The Role of Metal-Organic Framework Architecture in Hydrogen Storage

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Abstract. In recent years, human demand for energy has been increasing. However, the transitional use of currently used energy sources such as fossil fuels, for example, has had a very serious adverse effects on the environment and people's health. The development and widespread use of new and clean energy sources is an urgent necessity. As a clean, sustainable energy source, hydrogen has gained popularity as a potential replacement for fossil fuels. However, for hydrogen to be widely adopted as an energy source, it is imperative to create ways for storing hydrogen that are both practical and affordable. Due to the adjustable pore size, large surface area, and high porosity, metal-organic frameworks (MOFs) are receiving increasing attention in hydrogen storage. This paper aims to explore the potential of MOFs used in hydrogen storage and to provide insights into the optimization of the MOF architecture to design more suitable MOFs in this field.

Keywords: Metal-Organic Framework, Hydrogen Storage, Architecture Optimization.

1. Introduction

As science and technology continue to advance, mankind continues to expand the development and use of energy. However, the majority of the energy sources used by humanity today are fossil fuels, which have had many detrimental effects on both the environment and human health. For example, a World Health Organization (WHO) report claims that using coal, oil, and natural gas seriously harms human health because they contribute to air pollution and climate change. The heating value of hydrogen (33.3 kWh kg^{-1}) is roughly 3 times higher than that of gasoline (11.1 kWh kg^{-1}) even though the situation is the opposite on a volume basis [1]. After burning, it generates water vapour instead of other toxic gases such as sulphur dioxide. Due to its high energy density and clean burning characteristics, hydrogen is frequently regarded as a promising replacement for fossil fuels in both transportation and power generation.

Hydrogen is not an energy source from nature such as coals, which can easily gain from the subsurface of earth, it is generated from the natural energy sources in small quantity by gasifying coal, electrolyzing water, and reform methane steam [1,2]. It is therefore a challenge to store large quantities of hydrogen for the widespread adoption as an energy source. However, there are lower volumetric capacities and higher infrastructure costs associated with storage methods like liquefied storage and cryo-compression, which need high pressures and extremely low temperatures [2,3]. The U.S. Department of Energy set brenchmarks for onboard hydrogen distribution, 4.5 wt% for gravimetric storage capacity and a 30 g L^{-1} for volumetric storage capacity in the targets (2020) [4]. Therefore, it is important to find a way of storing hydrogen efficiently at normal temperatures and relatively low pressure.

MOFs, with metallic clusters and organic linkers, benefit from high surface area, crystallinity, and porosity as well as controlled architectural properties, have been viewed as a promising contender in hydrogen storage. On the one hand, MOFs are composed of many organic ligands and metal clusters, and on the other hand, they may undergo chemcial conversion to metal oxide composites through calcinating in N_2 or air under catalysis [5]. Furthermore, its special structure generates a huge potential to reach an extremely high specific surface area (SSA) and pore size, which are important in hydrogen storage [4]. This article is to explore the relationship between MOF architecture and hydrogen storage performance and seek for some methods to optimize the architecture of MOFs.

2. Characterization of MOF Architecture

MOFs have various structures because of diverse organic linkers and metal clusters. Thus, they have extremely high surface areas, adaptable structural properties, and abundant selectivity to load various functional elements to change their architectures for improved hydrogen storage. As a result, research into modifying or embellishing MOFs by architectural strategies in order to enhance hydrogen storage is crucial despite there are still many difficulties. Here are some methods for characterizing MOF architecture.

X-ray diffraction in powder (PXRD) has become an increasingly popular technique for describing materials in the nanotechnology. PXRD examination of a sample can offer important information in addition to a number of microscopic and spectroscopic methods, including phase verification and examination of the sample purity, crystallizable, size and shape. However, structural solution data from PXRD is more difficult compared to single crystal XRD, despite the fact that single crystals are not applicable to single crystal XRD because of processes caused by gases, temperatures, and solvents [6].

Transmission electron microscopy (TEM), which can observe atomic-scale structures and chemical environments, has been acknowledged as a helpful technique in advanced materials research since its debut in the 1930s. The increasingly popular analytical TEM techniques can be sorted into different categories such as scanning TEM and electron energy loss spectroscopy.

Variable-Temperature infrared spectroscopy responds to structural dynamics, which is an essential MOF phenomenon in crystal formation, negative thermal expansion, post synthetic exchange and catalysis, and the dynamic bonding can be seen by this way. In 15K, verifying the hydrogen framework interaction in MOF-5 was accomplished using variable-temperature infrared spectroscopy, at 4088-4093 and 4175-4181 cm^{-1}, two doublets were used to describe the interaction [1].

The dynamics of the entire sample are investigated by the quantitative spectroscopic method known as inelastic neutron scattering (INS). As opposed to Raman or other optical vibrational spectroscopies, which measure the energy exchange by photons that follow selected criteria, it measures the transferred energy of neutrons and is thus unrestricted by photon selection rules [7]. Additionally, unlike optical spectroscopies, which only sample the gamma point, INS samples the entire Brillouin zone, allowing it to resolve phonons that cannot be detected by them [8]. When hydrogen molecules are adsorbed on a MOF, information about the number of distinct binding sites can be obtained by using INS spectroscopy [1].

3. The Relationship between MOF Architecture and Hydrogen Storage Performance

3.1. Key Parameters in Hydrogen Storage

There are many key parameters that determine hydrogen storage performance in MOFs, including SSA, pore size, chemical composition, crystal structure, etc.

The surface area of a MOF is a critical factor in determining its hydrogen storage capacity. The higher it is, the more hydrogen the MOF can adsorb.

The pore sizes and shapes of MOFs also play an important role in hydrogen storage. Hydrogen molecules must be able to enter the pores easily, but they must be unable to quickly exit. The pore shape and size can also affect the adsorption energy of the hydrogen molecules. It is previously reported that the smaller the MOFs' pores are, the smaller the surface areas are [1]. In contrast, the larger pores are, the larger surface areas are [1].

The chemical composition of a MOF can influence its hydrogen storage capacity by affecting the adsorption energy of the hydrogen molecules. For example, the open metal sites or the organic linkers can influence the isosteric heat of hydrogen adsoption [1].

The crystal structure of MOFs influences its hydrogen storage performance by affecting the packing density of the MOF particles and the accessibility of the pores. Different crystal structures can also lead to different hydrogen adsorption energies and kinetics [1,2].

3.2. Research Progress

NU-100 was synthesized from 1,3,5-tris[(1,3-carboxylicacid-5-(4-(ethynyl) phenyl)) ethynyl]-benzene and copper SBUs which were shaped in paddle-wheel, and thus it was noncatenated, that is, non-interpenetrated [1,8,9]. Nonlocal density functional theory (NLDFT) was used for computing the pore size through Ar adsorption methods at 87 K, with peaks at 17, 24, and 30 Å [9]. Moreover, it had three different types of cavities, the longest open cage length reaching 48 Å [9]. In gas storage, it is critical to eliminate extraneous solvent molecules from the pores without lowering porosity [9]. As a result, NU-100 can eliminate certain guest solvent molecules [9]. Ahmed et al. found in the experiment that NU-100 has high volumetric working capacity, which is 35.5 g L^{-1} at 77 K from 5 to 100 bar [10]. Moreover, it has the greatest volumetric and gravimetric useable pressure-swing (PS) capability among the experimental materials the researchers used, and it is a promising MOF material because of its low capacity at 5 bars [10].

Zhang X et al. found that Nebraska Porous Framework (NPF)-200, which is regarded as cage-type, also has high working capacity with hydrogen, the working capacity measured in volumetric is 37.2 g L^{-1} [11]. Its largest cage occupies D/A≈2 to the total porosity, making it a promising material for gas storage [11]. Furthermore, Zhang X et al. pointed out that because the adsorbate and adsorbent interaction in larger pores becomes weaker, pore occupancy decreases as pore volume increases [12]. Besides, cage-like pores have a higher hydrogen adsorption capacity than the same pore volume channel-like pores [12]. NPF-200 has a Brunauer−Emmett−Teller (BET) area of 5,830 m^{2} g^{-1} in gravimetric, and 2,268 m^{2} cm^{-3} in volumetric, and it is synthesized from the Zr_6 assemble clusters and tetrahedral carboxylate ligands [13].

Chen Z et al. reported a MOF named NU-1501-M (M refers to Al or Fe), and NU-1501-Al, exhibits excellent hydrogen working capacities [4]. It is originated from NU-1500, a MOF with great stability and allowing metal iron such as Al^{3+} and Fe^{3+} to synthesize, and based on triptycene organic ligands and aluminium clusters [4]. NU-1501-Al has a BET area of 7310 m^{2} g^{-1} (2060 m^{2} cm^{-3}), and NU-1501-Fe of 7140 m^{2} g^{-1} (2130 m^{2} cm^{-3}) which volumetric one slightly smaller than NU-1501-Al due to the different metal clusters [4,13]. One of the most effective adsorbents for hydrogen storage is NU-1501 due to high SSA and high porosity (1.46 cm3 g^{-1} experimental total pore volume) [4,13]. NU-1501-Al has a gravimetric hydrogen deliverable capacity which is 14.0 wt% and its volumetric one is 46.2 g L^{-1} from 100 bar (77 K) to 5 bar (160 K) [4].

From the example MOFs above, SSA and pore volume are two most significant and determinant parameters for the hydrogen storage capacity. To improve the surface area, pore size or other parameters, the MOFs architecture can be designed by decorating the metal clusters or improve the shape of the structure, such as the examples NU-1501-M and NPF-200. Table 1 shows some porous MOFs and their BET areas, hydrogen working capacities and so on.

Table 1. Selected porous MOF materials' BET area, pore volume (PV), and H_2 working capacity [14].

Materials	BET area (m^{2} g^{-1})	Vol. BET area (m^{2} cm^{-3})	PV (cm^{3} g^{-1})	ΔH_2@(77 K/100 bar →160 K/5 bar)	
				wt %	g L^{-1}
MOF-5	3,510	2.070	1.36	7.8	51.9
SNU-70	4,940	2,030	2.14	10.6	57.9
NU-100/PCN-610	6,050	1,755	3.17	13.9	47.6
NPF-200	5,830	2,268	2.17	11.4	49.8
NU-1500-Al	3,560	1,770	1.46	8.2	44.6
NU-1501-Fe	7,140	2,130	2.90	13.2	45.4
NU-1501-Al	7,310	2,060	2.91	14.0	46,2

4. Optimization of MOF Architecture for Hydrogen Storage

For applications involving hydrogen storage, there are several ways to optimize MOF architecture. Fig.1 presents some important suggestions to improve a MOF's suitability for hydrogen storage by highlighting some key instances of how to build a MOF structure for hydrogen storage. All the methods below are related to these factors.

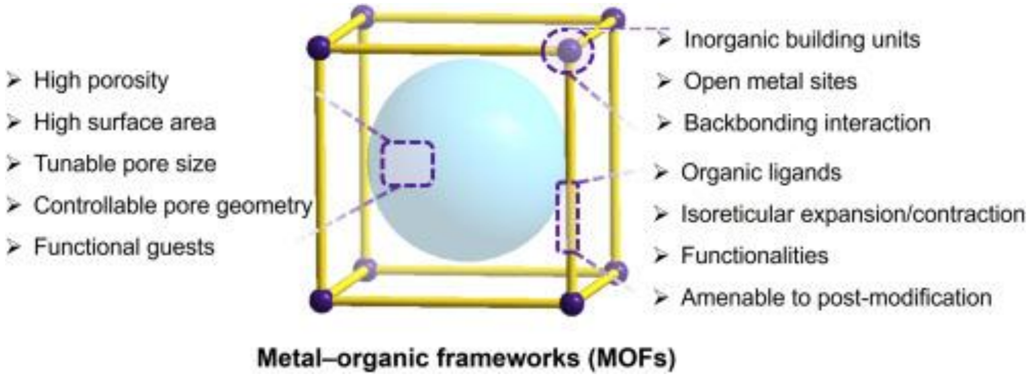

Figure 1. Illustrative instances of the creation of MOFs and their synthesis for hydrogen storage [14].

4.1. Post-Synthesis Modification

Post-synthesis modification was first suggested by Hoskins and Robson in 1990. Compared to PR functionalization which was widely used before, it is time-saving and it can maintain the framework structure because it is a modification after the MOF being synthesized [1]. In addition to covalent alteration of the metal clusters and the creation of open metal sites, post-synthesis modification also allows for amine or pyridine group modification of the organic ligands [1]. Thus, one can improve a MOF's hydrogen storage ability by metal center modification or ligand parts modification.

Hydrogen deliverable capacity is the uptake difference between two pressure conditions (basically 100 bar and 5 bar). Therefore, it is important to decrease the uptake at the minimum pressure [11,14]. For example, according to Farha et al., the open metal site of MOFs may be changed to increase or decrease the hydrogen storage capacity [1]. Besides, there are many other reports on the modification of the ligand parts. The amine groups MOFs can be modified to amides groups [1].

4.2. Ligands Elongation

The surface area of MOFs is able to be improved by elongating the ligands. Although MOFs with long ligands collapsed easily and the surface area reduced due to the interpenetration, researchers found that MOFs surface area increase by using elongated ligands [1]. For example, NU-100 has hexatopic ligands and Cu_2 paddle-wheel corners, and it processes an incredible hydrogen uptake capacity and stability [9]. This is due to the fact that the extended hexatopic ligands create a unique, 3,24-connected network that minimizes pore opening and network interpenetration [1]. Ligand elongation is a technique to increase the SSA of MOFs and keep stability.

4.3. Open Metal Site Generation

The process of hydrogen adsorption on MOFs is known as physical adorption, and there is very little van der Waals interaction between H_2 and MOFs [1]. Thus, the strong adsorption sites in MOFs to adsorb hydrogen molecules are crucial for hydrogen storage, especially at ambient temperature [1]. Depending on the type of metal and open metal site, MOFs can process persistent porosity and provide significant binding energy [2]. The terminal water linker of HKUST-1 in pores makes it possible to generate active site by removing the water molecules. Using thermal treatment leads to adsorption of other guest molecules including hydrogen. The reason why this is possible for HKUST-1 is that it is constructed of SBUs which is located at the nodes and followed by some guest molecules, the open metal site can be created at the secondary building units [1]. Although creating open metal sites can enhanced stability and binding energy of MOFs, it still has some limits such as the low corrosion resistance [2].

There are various other ways to optimize the MOF architecture besides the methods which are mentioned above. For example, embedding metals such as palladium and platinum, can increase the hydrogen uptake capacity of MOFs because of the spillover effect [1]. Moreover, MOFs can be mixed with other substances such as graphene oxide to create hybrid MOF materials with optimized hydrogen storage properties, but the linkers are always expensive and the MOF is less stable and lack of active centers [2]. By tailoring the architecture of MOFs to meet specific hydrogen storage needs, researchers can develop more efficient and effective hydrogen storage materials.

5. Conclusion

Hydrogen is a crucial energy source to reduce the use of fossil energy, and to store and transport hydrogen, MOF materials become a promising candidate due to its special architecture among other materials. A MOF's structure may be described in a variety of ways, and then its design can be optimized to increase its hydrogen storage capacity. Some key parameters such as the surface area, can affect the storage capacity, so these parameters should be taken into consideration in terms of the optimization to design an effective MOF for hydrogen storage.

In the future, more research should be done on the implications or the development and commercialization of MOFs as hydrogen storage materials in ambient temperature condition. It is hoped that more and more efficient, low-cost and widely available materials will be discovered in the future, so that hydrogen, as a clean energy source, will gain a wider use.

References

[1] Suh M P, Park H J, Prasad T K, et al. Hydrogen Storage in Metal–Organic Frameworks, 2012, 112 (2), 782 – 835.

[2] Shet S P, Priya S S, Sudhakar K, et al. A review on current trends in potential use of metal-organic framework for hydrogen storage. International Journal of Hydrogen Energy, 2021, 46 (21): 11782 - 11803.

[3] Barthélémy H, Weber M, Barbier F. Hydrogen storage: Recent improvements and industrial perspectives. International Journal of Hydrogen Energy, 2017, 42 (11): 7254 - 7262.

[4] Chen Z, Li P, Anderson R, et al. Balancing volumetric and gravimetric uptake in highly porous materials for clean energy. Science, 2020, 368 (6488): 297 - 303.

[5] Liao Y T, Matsagar B M, Wu K C W. Metal–organic framework (MOF)-derived effective solid catalysts for valorization of lignocellulosic biomass. ACS Sustainable Chemistry & Engineering, 2018, 6 (11): 13628 - 13643.

[6] Martí-Rujas J. Structural elucidation of microcrystalline MOFs from powder X-ray diffraction. Dalton Transactions, 2020, 49 (40): 13897 - 13916.

[7] Cavalcante L S R, Dettmann M A, Sours T, et al. Elucidating correlated defects in metal organic frameworks using theory-guided inelastic neutron scattering spectroscopy. Materials Horizons, 2023, 10 (1): 187 - 196.

[8] Farha O K, Eryazici I, Jeong N C, et al. Metal–organic framework materials with ultrahigh surface areas: is the sky the limit? Journal of the American Chemical Society, 2012, 134 (36): 15016 - 15021.

[9] Farha O K, Özgür Yazaydın A, Eryazici I, et al. De novo synthesis of a metal–organic framework material featuring ultrahigh surface area and gas storage capacities. Nature chemistry, 2010, 2 (11): 944 - 948.

[10] Ahmed A, Seth S, Purewal J, et al. Exceptional hydrogen storage achieved by screening nearly half a million metal-organic frameworks. Nature communications, 2019, 10 (1): 1568.

[11] Zhang X, Lin R B, Wang J, et al. Optimization of the pore structures of MOFs for record high hydrogen volumetric working capacity. Advanced Materials, 2020, 32 (17): 1907995.

[12] Stoddart A. Predicting perfect pores. Nature Reviews Materials, 2020, 5 (5): 331 - 331.

[13] Chen Z, Kirlikovali K O, Li P, et al. Reticular chemistry for highly porous metal-organic frameworks: the chemistry and applications. Accounts of Chemical Research, 2022, 55 (4), 579 - 591.

[14] Chen Z, Kirlikovali K O, Idrees K B, et al. porous materials for hydrogen storage. Chem, 2022.