

# The synthesis, activation, and adsorption capacity of metal-organic frameworks for hydrogen storage

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**Abstract.** Metal-organic frameworks (MOFs) comprise both organic and inorganic parts, allowing for immense diversity and tunability for specific purposes. Hydrogen has a hopeful prospect of being a clean energy carrier because of its lightness and therefore energy density, and it has been reported that MOFs already effectively adsorb hydrogen at cryogenic temperatures. In this article, the main synthesis methods for MOFs for hydrogen storage will be outlined, including the solvothermal, sonochemical, electrochemical and microwave methods. Methods of activation and stability concerns (thermal, mechanical and moisture) will also be addressed. The main focus of the article will be on increasing hydrogen capacity in MOFs at room temperature as opposed to cryogenic. The main ways to achieve this are adjusting pore size and strengthening hydrogen-MOF interaction. Recent research has shown that the most important effects in this regard are generating active metal sites, the spillover mechanism, and adjusting organic linkers.

**Keywords:** Hydrogen storage; metal-organic framework; synthesis; activation.

## 1. Introduction

As fossil fuels are depleted and the climate crisis becomes more pressing, hydrogen has been receiving increasing attention as a vector for renewable energy [1-3]. There are three main ways of storing hydrogen. One way is as a compressed gas, which requires very high pressures, and another is liquefaction, which calls for heavy and expensive cooling mechanisms. Both methods present obvious safety risks and are unsuitable for everyday applications. The third way is stored in solid materials, and metal hydrides (e.g.,  $\text{LiBH}_4$ ,  $\text{LaNi}_5\text{H}_6$ ) are one class of solid materials that have been considered [1]. Whilst these have high storage capacity, they work by chemisorption of hydrogen and so extreme temperatures are necessary for the hydrogen to desorb [1]. Materials that adsorb by physisorption include carbon nanotubes and zeolites, but they turned out to have insufficient hydrogen capacity.

Metal-organic frameworks (MOFs) are investigated for gas adsorption because of their porosity and therefore large surface area. However, what makes them special is their vast variability in terms of pore volume, structure, and composition. In essence, MOFs are made from metal ions/complexes joined by organic linkers, and this allows for high tunability to specific applications. Researchers have already used a variety of metal ions like  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Cr}^{3+}$ , in combination with organic ligands including carboxylates, imidazolates, triazolates, and tetrazolates to build many different MOFs [2]. More recently, more focus has been put on pre- and post-synthetic modifications to achieve desired characteristics.

To be accepted to store hydrogen in vehicles, the US Department of Energy (DOE) goals need to be met, that is a capacity of 5.5 wt.% (gravimetric), or  $40 \text{ g L}^{-1}$  (volumetric) [4]. MOFs that satisfy the DOE capacity requirement at cryogenic temperatures have already been successfully prepared. For example, the high surface area MOF DUT-32 had 7.8 wt.% capacity at 77K, 53 bar [5]. However, storage capacities are generally below 1 wt.% at ambient temperature due to relatively low  $\text{H}_2$ -MOF binding energy. To meet the DOE target temperature, higher isosteric heat of adsorption is therefore required, as it indicates stronger attraction between the hydrogen and the MOF. A plethora of ways to achieve this have been reported, including the creation of active metal sites at SBUs and/or organic linkers, the spillover effect, functionalization of organic ligands and manipulation of pore size. In recent research, the spillover effect involving hydrogenation catalysts such as Pt and Pd are proving important, as well as altering ligands to control pore size through catenation [1,2].

In the hydrogen storage field, besides adsorption capacity, other goals for MOFs including high stability, high capacity, cyclability, and fast kinetics also are important. For use as on-board fuel storage in vehicles, it must also be lightweight but simultaneously dense, to maximize hydrogen content in storage tanks. Even if all these are met, MOFs need to be cheap enough for widespread use, so energy efficiency and relatively simple synthesis are therefore required.

In this article, the main ways to synthesize MOFs for hydrogen storage are summarized, as well as how they are activated after synthesis. Methods of increasing capacity, especially controlling pore volume, and increasing hydrogen binding strength, will be described. Some stability concerns will also be discussed.

## 2. Synthesis of MOFs

MOFs comprise metal ions/complexes and organic linkers. To synthesize, the most commonly used are the solvothermal, sonochemical, electrochemical and microwave methods which will be outlined here.

### 2.1 Solvothermal Method

The solvothermal approach is considered the conventional method and involves dissolving the reactants in a suitable solvent before heating to above its boiling point at above atmospheric pressure. Glass vials are generally used for mild temperatures and pressures, and acid digestion vessels for higher temperatures and pressures [6]. Commonly used solvents are DMF (dimethylformamide) and DEF (diethylformamide), which have comparably high boiling points; generally, 80-130 °C is required to ensure full dissolution of reactants [2]. This method is popular owing to its relative simplicity, but some disadvantages exist, such as the amount of waste and the risk of oxidation and corrosion hazards [7].

### 2.2 Sonochemical Method

Ultrasound waves are to drive sonochemical synthesis. When these waves hit liquids, bubbles are created and waves oscillate in the liquid, causing energy to build up. When the bubbles collapse, large amounts of energy are released rapidly, causing local increases in temperature of up to 500 K and pressure reaching 1000 bar, driving MOF synthesis [6]. An example would be the Cu-BDC-NH<sub>2</sub> MOF where sonochemical synthesis improved its hydrogen capacity and efficiency of activation [8]. Other advantages include short reaction time, cheapness, and lower energy input due to mild temperature and pressure requirements. A problem is the formation of free radicals due to the huge local temperatures and pressures generated, and the immediate formation of unneeded crystallization nuclei need to be encouraged [6].

### 2.3 Electrochemical Method

The electrochemical method involves the creation of metal cations by immersion of an electrode in a chosen ligand-electrolyte solution. Metal ions will be formed when a voltage is applied which reacts with the deprotonated linkers to form MOFs. The main advantages of this method are mild conditions, quicker crystallization and easily scale-up due to its continuous nature. However, the reduction reaction causes the formation of reduced metal which could increase impurities [6]. HKUST-1 has been investigated as a MOF for hydrogen storage [2] and can be prepared particularly quickly by the electrochemical method involving the anodic dissolution of copper and ethanol/H<sub>2</sub>O as the solvent for 1,3,5-tricarboxylic acid [19].

### 2.4 Microwave Method

The microwave method utilizes the interaction between microwave energy and mobile charged particles in the solution, causing the reaction mixture to heat quickly and evenly. An example would be the microwave synthesis of a zirconium-based MOF, which had similar hydrogen storage capacity,

but a shorter synthesis time compared to products of conventional solvothermal methods [10]. However, it is not certain whether this is true for larger batches. Also, the main drawback is that the solvent is heated above its boiling points so high pressure is needed to prevent vaporization. The MOF product will exhibit morphologies and adsorption characteristics similar to that of the solvothermal method [6].

### 3. Activation of MOFs

Here, activation involves removing guest molecules after MOF synthesis. The guest molecules are generally solvent molecules or unreacted precursors still inside pores (sometimes due to open metal sites) after synthesis. This step is important as it ensures maximum hydrogen capacity. The three main methods of doing so are heat evacuation, guest molecule exchange, and supercritical CO<sub>2</sub> drying [2].

#### 3.1 Thermal Evacuation

Thermal evacuation, or simply the heating process, involves heating the MOF under a vacuum until the interaction between the guest molecule and the MOF is overcome, thereby evaporating and leaving the structure. However, this involves high temperatures, which could cause the MOF to collapse, especially if the pores are large [2]. This is why it is a good idea to identify the temperature where the MOF decomposes by thermogravimetric analysis before heating to half the decomposition temperature [6]. The evacuation rate should also be controlled and gradual, as the leaving of guest molecules involves exerting high surface tension (from the change from liquid to gas) on the structure, potentially causing collapse [11].

#### 3.2 Solvent Exchange

Solvent, or guest molecule, exchange involves placing the MOF in a solvent that will not cause collapse upon activation, so it should have a lower boiling point. As mentioned above, exertion of force on the MOF upon evacuation could also cause collapse, so a lower surface tension solvent would be desirable [11]. The MOF can then be activated at an appropriate temperature, usually in a vacuum [6]. This method would be applied if the temperature needed to fully activate the MOF by pure thermal evacuation would damage the MOF. For example, IRMOF-16 was nonporous when thermally evacuated at high temperatures. However, after guest molecule exchange and activation under ambient temperature, it became porous and could adsorb gases (gas-accessible surface area of 470 m<sup>2</sup> g<sup>-1</sup>) [12].

#### 3.3 Supercritical CO<sub>2</sub> Drying (SCD)

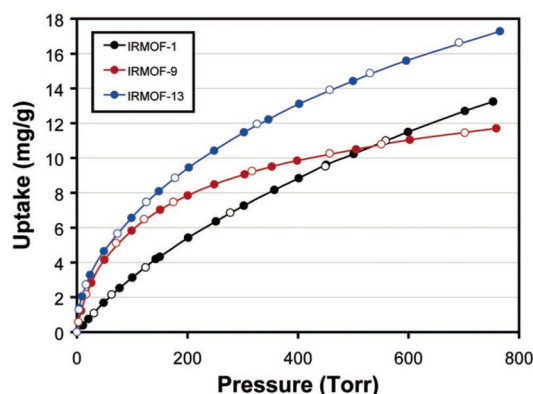
SCD involves soaking the MOF powder in ethanol, which is replaced every 24 hours to ensure thorough exchange. The sample is then soaked in liquid CO<sub>2</sub> at around 0 °C before heating to above the CO<sub>2</sub> boiling point to release the gas. This method is more time-consuming than the other two and would only be used if there is no suitable solvent to exchange in the guest molecule exchange method. Strikingly, for some zinc nitrate-based MOFs, the gas-accessible surface area increased by up to 12 times by SCD activation as opposed to thermal as pore collapse was prevented [12].

## 4. Increasing Storage Capacity of MOFs for H<sub>2</sub>

The surface area is generally not a concern due to the porous nature of MOFs. Therefore, the main way to improve capacity is through strengthening the H<sub>2</sub>-MOF interaction, which can be through controlling pore size and increasing binding energy. Investigating and utilizing these factors are essential to meet the DOE targets.

#### 4.1 Surface Area and Pore Size

When it comes to adsorption, a high surface area is crucial. According to Chahine's rule, for every  $500 \text{ m}^2\text{g}^{-1}$  increase in surface area, there is a 1 wt.% increase in hydrogen uptake [3]. However, surface area and hydrogen uptake are not always positively correlated. For example, at 298K and 70 bar, Ni(HBTC)(4,4'-bpy) with a relatively low BET surface area of  $1590 \text{ m}^2 \text{ g}^{-1}$  possesses a rather high capacity at 1.20 wt.% [13]. This is because pore size will affect the strength of the binding of hydrogen onto the MOF. Organic linkers can be adjusted to control pore size so that it is similar to a molecule of hydrogen, meaning the hydrogen molecule interacts with all surrounding walls. An example would be through catenation, the entanglement of MOFs. This occurs with longer organic ligands and works to reduce pore size. As shown in Figure 1, catenated MOF IRMOF-13 was reported to have higher  $\text{H}_2$  uptake at all pressures examined at 77 K compared to non-catenated IRMOF-1. However, it is important to be aware that loss of porosity is possible if the extent of catenation is too high. We see from Figure 1 that the rate of increase of hydrogen uptake in catenated IRMOF-9 decreased as pressure increased above 100 Torr due to the collapse of MOF structure and loss of crystallinity [14].



**Fig. 1** Comparison between  $\text{H}_2$  adsorption isotherms of IRMOF-1, IRMOF-9, and IRMOF-13 at 77 K [14].

#### 4.2 Isothermic Heat of Adsorption

As previously mentioned, a major way to increase capacity is to strengthen  $\text{H}_2$ -MOF interaction. Abbreviated as  $Q_{\text{st}}$ , isosteric heat of adsorption measures the strength of interaction when hydrogen is adsorbed onto a surface and will be relatively low in hydrogen adsorption in MOFs as it is primarily a physisorption process. Therefore, it is necessary to increase  $Q_{\text{st}}$  so that higher adsorption can be achieved. Bhatia and Myers worked out that MOFs would need a  $Q_{\text{st}}$  of  $15.1 \text{ kJ mol}^{-1}$  to store hydrogen at room temperature [15]. The main ways to do this are outlined here, including the creation of active metal sites, the spillover effect, and the functionalization of ligands.

##### 4.2.1 Creation of active metal sites at SBUs

Generating active (or open) metal sites, which will be abbreviated here as AMS, is a major way to increase isosteric heat. As shown in Figure 2, MOFs with active metal sites tend to have higher hydrogen uptake at room temperature (those highlighted in yellow have high uptake due to lower pore size and so stronger interaction with hydrogen). Open metal sites can be formed at SBUs after the evacuation of solvent molecules from synthesis that coordinate with the metal ions. Suh et al. reported the comparison between the three isostructural MOFs SNU-4 and SNU-5' (no AMS), and SNU-5 (AMS present) which had  $Q_{\text{st}}$  of 5.96 to 7.24, 5.91 to 6.53 and 4.43 to  $11.60 \text{ kJ mol}^{-1}$  respectively. At 77K and atmospheric pressure, the respective hydrogen uptakes were 2.07 wt.%, 1.83 wt.%, and 2.87 wt.%, clearly showing the improved capacity in active metal site MOFs [16].

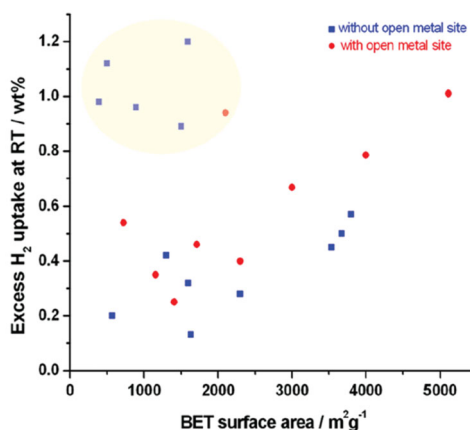


Fig. 2 A plot showing hydrogen uptake at room temperature against BET surface area [2].

#### 4.2.2 Introducing metal ions inside pores

Metal ions can also be introduced inside pores, for example through attaching metallated chelating groups to linkers, converting pendant alcohol groups into metal alkoxides, or porphyrin and Schiff base complexes [2]. Studies by Mulfort et al. have shown a modest increase in hydrogen uptake. they exchanged the hydroxyl proton in so-called DO-MOF for a lithium-ion, resulting in an increase in sorption from 1.23 to 1.32 wt.% at atmospheric pressure and cryogenic temperature. This increase corresponds to two additional H<sub>2</sub> molecules adsorbed to each Li<sup>+</sup> [17]. A problem is that much of the current data show only a slight increase with the impregnation of a metal ion, perhaps due to solvent molecules still being coordinated or weak interaction between hydrogen and the metal ion. Therefore, need MOFs that can be activated at higher temperatures, as well as utilize Sc, Ti, and V, which have been shown to have high isosteric heats of 21.9, 34.6 and 46.5 kJ mol<sup>-1</sup> respectively in MOFs [17].

#### 4.2.3 The spillover effect

Perhaps a better way to increase Q<sub>st</sub> is the spillover effect. This is where embedded hydrogenation catalysts such as Pt and Pd convert molecular hydrogen to atomic hydrogen. This results in a significant increase in isosteric heat as the interaction lean towards chemisorption and so the Q<sub>st</sub> will easily be higher than the required 15.1 kJ mol<sup>-1</sup> mentioned previously. Additionally, alumina and activated carbon (AC) can be used to link MOFs and adsorb some hydrogen themselves. As demonstrated in Figure 3, primary spillover is where the hydrogen interacts with the AC or alumina, and secondary describes interaction with the framework itself [1]. This effect is shown by Yang et al., reporting an approximately 3-fold increase in hydrogen storage at ambient temperature in IRMOF-1 and IRMOF-8 with the addition of platinum and activated carbon [18]. However, the space that the Pt and Pd take up could lead to lower porosity and surface area [2].

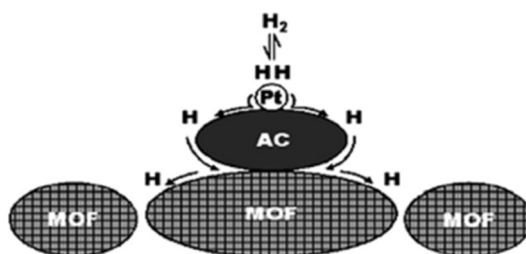


Fig. 3. The spillover effect of atomic hydrogen onto activated carbon (primary spillover) and the MOF itself (secondary spillover) [18].

#### 4.2.4 Changing Functional Groups

Different organic ligands will influence the surface area, pore size and interaction with hydrogen, and pre- or post-synthetic modifications can be introduced to modify functional groups. In general, aromatic groups interact more strongly with hydrogen, and it has been shown that interaction with

hydrogen is in the center of the ring. The comparison between gas sorption results of IRMOF-3 and its aromatic counterpart demonstrates this, with capacities being 1.51 wt% to 1.73 wt% respectively [19]. Following this, the incorporation of activating groups like amine and methyl groups will lead to stronger binding energies [2]. Oxygen and nitrogen will frequently appear in organic linkers due to their lone pair availability and therefore increased interaction with adsorbed hydrogen [2].

## 5. Stability of MOFs

Awareness of stability is essential in the densification of MOFs, as storage tanks must be filled with the largest amount of adsorbent; to increase overall volumetric capacity, its density must be increased. Having considered the relatively low stability of MOFs towards temperature, pressure, and moisture, it has been proposed that pelletization by mild compression is the most suitable densification method. In this method, as long as the pressure used does not cause porosity to be lost, densification will be directly proportional to the pressure applied [19]. Unstable MOFs are ones that, for some reason, collapse and become less porous or even nonporous, and thermal, moisture and mechanical stabilities will be discussed here.

### 5.1 Thermal Stability

Thermal stability is generally the first to be evaluated as it can be used to predict how stable the MOF is in other aspects. As previously mentioned, open metal sites can cause guest molecules to be strongly attracted to the MOF structure, and so high temperatures may be needed for their evacuation. Thermal degradation will be due to SBU-linker bond breaking, sometimes in combination with the combustion of the organic linkers. Metal-ligand bond strength can be increased by using oxyanion-terminated linkers and high valence metal SBUs, such as Ln(III) and Al(III), thereby increasing stability [20]. Evidence includes calculations of BET areas that have shown that Al-BDC (BDC = benzene dicarboxylate) maintained a higher surface area compared to lower valence chromium and vanadium counterparts after heating to 300 °C [21].

### 5.2 Moisture Stability

For gas storage, moisture stability is more relevant than other chemical concerns. Hydrogen sources will often contain some impurities, especially water, and there is a risk with MOFs that they interact with water molecules in the hydrogen supply instead of hydrogen itself. For example, Li and Yang reported an up to 10 wt.% uptake of water molecules in MOF-177 when exposed to water vapor and around 65% of the water adsorbed did not resorb at room temperature [22]. What this means is the sizeable loss in gravimetric capacity which would be best to avoid. Similarly, MOFs containing active metal sites may preferentially coordinate with water molecules rather than hydrogen, reducing hydrogen uptake. In some cases, such as SNU-5 [16], MOFs may partially dissociate upon exposure to water, leading to a significant loss in capacity. To improve stability against moisture, hydrophobic groups at organic linkers could be used. Zn-carboxylate MOFs are unstable in moisture [2], but it has been shown that the addition of methyl groups to a Zn-based MOF to form SCUTC-18 and SCUTC-19 resulted in little change in framework structure (shown by powder X-ray diffraction) after saturation in water vapor, indicating improved stability [23].

### 5.3 Mechanical Stability

The porous nature of MOFs inevitably means relatively low mechanical stability. It has been reported that zirconium-based MOFs are generally more mechanically stable due to their high coordination number and high strength of SBU-linker bonds. The shear and bulk moduli measure the susceptibility of a material to distortion under a shear force and uniform compression respectively and could indicate high mechanical stability in MOFs. For example, computational models have shown that Hf-UiO-66, which has high bulk and shear moduli, was among the most mechanically stable [24]. As mentioned in section 3, the surface tension or capillary force exerted on the structure

when guest molecules leave during activation can lead to collapse, and this is mechanical degradation as opposed to thermal. This is overcome by the SCD method, which gets rid of any capillary forces.

## 6. Summary

In conclusion, metal-organic frameworks are worth looking into as a material to store hydrogen because of their inherent large surface area and mainly their diversity and organic-inorganic nature. In this article, the main methods of MOF synthesis (solvothermal, sonochemical, electrochemical, microwave) have been discussed. The most widely used method has been the solvothermal method, although newer methods do have their advantages. Activation is an essential process after synthesis to remove the guest molecules and maximize storage capacity. The most common method is thermal evacuation, but sometimes low thermal stability of the MOF will mean that guest molecule exchange of supercritical CO<sub>2</sub> drying, which involves lower temperatures, will be necessary. As mentioned, there have been MOFs already synthesized that have storage capacities that meet the DOE targets at cryogenic temperatures, but at ambient temperatures, adsorption is significantly lower due to the weak nature of physisorption. So, much attention has been directed to increasing hydrogen binding energy, by considering open metal sites, the spillover effect and modifying linkers. In particular, the spillover effect has been associated with a considerable increase in uptake of up to 3-4 wt.%

Stability is also a main concern and as discussed, the main types associated with MOFs in hydrogen storage are thermal, moisture and mechanical. Thermal stability can be increased by strengthening SBU-ligand interaction, which can be through using high valence metals. Similarly, a good way to increase mechanical stability is through zirconium-based MOFs that have stronger SBU-linker bonds. Moisture stability could be dealt with by adding hydrophobic groups to organic ligands and avoiding those that readily dissociate in the presence of water.

Whilst considerable progress has already been made, there is a lot more research that needs to be done. Meeting the U.S. DOE targets is the main goal, and so continuous research needs to be made to increase hydrogen capacity at ambient temperature. On top of this, MOFs also need to be stable and able to withstand many adsorption-desorption cycles. Low cost is also necessary, meaning that simple synthesis and common precursors would be preferable. Nevertheless, MOFs still have a high potential for hydrogen storage.

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