected materials, particularly metal hydrides, as demonstrated in this comparative study. The primary objective should be to optimize or sustain the increased gravimetric uptake under ambient circumstances, replicating real-world scenarios for hydrogen storage in automobile implementations. Besides, materials cost, scalability, transportation and safety issues are all significant factors that should be considered when designing and operating hydrogen storage. The aforementioned factors contribute to the preference for MOFs materials in terms of their designability, cost-effectiveness, ease of transportation and safety. Clearly, the information provided in this review article shows that copper-based MOFs with open metal sites are promising materials for hydrogen storage applications in real-life conditions.

Future research into the subject is required to optimize metal hydrides and MOFs to operate better under normal operating conditions to meet the recommendations of the United States Department of Energy. Researchers are strongly encouraged to continue down the road toward creating MOFs with unsaturated open metal sites for working at room temperature. To enhance hydrogen storage capacity, future research should concentrate on active Cu(I) sites and methods of increasing their density. This suggestion is made after careful consideration and in an effort to pool resources in order to meet specific DOE standards.

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AVTOMOBİL TEXNİKASINDA HİDROGENİN SAXLANMASI ÜÇÜN METAL HİDRİDLƏR VƏ METAL-ÜZVİ KARKASLAR: İCMAL

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Xülasə: Hidrogen cəlbedici avtomobil yanacağıdır, çünki o, karbonsuzdur, xeyli miqdarda suda mövcuddur və müstəsna kütlə və enerji sıxlığına malikdir. Ətraf mühit şəraitində hidrogenin tez və dönən olaraq saxlanması üçün ucuz və asan materialların yaradılması son illərdə aktual mövzuya çevrilmişdir. Bu məqsədlə, metal hidridlər və metal-üzvi karkaslar kimi müxtəlif material əsaslı sistemlər təqdim edilmişdir. Bu məqalədə hidrogenin saxlanma həcmi, kinetikası və davamlılığı baxımından materiallar müzakirə və müqayisə edilir. Maqnezium hidridləri, kompleks hidridlər və intermetal hidridlər kimi müxtəlif növ metal hidridlər nəzərə alınır. Bundan əlavə, sink və mis əsaslı perspektivli metal-üzvi karkaslar qeyd olunur. Nəticələr göstərir ki, metal hidridləri əldə etmək və saxlamaq çətin olan optimal saxlama qabiliyyətinə nail olmaq üçün yüksək təzyiq və temperatur tələb olunur. Digər tərəfdən, metal-üzvi karkasların böyük səth sahəsi, böyük məsamə həcmi və həmçinin çoxlu sayda açıq metal sahələri kimi bəzi üstünlükləri var. Bununla belə, metal-üzvi karkasların təklif etdiyi bu xüsusiyyətlər ətraf mühit temperaturunda hidrogenin saxlanması üçün aşağı udulma ilə məhdudlaşır. Bu məhdudiyyət doymamış metal bölgələri olan metal-üzvi karkaslar yaratmaqla aradan qaldırılır.

Açar sözlər: yaşıl enerji; metal-üzvi karkaslar; metal hidrid; qaz anbarı; hidrogenin udulması

ГИДРИДЫ МЕТАЛЛОВ И МЕТАЛЛООРГАНИЧЕСКИЕ КАРКАСЫ ДЛЯ ХРАНЕНИЯ ВОДОРОДА В АВТОМОБИЛЬНОЙ ТЕХНИКЕ: ОБЗОР

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Аннотация: Водород является привлекательным автомобильным топливом, поскольку он не содержит углерода, в изобилии доступен из воды и обладает исключительной плотностью массы и энергии. Хранение водорода стало модной темой в последние годы благодаря возможности создавать недорогие и легкие материалы, которые могут обратимо и быстро хранить водород при условиях окружающей среды. Были внедрены различные системы на основе материалов, такие как гидриды металлов и металлорганические каркасы (MOFs). В этой статье обсуждаются и сравниваются материалы с точки зрения емкости хранения водорода, кинетики и жизнеспособности. Рассмотрены различные типы гидридов металлов, такие как гидриды магния, комплексные гидриды и гидриды интерметаллических соединений. Кроме того, упоминаются перспективные материалы MOFs, такие как MOFs на основе цинка и меди. В статье также сравниваются материалы с точки зрения стоимости хранения, что редко обсуждается в литературе. Результаты показывают, что гидриды металлов требуют высоких давлений и температур для достижения оптимальной емкости хранения, которую трудно получить и поддерживать. С другой стороны, MOFs имеют некоторые преимущества, такие как большая площадь поверхности, большой объем пор, а также большое количество открытых металлических участков. Однако эти свойства, предлагаемые с помощью MOFs, имеют ограничение в виде низкого поглощения водорода при температуре окружающей среды для хранения водорода. Это ограничение преодолевается путем создания MOFs с ненасыщенными открытыми металлическими участками.

Ключевые слова: зеленая энергетика; металлоорганические каркасы; гидрид металла; хранилище газа; поглощение водорода