

MOF Used for Hydrogen Storage and Applied in Hydrogen-Powered Vehicles

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Abstract. Hydrogen is considered to be a major energy carrier for low-carbon transportation in the future, but its real application in fuel-cell vehicles is limited by difficulties in storing it onboard. Metal - organic frameworks (MOFs) have become key candidates for solid state hydrogen adsorption materials because of their tunable pore structures, high surface areas, and chemically tunable binding environments. This work provides a review of the structural influences on the uptake of hydrogen in MOFs such as pore size, specific surface area, open metal sites and linker functionalization and how these characteristics can be optimized to meet the stringent performance targets for automotive applications. Recent progress in the pore engineering, functional modification and metal site design are discussed along with experimental case studies showing improved storage capacities. Finally, potential application scenarios are considered, such as low-pressure tanks on board, cryo-adsorption hybrid systems, boil-off management of liquid hydrogen as well as the hydrogen transport infrastructure. Overall, these results demonstrate all the potential of MOF-based hydrogen storage technology, as well as the challenges it faces. They also clearly indicate that it is necessary to implement integrated material system design in the next generation of hydrogen-powered vehicles.

1 Introduction

Globally, the major trend of transitioning to sustainable and low-carbon energy systems has sparked greater interest in using hydrogen as a clean energy carrier in the process of energy transition for transportation. The attraction of hydrogen is its high gravimetric energy density, the potential to utilize the hydrogen from renewable sources, and the ability to power fuel cell vehicles while not contributing to global warming through greenhouse gas emissions. As countries seek ways to become carbon neutral, the use of hydrogen as a fuel for mobility has revealed itself as a potentially viable alternative to the traditional form of transportation fuelled by fossil fuels [1].

Despite these benefits, the use of hydrogen on board vehicles is seriously limited by the difficulty in storing it. Hydrogen has a very low volumetric density under ambient conditions, that is, we usually need to go through very large steps of compression or liquefaction to store sufficient fuel. Current energy storage technologies, i.e., high-pressure compressed gas (350-700 bar), cryogenic liquid hydrogen (20 K), and metal hydride, have problems such as high

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energy consumption, safety concerns, heavy system mass, poor kinetics, and high cost. As a result many of the existing approaches are still not able to fully meet the U.S. Department of Energy (DOE) performance targets for use as onboard storage—6.5 wt% and 50 g L⁻¹—under practical operating conditions [2].

In recent years, metal-organic frameworks (MOFs) have received a great deal of attention as a new class of porous materials that may overcome these limitations. MOFs are composed of metal nodes and organic linkers and, as a result, build crystalline materials with extremely high surface areas and adjustable pore geometries. These characteristics make MOFs interesting candidates for solid-state adsorption of Hydrogen, and particularly at low temperatures where physisorption is most effective [3]. Unlike many traditional adsorbents, MOFs provide crazoation on molecular level and are able to design a pore enclosure environment, customise chemical functionality and experiment with structure variations potential to improve hydrogen storage (H₂O) efficiency.

2 Key factors affecting hydrogen storage performance in MOFs

Metal-organic frameworks (MOFs) have tuneable structure and chemical environment in which MOFs are focal candidates for solid state hydrogen storage. Their storage behavior - capacity, adsorption enthalpy, diffusion, and reversible working capacity - is determined by several structural parameters in joint dependence. This chapter discusses four main factors: pore size, specific surface area, open metal sites and linker functionalization. Understanding how these factors interact is the scientific basis for the design of MOFs for the demanding requirements of hydrogen powered vehicles.

Beyond the performance requirements at the material level, MOFs must ultimately meet the performance requirements at the system level imposed by fuel-cell electric vehicles (FCEVs). According to the U.S. Department of Energy (DOE), for light-duty vehicles, the target weight fraction for the effective usable hydrogen in the on-board hydrogen storage systems (wh by weight) is about 6.5 wt% and the target for the system-level volumetric capacity is about and 50 g L⁻¹ (gallons per liter). These targets represent actual and practical limitations to vehicle mass and interior space as well as overall energy efficiency - issues which have a bearing on whether a hydrogen storage technology will be commercially viable [4].

In addition, storage systems must operate safely and reliably under a wide range of environmental conditions (typically from -40C to +85C while surviving hundreds of refueling cycles without a decrease in structural integrity). Rapid refuelling, constant production of hydrogen for the fuel cell, as well as compatibility with the on-board thermal management are further practical requirements. Meeting these operational standards is required for FCEVs to compete with existing technologies (battery-electric and internal-combustion).

Consequently MOFs made for hydrogen storage require not only high adsorption capacity at cryogenic conditions but also favourable kinetics, mechanical robustness and stability during repeated adsorption/desorption cycles. They must efficiently integrate into the real storage tanks without being too massive or voluminous, and their performance should be similar when taking samples out of the lab and into full size automotive systems. Only a combination of optimized design at the material level and constraints at the system level can bring the potential of MOFs out of the realm of promising experimental adsorbents to viable components of next-generation hydrogen storage technologies.

2.1 Pore size

The size of the pores is decisive both for the accessibility of the hydrogen molecules, and for the strength of the physisorptive interaction of hydrogen molecules with the internal surfaces of MOFs. Because of the weak van der Waals forces involved in taking up hydrogen, pore dimensions should be such that the molecules come close to the surface at an optimum distance.

Extensive computational screenings - such as those reported by- demonstrate that: Computational screening studies show that pore sizes in the sub-nanometer range, usually in a range of 0.6-1.0 nm, are optimal to maximize hydrogen adsorption by balancing the availability of diffusion and the adsorption potential. Pores smaller than this value impair the molecular diffusion, while larger pores impair the adsorption potential due to a lack of sufficient interaction strength.

Furthermore, pore size directly affects volumetric storage density which is an important metric for on-board vehicle applications where space is extremely limited. MOFs with a combination of micropores and mesopores - often termed hierarchical pores systems - can at the same time provide the two desirable properties: high packing density and mass transport speed resulting in enhanced working capacity under realistic operating conditions.

2.2 Specific surface area

As a rule, the larger the specific surface area (SSA) the higher the uptake of hydrogen will be, especially at cryogenic temperatures. Well-known high-surface-area MOFs, such as MOF-177, NU-100 and UCMC-9, are routinely more than 5000 m²/g, which can be used to realize exceptional gravimetric storage at 77 K conditions [5].

However, the correlation between SSA and storage performance decreases at near-ambient temperatures. Thermal motion makes the weak physisorption less effective and materials with no strong adsorption sites have a rapid desorption at room temperature. Thus, a high SSA while useful remains highly beneficial, but it must be complemented by characteristics that increase interaction energy such as open metal sites or polar functional groups.

A second limitation is that high SSA materials tend to have low bulk density, which has a detrimental effect on the volumetric efficiency, a key parameter for vehicle integration. Thus SSA optimization has to be countered by mechanical robustness/achievable pellet density.

2.3 Open metal sites (OMS)

Open metal sites, open unsaturated metal centres in the pore environment, greatly increase the strength of the hydrogen adsorption in comparison with organic linker surfaces. These sites lead to the production of localized electrostatic fields, which lead to higher binding energies of hydrogen than are obtainable with purely physisorptive interactions, which helps to improve usable capacity at higher temperatures, which can be used closer to room temperature [6].

Systems like Ni₂(m-dobdc) and V₂Cl₂·8(bttf) have been shown to be effective OMS-rich framework materials: under moderate pressures and temperatures their working capacities exceed the performance of classical MOFs like MOF-5 [7].

Despite all the benefits OMS may bring, these architectural treatments present various difficulties such the moisture sensitivity and possible framework degradation. This makes the design of chemically stable, water tolerant OMS an ongoing research priority, where the automotive application is a target, requiring long term cycling stability.

2.4 Functional groups

Chemical modification of MOF linkers provides another efficient way of tuning hydrogen adsorption. Functional groups affect the pore environment by changing polarity, charge distribution and surface chemistry.

Examples of useful functional modifications are the introduction of $-NH_2$ groups, which will increase the local polarity and reinforce the physisorption; the introduction of $-F$ or $-CF_3$ substituents, which will reinforce the induced dipole interactions; and the introduction of $-OH$ groups, which will provide supplementary weak binding sites. In some cases, the incorporation of alkali metal, such as Li^+ , can further produce cation–hydrogen interactions which is particularly beneficial to enhance the adsorption performance towards near-ambient operating conditions.

These modifications are not only beneficial for improving the adsorption but can also change the hydrophobicity, thermal stability, and the resistance to degradation by impurities [8]. Functionalization is therefore a flexible design tool, which allows MOFs to be used under realistic vehicular conditions. As shown in Fig. 1 The optimized adsorption geometries of H_2 on Li-functionalized Zn-MOF-5 are shown in this figure. Short Li– H_2 contact distances indicate higher cation– H_2 interactions and thus better physisorption.

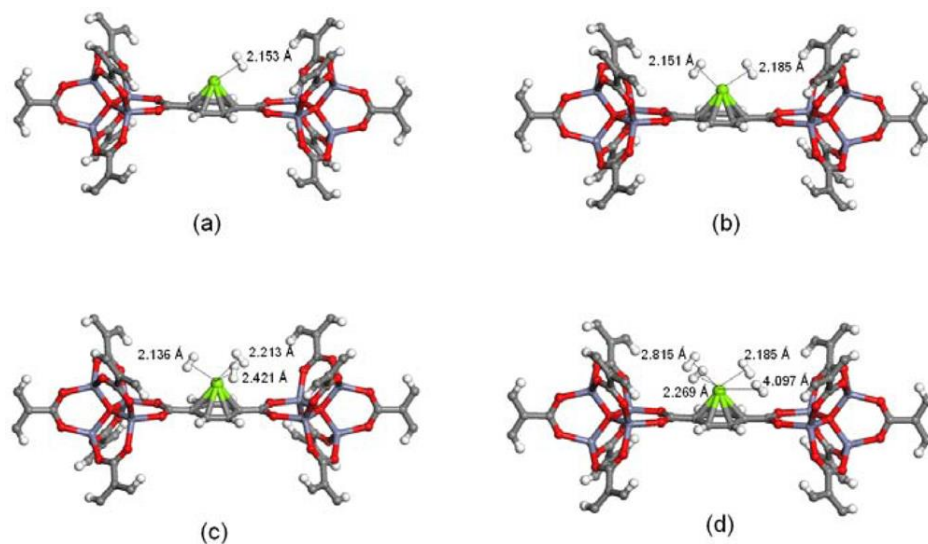


Fig. 1. Optimized geometries of H_2 adsorbed on Li-functionalized Zn-MOF-5, illustrating enhanced cation– H_2 interactions (charge-induced dipole / quadrupole). Reproduced under CC BY 3.0.

3 Strategies for optimizing MOF-based hydrogen storage and their application scenarios

In recent years, there has been great progress in the development of MOF-based hydrogen storage systems through structural and chemical optimization. For example, Expanded-pore metal-organic frameworks have been proved to contain higher hydrogen storage performance at the cryogenic condition, due to the increasing pore volume and surface area which will increase the available adsorption points. For instance, $M_2(dobpdc)$ frameworks ($M=Mg, Mn, Fe, Co, Ni, Zn$) exhibit seriously higher hydrogen uptakes than their smaller-pores

counterparts at 77 K, showing the importance of pore expansion as a structural design strategy [9].

The research results they obtained are crucial for achieving geometric tuning. Although this framework can only function under low-temperature conditions at present, this situation leads to some challenges when they want to apply it to in-vehicle storage.

Based on the research mentioned earlier, in the MOF-74 framework, The adsorption of hydrogen mainly interacts with those exposed open metal sites. These open metal sites act like primary binding centers, exerting a significant influence on the adsorption energy within the pores and the relatively favorable adsorption geometry, thereby enhancing the available capacity under moderate pressure. This strategy is effective in strengthening the host-guest interactions, but the high moisture sensitivity of the open metal site MOFs is still an obstacle to the long-term operational stability of MOFs in practical systems.

Further advances were reported by Linker functionalization has been widely explored as a strategy to modify the pore surface polarity and enhance the host-guest interactions. Electron-withdrawing substituents in particular have the ability to strengthen induced dipole interactions with hydrogen molecules resulting in better mid-pressure adsorption and working capacity, and the extent of induced dipole interaction there was measurable, leading to higher mid-pressure adsorption and better working capacity between 5-100 bar. However, this strategy adds synthetic complexity and could cause a reduction of mechanical robustness, in particular with repeated pressure cycling.

A complementary strategy is that of alkali-metal doping (represented by the work of Alkali-metal doping has been suggested as an alternative strategy for improving hydrogen binding by the introduction of interactions between cations and H₂, although issues related to ion stability, framework integrity and scalability need to be addressed.) the modified structures showed improved binding energies approaching 12–15 kJ mol⁻¹; thus improving the near-ambient adsorption performance significantly. Despite this progress, many challenges remain that will need to be overcome in order to see their direct application in automotive storage systems, including the migration of ions, destabilization of the framework, and the cost of scale-up, among others.

Collectively, these studies have shown how the different routes of pore engineering, open-metal-site incorporation, linker functionalization and cation doping offer unique pathways to improve the MOF-based hydrogen storage. At the same time, the trade-offs involved i.e. cryogenic needs, moisture instability, synthetic complexity & cycling durability point to the need for integrated design strategies balancing the performance of materials with the stringent operation demands of hydrogen-powered vehicles.

Although many MOFs have great potential properties, for practical use of hydrogen for fuel-cell vehicles, coordinated efforts are required in molecular design, structural engineering, and system-level integration. In this chapter, this article provides a general introduction to the main optimization strategies involved in MOF-based storage technology and the possible application fields.

3.1 Engineering of pore architecture

3.1.1 Precise control of pore apertures

By comprehensively adjusting the length of the linker, the geometry of the metal clusters, and the overall network topology, researchers can control the pore size within the ideal range suitable for hydrogen binding. High-throughput screening has demonstrated that even a minor adjustment to the pore diameter can significantly enhance the working capacity.

3.1.2 Construction of hierarchical porosity

This article holds that the framework structure that combines micropores and mesopores can achieve a strong adsorption capacity and also enable rapid diffusion of substances. Such a design is of great value for fuel cell vehicles because rapid refueling and efficient discharge are essential during the operation of fuel cell vehicles.

3.1.3 Enhancing packing density

In actual systems, MOF is not used as a loose powder but as particles or monomers. Methods such as solvent-assisted molding, mechanical pressing or polymer bonding must be adopted to increase its bulk density while maintaining its internal porosity.

3.2 Increasing adsorption enthalpy

Recently, the environmental hydrogen storage requirement has exceeded the adsorption enthalpy corresponding to traditional physical adsorption. This requirement has made enhancing the interaction between the host and guest the core goal in the design of advanced MOFs. One quite effective strategy is to combine high-density open metal sites, which can strengthen electrostatic interactions. It can also increase the binding energy. Another method that has been studied and explored by many people is to introduce electron-absorbing functional groups, which can cause polarization on the pore surface and enhance the interaction potential with hydrogen molecules. Metal doping, such as the doping of light cations like Li^+ or Mg^{2+} , can promote stronger cation- H_2 interactions, creating conditions for more favorable adsorption thermodynamics. In addition, hydrogen overflow is also regarded as a potential improvement mechanism. However, its role in reversible hydrogen storage in MOFs remains controversial and has not been ultimately confirmed under practical operation conditions. Generally speaking, these strategies all aim to transform the adsorption mechanism towards a stronger but still reversible interaction. Enable the MOFs to function effectively under conditions related to actual on-board hydrogen storage.

3.3 Improving structural stability and cycling durability

The hydrogen storage system of automobiles is exposed to a relatively large pressure fluctuation environment, is also affected by mechanical vibration, undergoes temperature changes, and comes into contact with trace impurities. Long-term structural stability and chemical stability are crucial requirements for MOF-based adsorbents. To overcome these obstacles, researchers have come up with various stabilization strategies. A relatively common strategy is to achieve metal clusters that are inherently robust, such as the Zr^{4+} -based nodes found in UiO-type MOFs, which have excellent resistance to mechanical and chemical degradation. Hydrophobic functionalization has also been used to minimize damage caused by moisture, while different types of cross-linking methods have been introduced to prevent framework collapse in repeated adsorption-desorption cycles. In addition, helping limit powder formation and attrition during operation is optimizing the mechanical strength of pellets by optimizing shaping and densification techniques. MOF powders are able to effectively molded into pellets (such as by extrusion) to improve mechanical strength and reduce attrition during cycling. As seen in Fig. 2, Fig. 2 shows how extrusion transforms MOF particles into tight pellets, increasing mechanical strength and minimising attrition.

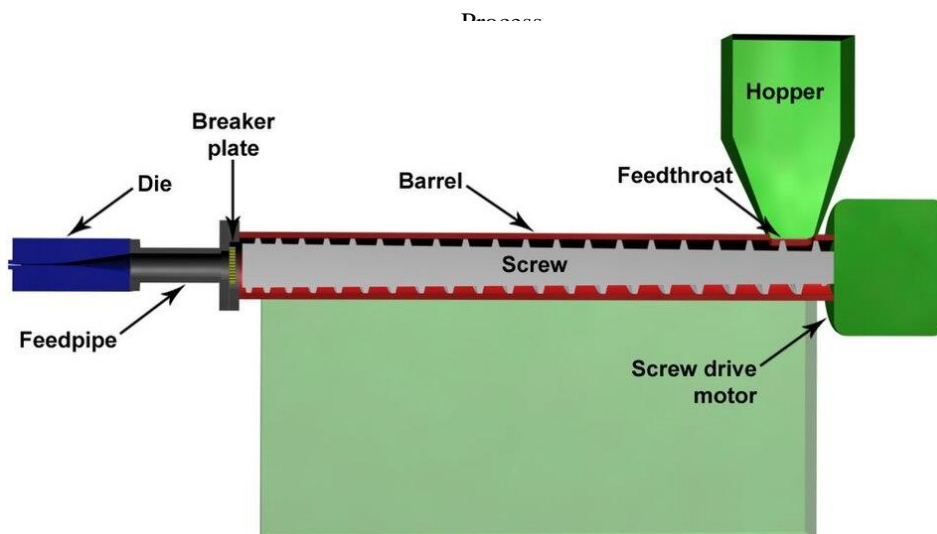


Fig. 2. van Lieshout, L. Extrusion process 1 (image). Wikimedia Commons, 2007; Public domain (released by copyright holder). Accessed January 8, 2026.

As discussed in it is not after all the maximum theoretical capacity of a material, but rather the cycling durability of a material that will determine its practical viability in a real hydrogen storage application.

3.4 Reducing production cost and enhancing scalability

For MOFs to be used in commercial vehicles, the cost of their production will have to be greatly lowered, which in turn requires the development of scalable and economically viable synthesis routes. Current strategies involve switching to water based solvothermal approaches that remove costly organic solvents, having continuous flow reactors with the capacity to produce product on a large scale and reproducibly, using inexpensive, earth-abundant metals like aluminum or magnesium instead of rare or costly metals, and optimizing linker synthesis to reduce the overall cost of manufacturing. Progress in these areas has given rise to the development of a number of low-cost MOF families, sometimes called "Type 3 MOFs," that show that high performance with low cost is technically possible.

4 Application scenarios of MOF-based hydrogen storage

Metal-organic frameworks(MOFs) have unique structural adjustability and adsorption performance, which increases their potential application possibilities in several fields of the emerging hydrogen economy. Metal-organic frameworks have the potential to store hydrogen under medium pressure, and they also have the ability to stabilize gas phase fluctuations. Moreover, they can perform efficiently at low temperatures. These features make it an ideal candidate material for mobile hydrogen storage systems and fixed hydrogen storage systems. In this chapter, four relatively key application scenarios of hydrogen storage technology based on MOF are discussed. These application scenarios, with the help of representative studies in recent literature, have demonstrated their practical significance.

On-board hydrogen storage in fuel cell vehicles is one of the applications that people pay particular attention to. The MOF, as the internal adsorbent of the composite hydrogen tank,

has been tested. Its working pressure is much lower than that of the existing systems used in commercial hydrogen fuel cell vehicles. The pressure of the existing systems is 700 bar, while the working pressure of the MOF is 100-250 bar. Low-pressure operation has benefits in terms of safety, in terms of compression energy requirements, and also in terms of refueling efficiency. Kapelewski et al. did an excellent work in 2017, which demonstrated that MOF Ni₂ (m-dobdc) has a high available hydrogen capacity at 100 bar and 77 K. Its performance is better than that of traditional activated carbon. Their research results indicate that it is feasible to apply high-capacity MOFs to sub-environment vehicle storage systems, which also demonstrates the role that customizable pore environments play in enhancing system-level performance.

A second pertinent case is the cryo-adsorption hybrid systems which work at intermediate cryogenic temperature (100-150 K). Under these conditions, MOFs show significantly improved adsorption capacities thanks to the improved physisorption energies. This hybrid approach combines the benefits of adsorption-based storage with partial cryogenic cooling, which can result in the use of higher volumetric densities that are suitable for heavy-duty vehicles, long-range transport fleet and aerospace platforms. tested MOFs, such as NU-111 and HKUST-1, at cryogenic pressure and achieved capacities of up to nearly 40–50 g L⁻¹ at temperatures of about 100 degrees Kelvin, which is close to DOE system-level targets. Their work highlights the potential of cryogenic-adsorption synergy for applications that require high energy density.

A third emerging application is in the management of liquid-hydrogen boil-off gas (BOG); an increasingly important application as the LH₂ vehicle platforms and fueling infrastructures are developed. During the storage of liquid hydrogen, unavoidable heat ingress creates a generation of hydrogen in vapour phase, which has to be vented or buffered in order to ensure tank safety. MOFs provide a way to adsorb this boil off gas on a temporary basis and stabilize tank pressure. Porous MOFs have been proposed as buffer material for the management of the liquid hydrogen boil-off gas by temporary adsorption of vapour phase hydrogen, allowing to stabilize tank pressure and to reduce venting losses in cryogenic conditions., reducing venting frequency and enhancing tank thermal balance. This work focuses on the contribution of MOFs not only in the field of hydrogen storage, but also system safety and operational stability in cryogenic environment.

Finally, owing to the ability of high-performance MOFs to store hydrogen at much lower pressure (below 700 bar), there is added benefit for mobile storage trailers, station-side buffer tanks and distributed renewable hydrogen systems. Early foundational studies such as Early experimental and computational studies on MOF-5 (IRMOF-1) established basic understanding of the hydrogen adsorption behavior in porous metal-organic frameworks and it could serve as the platform for further materials development. More recently, [10] simulated MOF-packed cylinders for hydrogen refueling stations, these results suggest that MOFs might improve current hydrogen distribution methods under some operational conditions. Such results strengthen the case for MOFs to play a vital role in the overall hydrogen distribution network to complement storage technologies onboard.

Taken together, these application scenarios represent the versatility of MOFs on the entire hydrogen value chain - from on-board vehicular storage application, to cryogenic hybrid storage applications, to liquid-hydrogen boil-off control, and to infrastructure-level storage applications. Although the hydrogen storage technology based on mof is currently facing many engineering challenges, such as scalability issues, anti-cycle stability problems, and system integration issues, there is an increasing amount of experimental and modeling evidence that can demonstrate that the hydrogen storage technology based on MOF has transformative potential in building a hydrogen economy.

5 Conclusion

This review has discussed metal organic frameworks (MOFs) for hydrogen storage as advanced solid state materials for hydrogen power automobiles. By analyzing systematically the key aspects of the structure-property relationships such as the pore size, the specific surface area, the number of open metal sites and the functionalization of the linkers, it becomes clear that the hydrogen adsorption performance of MOFs can be rationally designed through molecular and structural design. These parameters, taken together, control the adsorption capacity, adsorption enthalpy, diffusion behavior and reversible working capacity, which are significant in order to meet the storage requirements of the automotive sector.

Recent advances in engineering of pore size, introduction of open metal sites, chemical functionalization, and cation doping of MOFs prove that MOFs have an enhanced hydrogen binding energy and are superior for storage, especially under cryogenic and moderate pressure conditions. However, this review also calls attention to the fact that high theoretical uptake is not sufficient for practical deployment. System-level limits of relevant factors such as volumetric efficiency, mechanical stability, cycling durability, moisture resistance and cost-effective scalability are decisive in addressing the applicability of the system to the real world.

Potential application scenarios including low-pressure on-board storage, cryo-adsorption hybrid, liquid hydrogen boil-off gas and infrastructure level hydrogen buffering are further examples of the versatility of MOFs throughout the hydrogen value chain. Whilst there are still great challenges in this regard, especially in terms of realizing high reversible capacity close to ambient conditions and long-term operational stability, the fact that material design is becoming continuously coupled with engineering considerations provides a clear route forward.

Overall, MOFs are a highly tunable and promising platform for future hydrogen storage technologies and interdisciplinary efforts will continue to be critical in moving the technology from the laboratory to viable hydrogen storage solutions for future transportation systems.

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