Proceedings of 8th International Conference on Mechanical, Industrial and Energy Engineering 2024
02-04 January, 2025, Khulna, BANGLADESH

SciEn Conference Series: Engineering Vol. 3, 2025, pp 153-158 https://doi.org/10.38032/scse.2025.3.38

Strategies for Improved Efficiency of Hydrogen Storage in Metal-Organic Frameworks: A Comprehensive Review

Ahmadullah Hridoy, Rafid Bin Siddique, Md. Al-Riad Tonmoy, Md. Hasan Mahmud, A. K. M. Ahsanul Habib*

Department of Materials Science & Engineering, Rajshahi University of Engineering & Technology, Rajshahi-6204, Bangladesh.

ABSTRACT

Hydrogen energy has always been considered the cleanest and most sustainable means of energy supply technology, which is important for the energy portfolio of our civilization in the foreseeable future. However, typical storage systems have several drawbacks, such as the demanding conditions of high pressure and cryogenic temperature, which hinder their usage and efficacy. Metal-Organic Frameworks (MOFs) are a category of advanced materials characterized by their extensive surface area and adjustable pore architectures, which facilitate the storage of hydrogen at extremely high pressure and low temperatures. Despite all of these benefits, the weak physisorption of hydrogen under realistic conditions and rarely meeting up the condition of up taking hydrogen at room temperature nevertheless pose a significant obstacle to the usage of MOFs in energy storage devices. Some strategies used to improve MOFs' hydrogen sorption efficiency by modifications are covered in this paper. The main strategies are guest atom modification, the process which involves the use of foreign atoms which are inserted in the MOF pores to activate the unsaturated metal sites whereas metal doping utilizes d-block metals via ball milling to increase surface area and adsorption capacity. In particular, catalyst introduction causes the addition of metal nanoparticles so as to enhance hydrogen adsorption via spillover mechanisms, particularly at elevated temperatures. Additionally, MOF hybridization combines MOFs with materials like graphene oxide or zeolite, leveraging synergistic effects like optimizing pore size, enhancing microporosity, etc. to improve hydrogen binding energy. This review article focuses on the fundamental tactics that might enhance hydrogen storage qualities, enabling its use as a fuel source. Additionally, it explores potential avenues for further expansion to satisfy the growing energy requirements.

Keywords: Hydrogen energy, Hydrogen storage, Porous materials, Metal organic frameworks (MOFs), Modified MOFs.

1. Introduction

The energy demand is increasing everyday as the global population is increasing and energy consumption by them is also increasing to meet their modern lifestyle. Presently all of this energy demand is dependent on fossil fuels, but burning them causes serious environmental pollution. So, keeping climate change in mind, the biggest challenge is to develop a sustainable green energy source. Hydrogen can be a great alternative to green energy sources as it's renewable, eco-friendly, and has the potential to be a socially and economically sustainable fuel [1, 2]. There are some technical problems must need to be overcome before the hydrogen economy becomes a reality. A sustainable hydrogen storage system is one of them and the most challenging one. Storing hydrogen in a gaseous and liquid state requires very high pressure or extremely low pressure. However, when hydrogen gas is adsorbed onto suitable materials, it can achieve much higher storage densities compared to its bulk gas state [3, 4]. Using the right materials in storage tanks has the potential to increase storage density through chemisorption or physisorption. Metal-organic frameworks (MOFs) are nanoporous materials consisting of metal centers interconnected by organic ligands. In recent years, MOFs have garnered significant interest in hydrogen storage due to their exceptional characteristics. Fig. 1 presents a comprehensive description of hydrogen storage inside MOFs. [5].

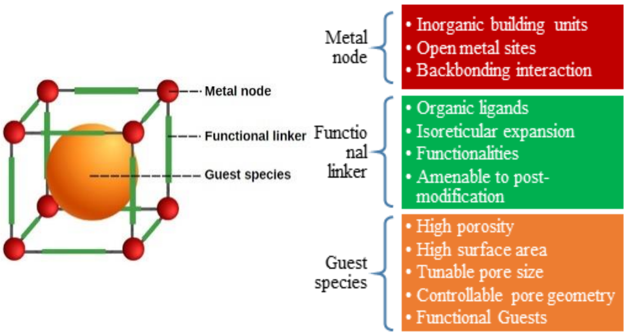

Fig. 1. An overview of the hydrogen storage in MOFs [5].

The majority of practical uses of MOFs rely on their specialized interactions with small molecules, where surface area and binding strength to metal centers are critical elements governing molecule absorption. At 77 K, MOFs have strong gravimetric hydrogen capabilities, and some of them have surpassed the Department of Energy (DOE) objective. Since MOFs have a lower hydrogen heat of enthalpy than fossil fuels, their storage capacity is lower at ambient temperatures, and their storage systems are heavier [6]. This review article is focused on the impact of adding guest atoms/species on the crystal structure and how the presence of catalysts affects the spillover mechanism. Metal ions form a robust connection with MOFs through induced

---

* Corresponding Author Email Address: alriadtonmoy@gmail.com

dipole moments, resulting in an enhanced rate of hydrogen absorption while maintaining feasible temperature and pressure conditions. It is believed that the addition of metal doping alters the chemical characteristics and enhances the capacity to adsorb hydrogen more efficiently. The inclusion of platinum-functionalized multi-walled carbon nanotubes (pt-MWCNTs) into MOF-5 results in the formation of a hybrid MOF. This hybrid MOF has improved surface area and pore volume, resulting in a greater total capacity for hydrogen storage.

2. Modification of guest atom

Guest atoms/species are the molecules that are introduced to the pores of MOFs but that are not part of the main structure. Guest atoms mainly follow two mechanisms to occupy the interstitial site; physisorption and chemisorption [7]. Physisorption method uses van der Waals forces to create the attraction between the MOF structure and guest atoms [8]. Chemisorption is stronger than physisorption. Metal sites within the MOF structure and guest atoms create chemical bonds between them. Ionic bonds are created when ions with opposite charges are drawn to one another, while covalent connections are created when electrons are shared [9]. Guest atoms/species have some important roles in storing hydrogen. Metal atoms or clusters (small groups of metal atoms) can be good guest atoms/species. These types of guest atoms can offer extra adsorption sites for H_2 molecules because of their ability to interact with H_2 molecules and increase the total storage capacity [10]. Again, polar molecules like metal ions create a very strong bond with the MOF by induced dipole moments. This leads to a higher rate of hydrogen uptake by maintaining the practical temperature and pressure (1 bar and 77 K). This is known as the polarization effect. Guest species help the MOF structure by preventing pores collapse. This is very important for the storage to stand without any changes after multiple cycles of adsorption and desorption [11].

Many unsaturated metal sites may be gained by introducing or changing the guest atoms into the MOF structure [12]. *Botas et al.* [13] replaced Zn in MOF-5 with Co (a cubic-shaped MOF; Formula: $Zn_4O(BDC)_3$) and prepared two samples namely Co8-MOF-5 ($Zn_{3.68}Co_{0.32}O(BDC)_3(DEF)_{0.75}$) and Co21-MOF-5 ($Zn_{3.16}Co_{0.84}O(BDC)_3(DEF)_{0.47}$) (BDC = benzene-1,4-dicarboxylate; DEF = diethylformamide). They found that Co21-MOF-5 had shown the highest hydrogen uptake and pristine MOF-5 did the lowest at 77K and 10 bar pressure. The presence of the active site of Co increased the surface area of the total cluster which led to the variation of this result. The differences were 7.4% to each other [13, 14]. However, the differences in H_2 adsorption between MOF-5 and Co-MOF-5 were nearly negligible at low pressure (<1 bar). Conversely, at higher pressures, Co-MOF-5's H_2 adsorption was significantly farther away than that of the parent MOF-5. The increase in pressure of the system would provide an extra driving force that allows for more hydrogen molecules to interact with MOF structures, this led to the adsorption capacities being increased [14]. Again, *Botas et al.* [13] carried out another experiment to investigate how the Zn/Co ratio affected the behavior of H_2 adsorption in MOF-74 ($Zn_2(C_8H_2O_6)(DMF)_2(H_2O)_2$) (DMF = N, N-dimethylformamide). They had analyzed $Zn_{1.72}Co_{0.28}(DHBDC)(DMF)_{0.1}$ (DHBDC = Dihydroxy-1,4-benzenedicarboxylate) (denoted Co14-MOF-74), $Zn_{0.78}Co_{1.22}(DHBDC)(DMF)_{0.1}$ (Co61-MOF-74), and $Co_2(DHBDC)(DMF)_{0.09}$ (Co100-MOF-74) and claimed that all the Co-containing MOF-74 is far more advanced than the parent Co-free MOF-74 for increased H_2 adsorption. As the amount of Co increased, so did the capacity of H_2 storage. The results of their investigation showed that the values for Co61-MOF-74, Co14-MOF-74, and Co100-MOF-74 were 26, 43, and 50% greater than those for MOF-74 [15]. For MOF-5 and MOF-74, the impact of the Zn/Co ratio on hydrogen adsorption was compared in Fig. 2. MOF-5 was shown to have higher capacity than MOF-74 at 10 bar pressure. Nevertheless, the exposed metal sites in MOF-74 materials altered the overall scenario below 1 bar. For Co14-MOF-74 compared to Co21-MOF-5 at 1 bar, the presence of exposed metal centers increased the H_2 adsorption capacity by up to 36% [16].

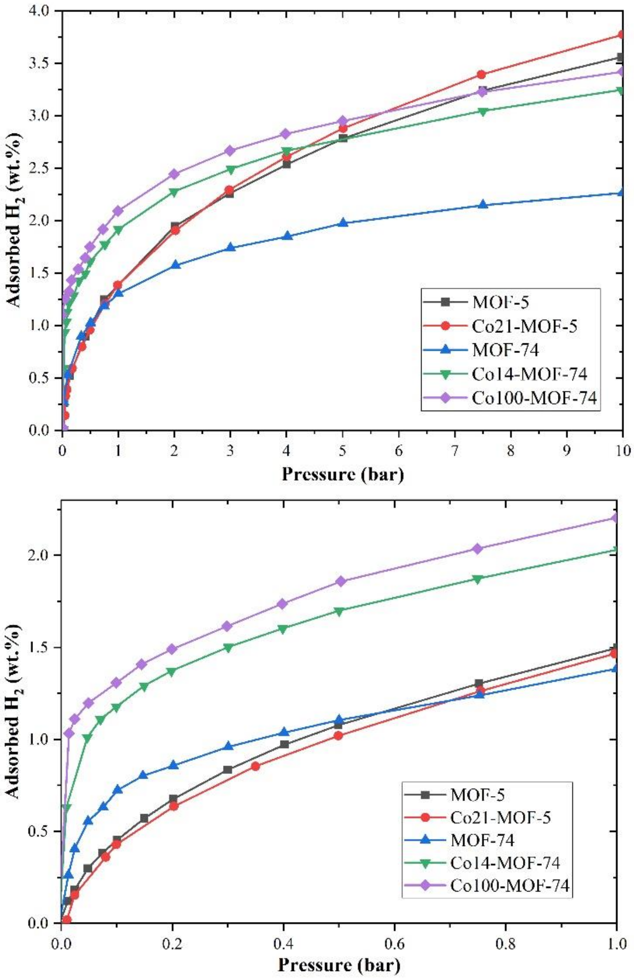

Fig. 2. At 77 K, MOF-74 and MOF-5 hydrogen adsorption isotherms are 10 bar (top) and 1 bar (bottom) [14, 15].

Dinca et al. [17] used some selected cations (Li^+, Cu^+, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}) instead of Mn^{2+} ions in $Mn_3[(Mn_4CI)_3(BTT)_8(CH_3OH)_{10}]_2$ (BTT = 1,3,5-benzenetristetrazolate). These MOFs demonstrated a significant H_2 storage capacity at 1.2 bar and 77 K, ranging from 2 to 2.29 wt.% [14, 17]. Almost all MOFs behave the same as we discussed increasing the hydrogen uptake by introducing or changing the guest atoms. Some other pieces of information are collected from different research papers and attached in Table 1.

Table 1 Variation of H_2 uptake in different MOF structures with the changes of guest species.

MOF name	Guest species	Temperature & Pressure	H_2 Uptake (wt %)	Ref.
DO-MOF	Parent	77 K & 1 bar	1.23	[18]
	Li		1.32	
MOF-74	Mg	77 K & 1 bar	2.2	
		77 K & 100 bar	4.9	
MIL-53	Al	77 K & 1 bar	3.8	[19]
	Cr		3.1	
CPO-27	Ni	77 K & 70 bar	1.8	[19, 20]
		298 K & 65 bar	<0.3	

3. Metal doping

Recently, different methods have been developed to improve the hydrogen storage capacity of MOFs and one of these methods involves metal doping [21, 22]. A variety of metals have been incorporated into microporous MOFs through doping [21]. Researchers have introduced various types of metals, such as platinum (Pt), palladium (Pd), ruthenium (Ru), and nickel (Ni) into MOFs to increase storage capacity [23, 24]. Various techniques have been employed for doping metals into MOFs, with incipient wetness and ball milling being the most common methods [21]. The process of metal doping is thought to change the porous materials' chemical properties, increasing their ability to adsorb hydrogen. Metal doping typically utilizes the large number of pores of MOFs to fulfill them with metal ions which is a big advantage for MOFs to bind H_2 by increasing binding energy [25].

Reardon et al. [25] found that Li^+ doping captures H_2 in MOFs with In(III) centers and tetracarboxylic ligands, comparing doped NOTT-201 and undoped NOTT-200 (NOTT = Nottingham) of MOFs series. As a result of doping, the adsorption enthalpy in NOTT-201 increased by 1kj/mol (reaching 10.1kj/mol at zero surface coverage) compared to NOTT-200 [25]. It has been shown that in MOFs, the quantity of stored H_2 is approximately equal to their extensive surface area. The maximum H_2 absorption (reaching the isotherm plateau at 77K) in MOFs typically increases linearly with a specific surface area [26]. Also, *Mandal et al.* [26] observed that a notable enhancement in hydrogen storage capacity at near ambient temperatures (30°C) has been forecasted for Li-doped MOF-C30, achieving a gravimetric absorption of 6 wt.% at 100 bar [26].

Fig. 3 represents the theoretical enhancements in gravimetric capacity for different Li-doped MOFs compared to their undoped counterparts. Introducing Li atoms into the MOFs is thought to functionalize organic linkers and lead to a predicted gravimetric absorption of 4.5 wt.% at room temperature and 10 wt.% at 77k at 100 bar in the framework through the strategy of this Li-doping [12]. Furthermore, Li-doped MOFs showed elevated binding energies of 16.7 kJ/mol with hydrogen, leading to significant hydrogen uptake at ambient temperature [27].

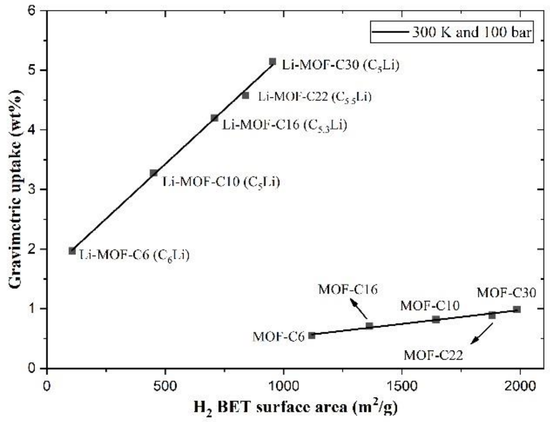

Fig. 3. MOF and Li-doped MOF gravimetric hydrogen uptake as a factor dependent on BET surface area at 300k and 100 bar [12].

Table 2 indicates that H_2 uptake at ambient temperature can be increased nearly times by doping MOFs with Li [27]. Because ab initio calculation presented that the energies involved in the interactions between hydrogen (H_2) molecules and Li-doped MOFs are three times higher compared to undoped MOFs [22]. On the other hand, *Sculley et al.* [28] found that the MOF doped with palladium nanoparticles (PdNPs) presented an improved capacity than the undoped MOF which is shown in Table 2 [28]. This is because doping nanoparticles in MOF impact H_2 storage by qualifying H_2 molecules to dissociate more effectively on the main MOFs' outer and inner surfaces [29].

Table 2 Hydrogen uptake results for Li-doped MOF-C30 and pure MOF-C30 at 300K and for PdNP-doped MOF and undoped MOF at 77K.

Materials	Pressure (bar)	H_2 uptake (wt.%)	Ref.
Li-MOF-C30	20	3.89	[27]
Pure MOF-C30	20	0.25	
Li-MOF-C30	50	4.56	
Pure MOF-C30	50	0.56	
Pd NP doped MOF	-	1.48	[28]

Also, *Sun et al.* [30] observed that the hydrogen storage capacity was observed to be favorable at 3.35 wt.% at 1.5 bar when the MOF of a $Zn_2(BDC)_2$dabco (dabco=1,4-diazabicyclo [2.2.2] octane) was doped with 5.0 wt.% Pt/Pd-loaded activated carbon (AC) [30]. On the other hand, *Lim et al.* [29] investigated the characteristics related to storing hydrogen of MIL-101 and MIL-53 (both chromium-based metal-organic frameworks) doped with 20 wt.% platinum (Pt/C). At 293K, the doped MIL-101 and doped MIL-53 exhibited hydrogen storage capacities of 0.75 wt.% and 0.43 wt.% respectively. These values are higher than those observed for their undoped counterparts [29]. Also, *Sculley et al.* [31] conducted computational studies to examine the impact of lithium doping on several MOFs, including IRMOF-14 (isoreticular metal-organic framework-14) [31]. *Froudakis et al.* [32] investigated through computational methods how the introduction of Li as a catalyst influences IRMOF-14 and the simulation result revealed that introducing a single Li atom per organic linker could enhance the storage capacity to 7.5 times that of undoped

IRMOF-14 [32]. Thus, metal doping in MOFs is a very promising method to improve the hydrogen storage capacity.

4. Introducing catalyst

The concept of hydrogen storage in porous materials utilizing the ‘spillover’ mechanism has been proposed and assessed [24, 28]. One of the most promising methods to increase hydrogen storage capacity in MOFs is the spillover mechanism [28, 30].

Hydrogen spillover is typically described as the diffusion of separated atoms from a metal surface to the surface of supporting materials [31]. This process generally involves using metal catalysts such as Pd, Pt, or Ni which facilitates hydrogen dissociation, generating atomic hydrogen [24]. Also, hydrogen spillover in MOFs is possible by incorporating metal nanoparticles [25, 30]. *Xiao et al.* [33] investigated that hydrogen spillover technology enhances the hydrogen storage capacity of MOFs at elevated temperatures [33]. The hydrogen spillover mechanism involves the adsorption of dihydrogen on a metal catalyst when it dissociates into hydrogen atoms that are subsequently transported to various active sites on the MOF that normally would not adsorb hydrogen at higher temperatures [33].

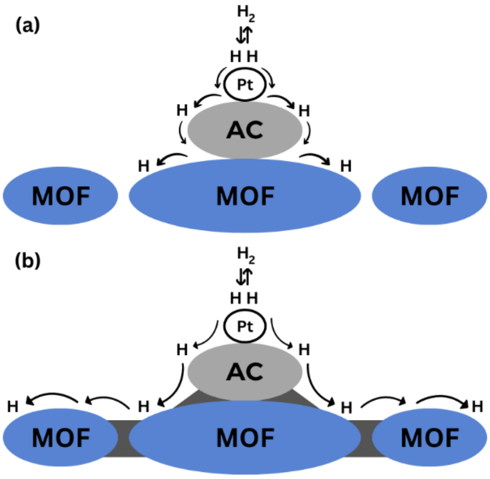

Fig. 4. Assumed mechanism of hydrogen spillover on MOF as receptor: (a) spillover is limited without bridge and (b) bridge facilities both primary and secondary spillover [33].

Fig. 4 illustrates the proposed adsorption mechanism of hydrogen spillover on MOFs [33]. Which is the ‘secondary spillover’ of H_2 onto the MOF surface that necessitates close contact between the involved materials due to the energy dynamics. Through a bridge-building method, hydrogen dissociates at the catalyst and subsequently diffuses onto the MOF receptor with the assistance of a carbon bridge [25].

Lim et al. [29] found that modifying porous materials with metal-supported catalysts via a carbon bridge significantly enhanced their hydrogen storage capacity [29]. *Mandal et al.* [26] found that hydrogen absorption increases eightfold in MOF-5 and IRMOF-8 (isoreticular metal-organic framework-8) using the spillover method [26]. This significant improvement was credited to the secondary spillover of hydrogen atoms from a platinum/activated carbon (Pt/AC) catalyst to the surface of the MOFs within a composite system [26]. *Zhao et al.* [18] found that using a 10wt.% Pt/AC catalyst (with 5 wt.% Pt on activated carbon) for hydrogen dissociation, the hydrogen storage capacity of isorecticular metal-organic frameworks-8 (IRMOF-8) significantly increased. This improvement, as shown in Table 3, highlights a remarkable advancement in storage performance. In comparison under the same conditions, the unmodified IRMOF-8 showed less hydrogen storage capacity from the alone Pt/AC catalyst [18].

Table 3 Hydrogen storage capacity of IRMOF-8 and Pt/AC catalyst.

Materials	H_2 storage capacity (wt.%)	Temperature (k)	Pressure (bar)	Ref.
IRMOf-8 (with 10 wt.% Pt/AC)	1.8	298	100	[18, 23]
Unmodified IRMOF-8	0.5	298	100	[18]
Pt/AC catalyst embedded MOF	1.0	298	100	[18, 23]

5. Hybridization of MOF

Hybrid MOF is one kind of porous crystalline material. Hybrid MOF is formed by two different components. One is the MOF structure and the other is hybridizing material. Organic polymers, nanoparticles, small molecules, etc. can be used as hybridizing materials. Hybrid MOF can be formed by adding the hybridizing materials at the time of synthesis of the main MOF structure (in-situ process) or introducing the hybridizing materials after the formation of the main MOF structure (post-synthetic process) [34].

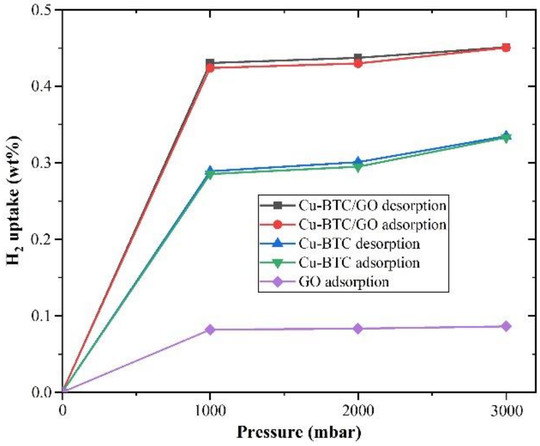

Fig. 5. H_2 adsorption isotherms of GO, Cu-BTC/GO, and Cu-BTC at 298 K, as well as H_2 desorption isotherm of Cu-BTC/GO and Cu-BTC [35].

Hybrid MOFs offer several advantages that surpass the advantages of conventional MOFs. *Karanikolos et al.* [35] introduced graphene oxide (GO) into the Cu-BTC (BTC = benzene-1,3,5-tricarboxylate) MOF and analyzed the performances of Cu-BTC/GO (hybrid), Cu-BTC (parent), and pure GO by gravimetric adsorption. The H_2 adsorption is shown in Fig. 5 at up to 3 bar and 298 K. For the GO, the H_2 storage capacity at 298 K is 0.039 and 0.044 wt % at 1and 3 bar [35]. The parent Cu-BTC exhibits an H_2 uptake of 0.29 and 0.35 wt.% at 1 and 3 bar, respectively, as illustrated in Fig. 5. Additionally, the uptake rate for the Cu-BTC/GO hybrid storage is significantly higher than that of Cu-BTC and GO, with increments of 59 and 40% at 1 and 3 bar, respectively. The enhanced H_2 uptake at hybrid MOF as opposed to parent MOF may be due to the increased surface area and more micropores at the interface.

Yang et al. [36] introduced Pt-MWCNT into the MOF-5 to create the Pt-MWCNT@MOF-5 (denoted as Pt-MOFMC). At 298 K and 100 bar, they discovered that the Pt-MOFMC had a higher H_2 storage capacity (0.55 wt%) than both the parent MOF (0.3 wt%) and the pt-MWCNTs (0.2 wt%) [36]. The incorporation of Pt-MWCNTs into MOF-5 demonstrates that MWCNTs act as effective spillover receptors, significantly enhancing the hydrogen storage capacity of Pt-MOFMC. Almost the same type of process was done by *Musyoka et al.* [37]. Through an in-situ procedure, they added zeolite templated carbon (ZTC) to the Cr-based MOF (MIL-101). As predicted, they discovered that at 1 bar, MIL-101(Cr)/ZTC had significantly higher hydrogen uptake than both MIL-101(Cr) and ZTC (Fig. 6).

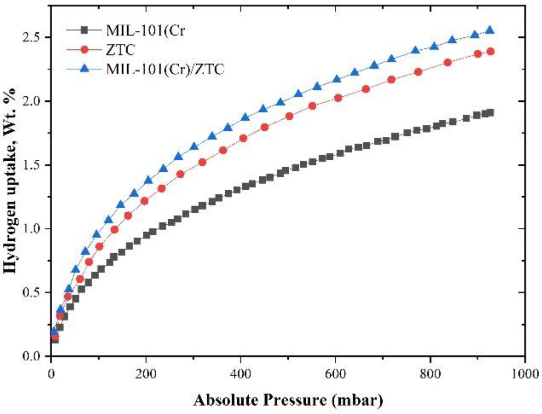

Fig. 6. MIL-101(Cr), ZTC, and MIL-101(Cr)/ZTC samples' H_2-sorption isotherms at 77 K [37].

The higher amount of H_2 uptake in hybrid MOF (MIL-101(Cr)/ZTC) was discussed in two parameters. A larger amount of H2 adsorption resulted from the ZTC's insertion into MIL-101(Cr) since it decreased the pore size of the MIL-101(Cr) and increased its surface area. Higher H_2 adsorption was primarily caused by the MOF's unsaturated metal sites being activated by the addition of carbon to the MOF structure. [38]. The summarized information of this section is presented in Table 4.

Table 4 Variations of H_2 uptake for introducing hybridizing materials into the MOF structure.

Hybrid MOF/ MOF/ Hybridizing materials	Temperature and pressure	H_2 uptake (wt.%)	Ref.
Cu-BTC/GO	298 K and 1 bar	0.46	[34]
Cu-BTC		0.29	
GO		0.039	
Pt-MWCNT@MOF-5	298 K and 100 bar	0.55	[39]
MOF-5		0.3	
Pt-MWCNT		0.2	
MIL-101(Cr)/ZTC	77 K and 1 bar	2.55	[37]
MIL-101(Cr)		1.91	
ZTC		2.39	

6. Future outlook

The hydrogen storage capacity of MOFs is significantly affected by variations in temperature and pressure. To increase the hydrogen storage capabilities of MOFs, it is essential to enhance factors that influence hydrogen adsorption, such as micropore volume, micropore width, isosteric heat of adsorption, and specific surface area. Researchers are particularly interested in modifying synthesis methods to achieve proper micropore distribution. As catalysts improve the kinetics of hydrogenation and dehydrogenation, there is a need to focus on investigating cost-effective solvents and catalysts except Pt. Experimental initiatives focused on discovering improved MOF adsorbents are increasingly being guided by high-throughput computational screening and data-driven forecasts that are effective under ambient conditions. Additionally, choosing open metal sites and organic linkers that optimize capacity, kinetics, and reversibility is a promising area of research. Ongoing studies explore using various catalysts, including doping and co-doping with different metal ions, to enhance hydrogen production efficiency while ensuring safety. Strategically utilizing the versatile nature of materials, serving as either physical adsorbents or catalytic/confining agents, is crucial for the advancement of sophisticated hydrogen storage systems.

7. Conclusion

The clean, efficient, and scalable nature of hydrogen energy has led to its widespread use in large-scale industrial production. Hydrogen storage technology, a key component of utilizing hydrogen energy, has recently gained significant attention as an important research area. This article investigates the impact of various modifications on hydrogen storage. Incorporating metal guest atoms can provide extra sites for the adsorption of H_2 molecules due to their interaction with hydrogen, thereby increasing overall storage capacity. Metal ions form strong bonds with MOFs, enhancing hydrogen uptake by maintaining practical temperature and pressure conditions. Metal doping in MOFs is also believed to improve hydrogen adsorption by utilizing a large number of pores, which increases binding energy. Metal catalysts like Pd, Pt, or Ni facilitate hydrogen dissociation, creating atomic hydrogen through the hydrogen spillover mechanism, where H_2 adsorbs on a metal catalyst and is then transported to various active sites. In hybrid MOFs, additional surface area and micropores at the interface likely contribute to increased H_2 uptake compared to parent MOFs. Among these modifications, MOF hybrids are particularly promising due to their ability to select materials with higher surface area, porosity, and stability. These insights are expected to guide future research in the field.

References

[1] Md. A.-R. Tonmoy, H. Mahmud, and A. K. M. Ahsanul Habib, "A Short Review on the Effects of Doping in TiO_2: A Potential Nano-photocatalyst for Hydrogen Production by Artificial Photosynthesis Process," in *2024 7th International Conference on Development in Renewable Energy Technology (ICDRET)*, IEEE, Mar. 2024, pp. 1–6.

[2] Y. Xu, Y. Deng, W. Liu, X. Zhao, J. Xu, and Z. Yuan, "Research progress of hydrogen energy and metal hydrogen storage materials," *Sustainable Energy Technologies and Assessments*, vol. 55, Feb. 2023.

[3] S. P. Shet, S. Shanmuga Priya, K. Sudhakar, and M. Tahir, “A review on current trends in potential use of metal-organic framework for hydrogen storage,” Mar. 23, 2021, *Elsevier Ltd.*

[4] A. K. M. A. Habib, A. N. Sakib, Z. T. Mona, M. M. H. Bhuiyan, P. Kazempoor, and Z. Siddique, “Hydrogen-Assisted Aging Applied to Storage and Sealing Materials: A Comprehensive Review,” *Materials*, vol. 16, no. 20, p. 6689, Oct. 2023.

[5] M. Hao and Z. Li, “Visible Light–Initiated Synergistic/Cascade Reactions over Metal–Organic Frameworks,” *Solar RRL*, vol. 5, no. 2, Feb. 2021.

[6] X. Gao *et al.*, “The role of transition metal doping in enhancing hydrogen storage capacity in porous carbon materials,” *Nano Energy*, vol. 118, Dec. 2023.

[7] M. Allendorf, R. Medishetty, and R. Fischer, “Guest molecules as a design element for metal–organic frameworks,” *MRS Bull*, vol. 41, pp. 865–869, Nov. 2016.

[8] S. Zuluaga, P. Canepa, K. Tan, Y. Chabal, and T. Thonhauser, “Study of van der Waals bonding and interactions in metal organic framework materials,” *J Phys Condens Matter*, vol. 26, p. 133002, Mar. 2014.

[9] P. Mercandelli and S. Racioppi, “CHEMICAL BONDING IN METAL-ORGANIC SYSTEMS: NATURE, STRUCTURES AND PROPERTIES,” Jan. 2018.

[10] K. Srinivasu, S. Ghosh, R. Das, S. Giri, and P. Chattaraj, “ChemInform Abstract: Theoretical Investigation of Hydrogen Adsorption in All-Metal Aromatic Clusters.,” *RSC Adv.*, vol. 2, pp. 2914–2922, Mar. 2012.

[11] Y. Cheng *et al.*, “Chemical Science modes of 2-D MOF nanosheets †,” pp. 4106–4113, 2024.

[12] P. Dietzel, R. Johnsen, R. Blom, and H. Fjellvåg, “Structural Changes and Coordinatively Unsaturated Metal Atoms on Dehydration of Honeycomb Analogous Microporous Metal–Organic Frameworks,” *Chemistry*, vol. 14, pp. 2389–2397, Feb. 2008.

[13] J. A. Botas, G. Calleja, M. Sánchez-Sánchez, and M. G. Orcajo, “Cobalt doping of the MOF-5 framework and its effect on gas-adsorption properties,” *Langmuir*, vol. 26, no. 8, pp. 5300–5303, 2010.

[14] H. W. Langmi, J. Ren, B. North, M. Mathe, and D. Bessarabov, “Hydrogen storage in metal-organic frameworks: A review,” *Electrochim Acta*, vol. 128, no. 2013, pp. 368–392, 2014.

[15] J. A. Botas, G. Calleja, M. Sánchez-Sánchez, and M. G. Orcajo, “Effect of Zn/Co ratio in MOF-74 type materials containing exposed metal sites on their hydrogen adsorption behaviour and on their band gap energy,” *Int J Hydrogen Energy*, vol. 36, no. 17, pp. 10834–10844, 2011.

[16] J. L. C. Rowsell and O. M. Yaghi, “Effects of functionalization, catenation, and variation of the metal oxide and organic linking units on the low-pressure hydrogen adsorption properties of metal-organic frameworks,” *J Am Chem Soc*, vol. 128, no. 4, pp. 1304–1315, 2006.

[17] M. Dincă and J. R. Long, “High-Enthalpy Hydrogen Adsorption in Cation-Exchanged Variants of the Microporous Metal−Organic Framework Mn3[(Mn4Cl)3(BTT)8(CH3OH)10]2,” *J Am Chem Soc*, vol. 129, no. 36, pp. 11172–11176, Sep. 2007.

[18] D. Zhao, X. Wang, L. Yue, Y. He, and B. Chen, “Porous metal-organic frameworks for hydrogen storage,” *Chemical Communications*, vol. 58, no. 79, pp. 11059–11078, 2022.

[19] B. Xiao and Q. Yuan, “Nanoporous metal organic framework materials for hydrogen storage,” *Particuology*, vol. 7, no. 2, pp. 129–140, 2009.

[20] P. D. C. Dietzel, B. Panella, M. Hirscher, R. Blom, and H. Fjellvåg, “Hydrogen adsorption in a nickel based coordination polymer with open metal sites in the cylindrical cavities of the desolvated framework,” *Chemical Communications*, no. 9, pp. 959–961, Feb. 2006.

[21] R. Zacharia and S. U. Rather, “Review of solid state hydrogen storage methods adopting different kinds of novel materials,” *J Nanomater*, vol. 2015, 2015.

[22] S. Niaz, T. Manzoor, and A. H. Pandith, “Hydrogen storage: Materials, methods and perspectives,” *Renewable and Sustainable Energy Reviews*, vol. 50, pp. 457–469, 2015.

[23] H. W. Langmi, J. Ren, B. North, M. Mathe, and D. Bessarabov, “Hydrogen storage in metal-organic frameworks: A review,” *Electrochim Acta*, vol. 128, no. 2013, pp. 368–392, 2014.

[24] J. Ren, N. M. Musyoka, H. W. Langmi, M. Mathe, and S. Liao, “Current research trends and perspectives on materials-based hydrogen storage solutions: A critical review,” *Int J Hydrogen Energy*, vol. 42, no. 1, pp. 289–311, 2017.

[25] H. Reardon, J. M. Hanlon, R. W. Hughes, A. Godula-Jopek, T. K. Mandal, and D. H. Gregory, “Emerging concepts in solid-state hydrogen storage: The role of nanomaterials design,” *Energy Environ Sci*, vol. 5, no. 3, pp. 5951–5979, 2012.

[26] T. K. Mandal and D. H. Gregory, “Hydrogen storage materials: Present scenarios and future directions,” *Annual Reports on the Progress of Chemistry - Section A*, vol. 105, pp. 21–54, 2009.

[27] Y. H. Hu and L. Zhang, “Hydrogen storage in metal-organic frameworks,” *Advanced Materials*, vol. 22, no. 20, pp. 117–130, 2010.

[28] J. Sculley, D. Yuan, and H. C. Zhou, “The current status of hydrogen storage in metal-organic frameworks - Updated,” *Energy Environ Sci*, vol. 4, no. 8, pp. 2721–2735, 2011.

[29] K. L. Lim, H. Kazemian, Z. Yaakob, and W. R. W. Daud, “Solid-state materials and methods for hydrogen storage: A critical review,” *Chem Eng Technol*, vol. 33, no. 2, pp. 213–226, 2010.

[30] Y. Sun *et al.*, “Hydrogen Storage in Metal-Organic Frameworks,” *J Inorg Organomet Polym Mater*, vol. 23, no. 2, pp. 270–285, 2013.

[31] J. Sculley, D. Yuan, and H. C. Zhou, “The current status of hydrogen storage in metal-organic frameworks - Updated,” *Energy Environ Sci*, vol. 4, no. 8, pp. 2721–2735, 2011.

[32] A. Mavrandonakis, E. Tylianakis, A. K. Stubos, and G. E. Froudakis, “Why Li doping in MOFs enhances H2 storage capacity? A multi-scale theoretical study,” *Journal of Physical Chemistry C*, vol. 112, no. 18, pp. 7290–7294, 2008.

[33] B. Xiao and Q. Yuan, “Nanoporous metal organic framework materials for hydrogen storage,” *Particuology*, vol. 7, no. 2, pp. 129–140, 2009.

[34] G. N. Karanikolos, A. M. Varghese, and K. S. K. Reddy, “An In-Situ-Grown Cu-BTC Metal−Organic Framework / Graphene Oxide Hybrid Adsorbent for Selective Hydrogen Storage at Ambient Temperature,” *Ind Eng Chem Res*, vol. 61, no. 18, pp. 6200–6213, 2022.

[35] G. N. Karanikolos, A. M. Varghese, and K. S. K. Reddy, “An In-Situ-Grown Cu-BTC Metal−Organic Framework / Graphene Oxide Hybrid Adsorbent for Selective Hydrogen Storage at Ambient Temperature,” *Ind Eng Chem Res*, vol. 61, no. 18, pp. 6200–6213, 2022.

[36] S. J. Yang, J. H. Cho, K. S. Nahm, and C. R. Park, “Enhanced hydrogen storage capacity of Pt-loaded CNT@MOF-5 hybrid composites,” *Int J Hydrogen Energy*, vol. 35, no. 23, pp. 13062–13067, 2010.

[37] N. M. Musyoka *et al.*, “Synthesis of a hybrid MIL-101(Cr)/ZTC composite for hydrogen storage applications,” *Research on Chemical Intermediates*, vol. 42, no. 6, pp. 5299–5307, 2016.

[38] P. B. Somayajulu Rallapalli, M. C. Raj, D. V Patil, K. P. Prasanth, R. S. Somani, and H. C. Bajaj, “Activated carbon@ MIL-101 (Cr): a potential metal-organic framework composite material for hydrogen storage,” *Int J Energy Res*, vol. 37, no. 7, pp. 746–753, 2013.

[39] B. Panella, M. Hirscher, H. Pütter, and U. Müller, “Hydrogen adsorption in metal–organic frameworks: Cu-MOFs and Zn-MOFs compared,” *Adv Funct Mater*, vol. 16, no. 4, pp. 520–524, 2006.