

Applications of Metal–Organic Frameworks (MOFs) in Hydrogen Storage: Mechanisms, Challenges, and Performance Enhancement Strategies

Jing Li*

School of Energy and Power Engineering, Xi'an Jiaotong University, 710000, Shaanxi China

Abstract. Hydrogen holds immense promise as a clean energy vector, but inadequate storage technologies limit its large-scale application. To address this, metal-organic frameworks (MOFs) have attracted substantial interest for solid-state storage, benefiting from their exceptional surface areas and highly tailorable structures. However, their performance at ambient temperature remains insufficient. This work reviews recent advances in the field of hydrogen storage using MOFs, with the aim of elucidating the relationship between structure and performance and providing guidance for targeted material design. Key factors affecting hydrogen storage and the major practical challenges are summarized and three critical material design dimensions are proposed in this work: optimizing the specific surface area and pore structure; selecting and rationally doping metal centers; and constructing multifunctional composite systems. The underlying mechanisms and enhancement effects of MOF-based hydrogen storage at low and room temperature are also systematically discussed. Notably, metal-ion doping can effectively increase the adsorption enthalpy of a material and is a key method for improving hydrogen storage performance at ambient temperature. Further research is still needed for future development, and combining different modification methods will be necessary. Ultimately, this will help MOFs move from lab research to real engineering use in hydrogen storage and transport.

1 Introduction

With the continued depletion of fossil fuels and increased environmental issues, it is imperative to develop energy sources which are safe, clean, and sustainable. As it has extremely high heating quality, Hydrogen is fully emitting upon burning; Hydrogen will be an intermediary substance moving toward decarbonized power network. But it's very volatile and flammable, so that makes storing and delivering much more difficult. Compared to traditional gas compression or Cryogenic liquefaction, solid-state containment has a better volumetric benefit and also much safer. Therefore, now it has become the main focus to make such highly effective hydrogen-absorbing super advanced solids.

* Corresponding author: li_jing105@stu.xjtu.edu.cn

Metal–organic frameworks (MOFs) — with their very high surface area, tunable porosity, and ease of solvothermal synthesis — are now regarded as promising solid-state hydrogen storage materials. They are crystalline porous structures composed of metal nodes and organic linkers. It is a kind of crystalline porous structure composed of both metal nodes and organic linkers Yaghi group first reported on the hydrogen storage in MOFs systematically back in 2003, and MOF-177, MIL-53, MIL-100 and MIL-101 are some examples of these. For instance, MIL-101 has big surface area and lots of open metal spots, it demonstrates high adsorption enthalpy and good structural stability at 77 K, [1] showing the focus is more on getting best overall grab, rather than just highest surface area.

Even if there are good low-temp properties of MOFs, they don't really work for hydrogen storage, because the interaction between H₂ and the framework is generally very weak. This is because they only bind very weakly to the molecule in general. To improve both how strongly hydrogen binds and how easily it moves through the material, researchers have explored different metal nodes, ligands, structures, and pore sizes [2]. It is challenging but necessary to understand microscopically how the material stores at room temperature or above

At the same time, this study examines the physical properties of hydrogen adsorption in MOFs, focusing on the factors that determine this process. Ultimately, three main strategies can be proposed to address these issues. By comparing the performance of different methods under various temperature conditions, this study elucidated the relationship between the molecular framework and the physical structure of MOFs, thereby laying the groundwork for the rational design of high-performance hydrogen storage materials.

2 Key factors influencing hydrogen storage in MOFs

The MOFs is a class of ordered crystalline materials formed by metal centers and organic ligands through coordination. This type of framework has a large surface area and a customized pore structure, which enables the gas H₂ to be effectively captured towards the interior through the effect of van der Waals force. However, due to the inherent limitations of these interactions, the hydrogen storage capacity of MOFs is largely determined by their framework structure and surface physicochemical properties. Key parameters such as specific surface area, pore size distribution, metal active sites, and framework stability all directly influence the final hydrogen storage performance. Therefore, the hydrogen absorption behavior of the MOF is determined by the complex combination of these structural features.

2.1 Pore size and surface area

Studies show that when the pore size is roughly equal with kinetic diameter of adsorbate, best interactions will be created among the adsorbate and every single surrounding pore walls to get maximum van der Waals force [3]. Hydrogen's ideal pore size then should be very near 2.89 Å which is its kinetic diameter [4]. If it's bigger, there will be voids in center, reducing volume packing. E.g., In MOF-5 there are spheres of 15 Å, much larger than the 2.89 Å diameter of H₂, so even at a monolayer there would be unoccupied porosity.

However, smaller pores do not necessarily lead to higher overall storage performance. The Hydrogen storage can be given in terms of the Gravimetric(wt%) or volumetric (kg-H₂ /m³). A substance with a higher molecular weight has a greater density, while a smaller substance has a lower density. Therefore, reducing the porosity is necessary to obtain the volume capacity, but increasing the capacity by the percentage of mass. Hence there must be a balance between pore size framework density and how much is stored.

Specific surface area is directly related to hydrogen adsorption. This is because a larger specific surface area provides more available adsorption sites. A research team led by Antonio investigated the adsorption capacities of typical porous materials—including HKUST-1, ZIFs, IRMOF, UiO-66/67, and MIL-101—at a pressure of 18 MPa and a temperature of 77 K. They found that as temperature decreases and pressure increases, the amount of water stored is proportional to the square root of the specific surface area, which means a surface area of 500 square meters can store approximately 1% more hydrogen. However, an excessively large surface area may cause pore expansion, thereby reducing the efficiency of hydrogen storage [5].

2.2 Open metal sites

Adding some open metal sites makes MOFs much better at storing hydrogen. Exposure of some unsaturated metal center, it is bind H₂ molecule strongly, so greatly enhanced adsorption in general but especially in physisorption. And open metal site can make the isosteric enthalpy of adsorption bigger, so the thermodynamic driving power becomes higher which could improve stability and efficiency of storing hydrogen. Moreover, in terms of the open metal site, a regular order is better than a disorder. Wang et al. prepared PCN -12 with ordered open metal sites and found it had an H₂ uptake of 3.05 wt% at 77 K, 1bar as opposed to unstructured PCN -12' which exhibited only 2.40 wt%. This result demonstrated the effect of site ordering on storage performance [6]. Therefore, engineering and regulating more exposed metal sites can provide more storage sites and better reversible performance, which is an effective way to improve hydrogen storage in MOFs.

2.3 Guest metal species

In MOF-based hydrogen storage systems, guest metal ions are introduced by partially replacing the original metal nodes or by exchanging charge-balancing cations. They can tune hydrogen storage performance by unsaturated coordination sites, altering the electrostatic field of the framework, or adjusting the pore structure. Botas et al. pointed that replacing 10% of the Zn in MOF-5 with Co under conditions of 77 K and 10 bar increases the H₂ adsorption capacity by 7.4% [7], when the Co content in MOF-74 reaches 100%, its capacity increases by 50% compared to the original ZnO-MOF. This is because Co has a strong binding affinity for H₂ and compensates for the low porosity of the material. The effect of guest ions depends on their type, size, and loading: they may enhance adsorption by increasing active sites or electrostatic interactions, but they may also reduce performance by occupying pore channels. Thus, guest metal species constitute an important tunable variable for optimizing hydrogen storage in MOFs.

2.4 Isosteric heat of adsorption

Isothermal adsorption enthalpy reflects the binding strength between hydrogen molecules and MOF structures, and affects low-pressure hydrogen storage performance. High adsorption enthalpy strengthens low-pressure hydrogen storage but may impede release, and the ideal range for room-temperature storage is 15–25 kJ/mol. In most MOFs, hydrogen uptake rises with adsorption enthalpy, especially in metal-containing samples at high saturation. Himsl et al. showed that Li⁺ in MIL-53(Al) raised its enthalpy from 4.4–5.8 to 6.4–11.6 kJ/mol [8], and aromatic rings or polar B–N bonds further enhance interaction energy. Most pristine MOFs show adsorption enthalpy below 12 kJ/mol, still below the 25 kJ/mol required, so their room-temperature capacity is generally below 1 wt% [9].

3 Challenges of MOFs in hydrogen storage

Although MOF has a large area and a controllable porous structure, their performance at room temperature is poor. For most MOF materials the adsorption enthalpy ranges from 4 to 12 kJ/mol, which is far below the approximately 15–25 kJ/mol required for efficient adsorption at room temperature, furthermore, their adsorption capacity (<1 wt%) is far below the 5.5 wt% target set by the OBS [10].

MOFs also have very little adaptation between pressures. Small-pore MOFs do fine at low pressure but have insufficient pore volume for the high-pressure regime, whereas large-pore, high-surface-area MOFs are favored by the high-pressure adsorption process yet suffer from weak interaction at low pressures due to pore size $>6\text{\AA}$, and there are some MOFs only reach 1.79 wt% at 77K/1bar [11].

Besides, It is challenging to achieve both structural stability and reactivity in MOFs. Some MOFs are prone to framework collapse following functionalization or high-temperature activation.

Finally, MOFs still face serious practical limitations. Many MOFs show poor water and thermal stability and are hence hard to apply in working situations. The mechanism of hydrogen spillover remains controversial, and excessive metal nanoparticles may block the internal pores. In addition, high-performance MOFs can be very costly and difficult to manufacture on a large scale. All these problems prevent us from putting MOFs to use in storing hydrogen.

4 Targeted design of MOFs for enhanced hydrogen storage

As discussed above, the efficiency of hydrogen uptake in MOFs depends largely on their porosity, surface characteristics, and building blocks. Therefore, in the future, efforts must be made to synthesize hydrogen storage materials with superior performance by adjusting these properties.

4.1 Optimization of surface area and pore structure

The specific surface area and porosity of MOFs enable them to store greater amounts of hydrogen. As stated above, a larger specific surface area provides more adsorption sites, and pores with sizes close to the kinetic diameter of H_2 (2.89 Å) will achieve higher adsorption capacities.

Therefore, increasing the weight-based surface area and appropriately adjusting the pore structure is effective, whereas increasing the volume-based surface area is not. High-throughput screening and experimental studies have shown that this method is effective when non-interpenetrating framework structures are formed by altering the type of ligands used or by controlling the degree of interpenetration. Frameworks such as SNU-70, PCN-610/NU-100, and UMCM-9 are also excellent examples, they exhibit outstanding specific surface area (6050 m^2/g) and pore volume (3.17 cm^3/g), far exceeding those of classical MOFs such as MOF-5 and IrMOF-20 [12].

At the same time, MOFs often have a relatively smaller amount of metal-ligand due to higher volume-surface-area. For example, the volume surface area for PCN-610/NU-100 is just 1603 m^2/cm^3 whereas MOF-5 has a specific surface area of 2,172 m^2/cm^3 which allows the former to accommodate more hydrogen [13].

In short, maximizing the specific surface area and pore volume of non-interconnected pores is a key characteristic that enables MOFs to exhibit good hydrogen storage capacity.

4.2 Selection and doping of metal centers

Metal centers strongly affect the pore stability and hydrogen adsorption behavior of MOFs, so rational selection is important for optimizing storage performance. The Zn_4O cluster is a typical building unit for high-performance hydrogen storage MOFs like MOF-5, IRMOF-20, UMCM-9 and SNU-70, due to its non-interpenetrated framework. Cu- and Zr-based clusters also have clear advantages: Cu sites offer abundant coordination sites and better stability, while Zr-based MOFs show excellent hydrothermal and activation stability from strong metal-ligand bonds [13]. Metals such as Mg, Pd and Pt can also be used to prepare new MOF hydrogen storage materials.

Metal- ion doping is a key approach for enhancing the hydrogen storage performance of MOFs at room temperature. Doping can alter the electrostatic field of the MOF framework and introduce a large number of new unsaturated metal sites. This enhances the interaction between H_2 and the framework and optimizes the adsorption enthalpy. The property is difficult to achieve in pristine undoped MOFs. For example, doping with Ni or Co can create a large number of additional pore structures and increase the adsorption enthalpy, improving hydrogen uptake under room- temperature conditions.

4.3 Application of composite systems

4.3.1 Composites of nanomaterials and MOFs

As for studies they have shown the incorporation of MOFs with metals like (Pt, Pd) or with carbon materials (carbon nanotubes, graphene). Hydrogen adsorption was improved. Metal nanoparticles causing the breaking up of H_2 and giving an atom formed there to a MOF, called spill - over, increasing how much H_2 can be taken. Like in Kim's report, he stated that adding Pt nanoparticle with MOF 5 increase the hydrogen storage capacity from 0.44wt% to 0.62wt% and also improve its adsorption kinetics [14]. Experiment results also show that adding both Pt and carbon black is better than just hydrogen uptake for the improvement of hydrothermal stability of MOF.

4.3.2 Composites of metal hydrides and MOFs

At the same time, the introduction of metal hydride nanocrystal can also demonstrate excellent performance in hydrogen storage. Metal hydrides such as $NaAlH_4$ and MgH_2 store hydrogen through chemical reactions and usually store large amounts of hydrogen; when these metal hydrides are mixed with MOFs, the total hydrogen storage capacity will significantly increase. Simmons demonstrated that nanoconfined MgH_2 within MOFs exhibited a much higher hydrogen storage capacity than bulk MgH_2 . [15] bulk metal hydrides normally release hydrogen at quite high temperature, but when metal hydride nanocrystal is combined with the MOFs, it could release hydrogen fast at low temperatures., thereby improving hydrogen adsorption and desorption performance.

5 Conclusion

This paper systematically outlines the progress made over the last twenty years in the use of MOFs for hydrogen capture and storage. It focuses on the key factors influencing hydrogen storage, the main limitations of current MOFs, and targeted strategies aimed at performance enhancement. The main conclusions are:

1. Pore size and surface area, open metal sites, guest metal species, and adsorption heat are the four main players in hydrogen storage by MOFs, but they do not act independently but rather work in concert.
2. Currently, there are four major challenges in MOF-based hydrogen storage: extremely low storage capacity at room temperature, limited performance across temperature ranges, the trade-off between structural stability and activity, and insufficient mechanical properties for large-scale industrial applications.
3. Three targeted design routes—optimizing specific surface area and pore structure, selecting appropriate metal centers, and developing composite systems based on MOFs. And they all have been proven effective in improving hydrogen storage.
4. As for further improvements: it is essential to take into account the relationship between structure and attributes, and optimization plans must be developed based on actual needs, rather than simply to maximize floor area.

These results offer valuable insights for investigators studying porous materials and hydrogen storage, which will contribute to the design and optimization of hydrogen storage materials based on MOFs. Since that hydrogen plays a critical role in large-scale clean energy applications, it can be assumed that if there's more progress in the MOFs world, new breakthroughs are expected in the field of hydrogen storage and transportation technology.

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