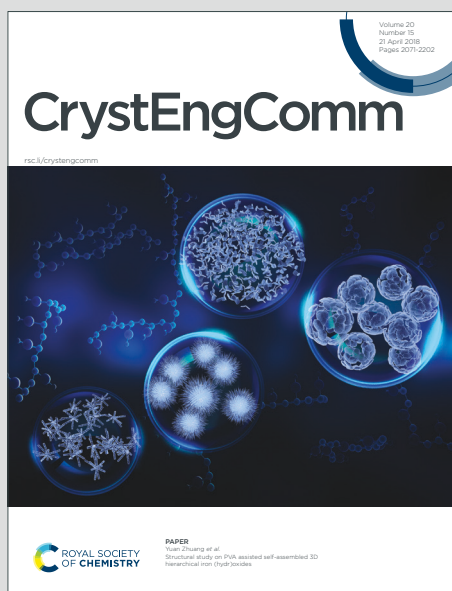


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MOFs as a partner for H₂ industry

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Abstract

Metal-organic frameworks (MOFs) are hybrid organic-inorganic porous materials composed of transition metal cations and polydentate organic ligands, forming modular architectures with high porosity and surface areas. These properties make MOFs promising candidates for hydrogen (H₂) storage and production, catalysis, sensing and gas separation, in between others. Since their conceptualization in 1995 by Omar Yaghi, MOFs have evolved significantly, with over 100,000 types reported, exhibiting surface areas ranging from 500 to 8000 m²/g. Their structural versatility, governed by secondary building units (SBUs) and ligand geometries, allows for tailored pore sizes and functionalities, critical for optimizing H₂ storage. MOFs with open metal sites (OMS) enhance H₂ adsorption by providing stronger binding sites, while advancements in synthesis methods, such as solvothermal, microwave, and spray drying, have improved scalability and efficiency. Recent developments include



MOF composites and bimetallic frameworks, which exhibit synergistic effects for enhanced H₂ storage and catalytic performance. For instance, NU-1501 achieves a H₂ gravimetric capacity of 14 wt%, while bimetallic MOFs like Zr/Hf-UiO-66 demonstrate superior catalytic activity. Additionally, MOFs are being explored for H₂ production via electrocatalysis and photocatalysis, leveraging their tunable electronic properties and high surface areas. Despite challenges in scalability and stability, startups like H₂MOF and Rux Energy are pioneering MOF-based H₂ storage solutions, aiming to meet U.S. Department of Energy targets for on-board H₂ storage. Computational modeling and reticular chemistry further accelerate the design of MOFs with optimized H₂ storage capacities, paving the way for their integration into sustainable energy systems. While commercial applications remain limited, ongoing research and industrial collaborations continue to advance MOFs toward practical H₂ storage and energy conversion technologies.

Introduction

Rapid industrialization has played a crucial role in driving economic wealth and population growth, leading to technological advancements, improved infrastructure, and higher living standards. However, this rapid expansion has also resulted in severe environmental consequences, including rising greenhouse gas emissions, escalating global temperatures, and increasing energy shortages^{1,2}. One of the most pressing challenges is climate change, which has led to extreme weather patterns, melting ice caps, and rising sea levels, posing serious threats to ecosystems and human societies worldwide³.

To combat the adverse effects of climate change, there has been a growing global initiative to implement rigorous environmental policies aimed at reducing greenhouse gas emissions. Many countries have set ambitious targets to transition towards cleaner and more



sustainable energy sources. For instance, France enacted Law No. 2015-992, which mandates a 40% reduction in greenhouse gas emissions by 2030 compared to 1990 levels⁴. This legislation reflects a broader international commitment to mitigating climate change through policy-driven efforts, increased investment in renewable energy, and technological innovations that promote energy efficiency.

While various factors contribute to greenhouse gas emissions, the burning of fossil fuels remains the primary culprit. Coal, oil, and natural gas have long been the pillars of industrial growth and energy production, but their extensive use has led to massive carbon dioxide emissions, exacerbating global warming. According to the United States Environmental Protection Agency (EPA), fossil fuel combustion is responsible for approximately 76% of all U.S. emissions resulting from human activities⁵. This alarming statistic underscores the urgent need to transition away from fossil fuel dependency and embrace cleaner alternatives such as wind, solar, and H₂-based energy systems⁶.

As nations continue to grapple with the dual challenge of sustaining economic growth while reducing environmental harm, see Figure 1, it is imperative to accelerate the adoption of sustainable energy solutions and reinforce policies that promote carbon neutrality. The path forward requires a collaborative effort between governments, industries, and individuals to create a cleaner, greener future for generations to come.

To address the pressing challenges of climate change and the growing energy crisis, it is imperative to explore alternative clean energy sources and gradually transition away from traditional fossil fuels such as oil and coal. These conventional energy sources, while historically essential for industrialization and economic growth, have significantly accelerated the environmental decline in a considerably way in the last decades. As global



energy demands continue to rise, finding sustainable and carbon-neutral alternatives has become a priority for researchers, policymakers, and industries equally.

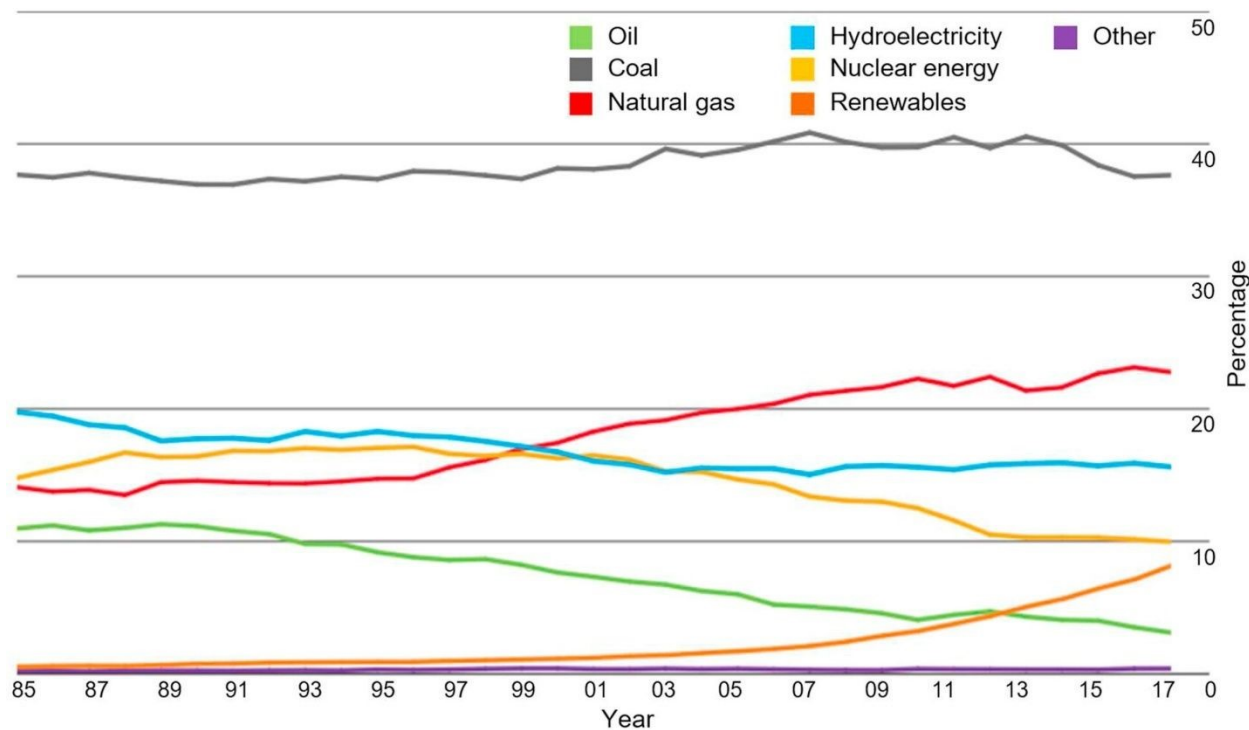


Figure 1. Global electricity generation source. Adapted from ref.⁷. Copyright 2024 Sciencedirect.

Among the various emerging energy solutions, H_2 has garnered considerable attention as one of the most promising candidates for a sustainable energy transition. H_2 offers several key advantages that make it an attractive alternative to fossil fuels. It boasts an exceptionally high energy density of approximately 142 MJ/kg (Gasoline has 46 MJ/kg for example), making it a highly efficient energy carrier. Moreover, H_2 is an environmentally friendly option, as it produces only water as a byproduct when used in fuel cells⁸. Additionally, H_2 can be derived from a variety of renewable sources, including water electrolysis powered by solar, wind, or hydroelectric energy, further reinforcing its potential as a clean and sustainable fuel^{9–11}.

Despite its potential, the widespread adoption of H₂ as a primary energy source faces significant challenges, particularly in its generation and storage. H₂ gas is highly reactive and has a low volumetric density, making its storage and transportation complex and costly. Traditional storage methods, such as compression and liquefaction, require high pressures and extremely low temperatures, increasing both energy consumption and operational costs. Additionally, H₂ production methods, including steam methane reforming (SMR) and water electrolysis, still face efficiency and cost barriers that hinder large-scale implementation¹¹. Several reports cover the implementation of different kind of catalysts to produce H₂.^{12–14} In general, these catalysts could be homogeneous, heterogeneous or biocatalysts. The selection of this catalyst is based on the synthesis method selected to produce H₂. The main limitation of these catalysts arose from the cost associated with their production and modification.

To overcome these challenges, Metal–Organic Frameworks (MOFs) have emerged as a promising alternative for both H₂ storage and generation. MOFs are highly porous materials with tunable structures, offering exceptional surface area and gas adsorption properties. These characteristics make them ideal candidates for efficiently storing H₂ at lower pressures and ambient temperatures, thereby addressing the limitations of conventional storage technologies. Additionally, recent research has explored MOFs as catalysts for H₂ production, providing new pathways to enhance the efficiency and sustainability of H₂ generation. By leveraging MOFs, the H₂ economy can move closer to achieving practical, scalable, and cost-effective energy solutions⁵. One of the most remarkable properties of MOFs is their tunable electronic properties, which can be modulated by adjusting the metal centers in the nodes or the organic ligands that serve as linkers¹⁵.



From a technoeconomic perspective, the current state of H₂ storage and generation still struggles to compete with conventional fossil fuels in terms of cost-effectiveness and infrastructure readiness. The high production and storage costs remain key obstacles to the widespread commercialization of H₂ energy. Therefore, advancing technologies that can reduce these costs is crucial to making H₂ a viable competitor in the global energy market. MOFs, with their ability to enhance storage efficiency and production processes, represent a cutting-edge solution that could drive the H₂ economy forward. Continued research, investment, and policy support are necessary to refine these technologies and pave the way for a cleaner and more sustainable energy future⁹.

Among the various applications of H₂ storage technology, the automotive sector presents the greatest challenge. Unlike portable electronic devices such as laptops and mobile phones, which can efficiently utilize compact fuel cells for power generation, H₂ storage for vehicles requires significantly larger energy capacities and must meet stringent safety, efficiency, and economic viability standards. Similarly, while non-automotive transportation applications, such as motorbikes and small-scale H₂-powered transportation, have shown promise, the large-scale adoption of H₂ as a fuel for automobiles remains a critical hurdle due to the complexities associated with storage, infrastructure, and cost-effectiveness¹⁶.

Research and development in H₂ storage technology have been ongoing for several decades, with numerous breakthroughs aimed at enhancing H₂ storage efficiency, safety, and scalability⁹. Scientists and engineers have explored various storage methods, including high-pressure gas cylinders, cryogenic liquid H₂ storage, and solid-state H₂ storage using advanced materials. Among these, nanoporous materials such as MOFs have attracted particular attention due to their high surface area, tunable porosity, and superior H₂ adsorption capabilities. MOFs offer a promising alternative for efficient H₂ storage,



potentially enabling vehicles to store sufficient H₂ for long-range travel while maintaining safety and cost efficiency^{1,17-19}.

To date, a substantial body of research has reviewed the applications and future directions of H₂ storage materials, including nanoporous H₂ storage materials and MOFs. These reviews have highlighted the technological advancements and limitations of existing materials, providing valuable insights into their potential for real-world applications. However, despite these extensive studies, a detailed structural analysis of MOFs, focusing on the relationship between their framework architecture and H₂ storage capabilities, remains lacking. Understanding this structure-activity relationship is crucial for optimizing MOFs to achieve higher H₂ uptake, improved stability, and enhanced adsorption/desorption kinetics.

In this report, we aim to provide a comprehensive analysis of the latest developments in MOFs for H₂ generation, storage, and real-life applications related to their structures. Our focus is to bridge the gap between material design and practical implementation by thoroughly examining how structural modifications in MOFs influence their H₂ storage and generation performance. By shedding light on the fundamental mechanisms governing H₂ interactions within MOFs, this report will contribute to advancing the field and paving the way for the next generation of efficient and scalable H₂ storage solutions.

Structure of a MOF. MOFs are a class of hybrid organic-inorganic porous materials, also called coordination complex polymers. MOFs are composed of transition metal cations and polydentate organic ligands with carboxylate, sulfonate, imidazolate and other ionic groups²⁰. These organic ligands bind orderly to the coordination sphere of metal cations replicating in space, resulting in modular architectures, with different topologies conferring a large internal surface area and high porosity. These topological characteristics of MOFs



coupled with their low density, high surface adaptability such as pore size and changes in their active sites, have made them interesting and promising heterogeneous catalysts, absorbing and storing materials for different gases such as CO₂, short chain hydrocarbons, or H₂^{21,22}.

These organo-inorganic materials were initially developed in 1989 by Richard Robert²³, who synthesized a three-dimensional coordination polymer $[Cu[C(C_6H_4CN)_4]]_n^{n+}$, but it was not until 1995 when Omar Yaghi first introduced the concept of MOFs²⁴. In this report he developed MOF-5 composed of terephthalic acid and zinc, which presented a high pore volume, great thermal stability, and was a good candidate for H₂ and methane storage. This finding was an achievement for reticular chemistry in the development of organometallic materials, since it was thought that these materials could only adopt amorphous structures, therefore, the advances in MOF synthesis opened a new window towards the formation of materials with high porosity. Currently, about 100,000 types of MOFs have been reported where their surface areas vary between 500-~8000 m²/g, with narrow pore size distribution, and low bulk density, which make them good candidates for H₂ storage.

The main structural characteristics of a MOF that provides it with high porosity and surface area are due to the different topologies that these materials acquire, so it is very important to decipher and understand their complex structure, for the design of new MOFs and to understand how their surface and porosity can be modified to improve their H₂ storage properties. By analyzing the topology of a MOF and unraveling its structure, a repetitive unit known as secondary building units (SBU) is defined²⁵, which (as its name implies) is the building block that by the repetition of this unit shapes the structure of a MOF. The SBUs corresponds to the metal clusters that adopt different geometries depending on the coordination number of the metal node and the anionic group of the used linker. SBUs are



classified according to their points of extension (POE), which means the number of possible connectors that can link an SBU to other SBUs through linkers. In Figure 2 it is shown some carboxyl-based SBUs commonly found in MOFs. Each SBU adopted a different geometry and form, which depends on the sphere of coordination of the metal cation used. Each carbon atoms of the carboxylic group in the SBUs represent a point of extension (POE) to connect with another SBUs where the minimum number of POE is 3 and the maximum is 18^{26,27}. Therefore, to understand the SBU geometry using POE, each carbon atom is taken as a vertex and is connected by edges with the other carbon atoms in the SBU, everything inside the vertices is represented by a green area. The shape of the metal cluster SBU is defined by the number and position of POEs in an SBU. For example, SBU $M_2(-COO)_4$ ($M=Zn$ and Cu) has POEs of four with a square paddlewheel SBU geometry. If the $M_2(-COO)_4$ SBU uses a carboxylic acid ligand such as benzene-1,4-dicarboxylic acid (H_2BDC) is replicated in a 2 dimension and the MOF-2 is obtained, which has a 2D structure. On the other hand, if the $M_2(-COO)_4$ SBU uses the benzene-1,3,5-tricarboxylate (H_3BTC) linker, the HKUST-1 is obtained, which is a 3D MOF. Although the topology of the MOFs is different, they both have the same square paddlewheel SBU geometry^{28,29}.



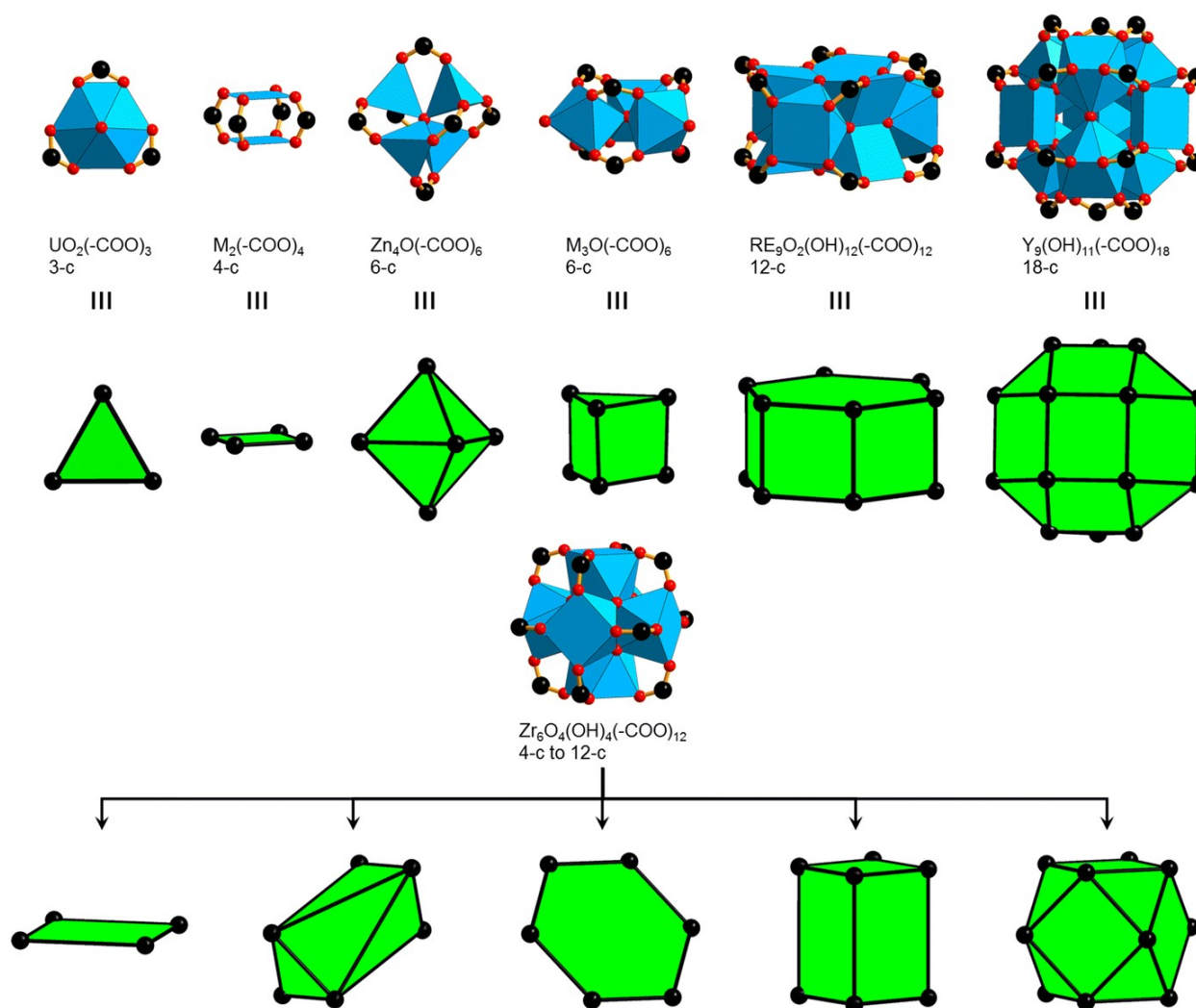


Figure 2. Common metal secondary building units (SBUs) to construct MOFs. Color code: black, C; red, O; blue polyhedra, metal. Adapted from ref.³⁰. Copyright 2024 Springer Nature.

Each SBU can be composed of different numbers of metals (from 1 to 6). Knowing the SBU that can form a metal cation with a type of organic ligand, different types of MOFs can be designed with different topologies by varying the geometry of the used ligand^{6, 7}. For example, in Figure 3, it is shown the SBU $\text{Zn}_4\text{O}(-\text{COO})_6$ formed by Zn(II) and carboxylic



acid ligand, this SBU has a POE of 6 and an octahedral geometry, depending on the carboxylic acid ligand employed to construct this SBU (terephthalic acid (H_2BDC), 1,4-naphthalenedicarboxylic acid (H_2NDC), or 4,4-biphenyldicarboxylic acid (H_2BPDC)) different MOFs can be obtained, MOF-5, UMCM-8, DUT-6, MOF-177, which will have different topologies, internal surface areas and pore volumes, and therefore will have different applicability's^{31–33}. Thus, knowing the SBU is of utmost importance to define the construction of a MOF, since the topology of the MOF is defined by the SBU formed and the geometry of the ligand used. This knowledge is crucial for the construction of MOFs used as H_2 storage, since some topologies will be more efficient than others for higher storage capacity^{34,35}.

The stability of the MOFs under different conditions will depend on many factors, such as rigidity of the ligand, geometry of the metal coordination sphere, length of the ligand, in between others.³⁶ The inherent stability of a MOF is related to the strength of the coordination bond between the ligand and the metal cluster, making this an important factor to design MOFs. If this coordination bond is weak, the MOF will have a low lifetime and will have low thermal and chemical stability. One of the theories that helps to predict the stability of the coordination bond in a MOF is the hard and soft acids and bases (HSAB) theory³⁷. In this theory acids and bases are subclassified into soft and hard categories, which will depend on the polarizability of the molecular electronic cloud, where hard acids/bases have low polarizability, and soft acids/bases have high polarizability. This theory indicates that the bonding of an acid-base pair of the same category (soft-soft, hard-hard) will be more favorable than the bonding of acid-base pairs of different categories (soft-hard). Considering that there are carboxylate base linkers, where their deprotonated form, carboxylate ion ($-COO^-$) is the species that coordinates to the metal clusters, this theory applies the formation of MOFs using these carboxylate ions polydentate ligands, which are



considered hard bases. According to HSAB theory the carboxylate (hard base) binds favorably to transition metals of high oxidation states ($>3+$). In this sense, the linker benzene-1,4-dicarboxylate (from terephthalic acid) binds to metals such as Cr(III), Fe(III), Al(III) or Zr(IV), to form different MOFs such as MIL-88B(Fe), UIO-66, MIL-101(Cr), MIL-53(Al), which have shown good thermal and chemical stability and have been applied as H₂ storage materials^{38–40}. The HSAB theory is useful to predict the stability that a MOF will have, since it predicts which metal-ligand bonds are more stable than others.



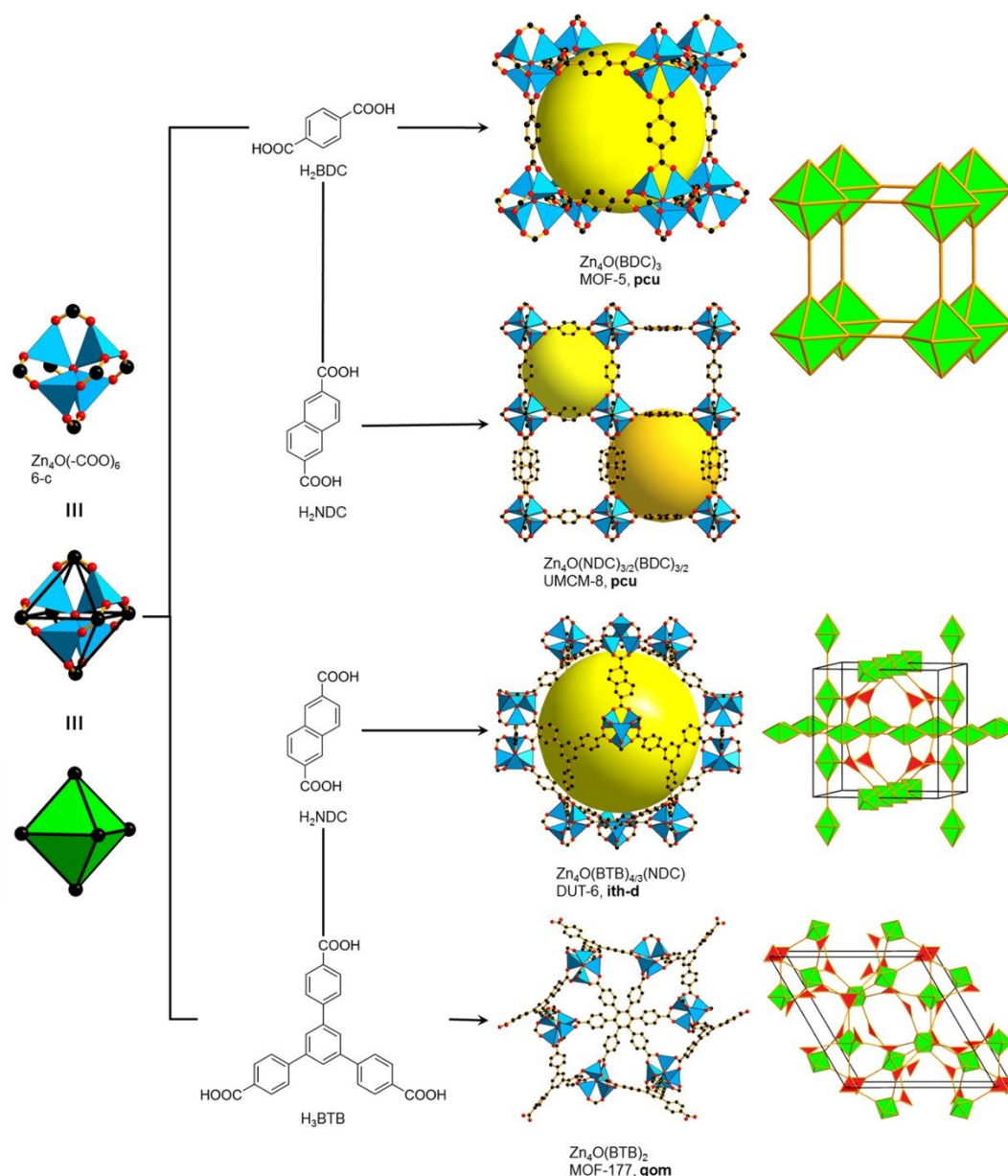


Figure 3. MOFs constructed from $\text{Zn}_4\text{O}(\text{-COO})_6$ SBUs. Color code: black, C; red, O; blue polyhedra, Zn. The yellow spheres represent the empty space in the framework. Hydrogen atoms are omitted for clarity. Adapted from ref.³⁰. Copyright 2024 Springer Nature.

There are different methods in MOF preparation, such as solvothermal/hydrothermal, microwave, electrochemical, ultrasonic, mechanochemical, chemical flow, stray drying,



etc.²⁰. We will highlight those that have been most commonly used and those that have the largest potential for large size synthesis. Each method has its advantages and disadvantages in MOF synthesis. Conventional synthesis methods, such as solvothermal methods, were initially proposed on MOFs preparation. The solvothermal method consists of a stoichiometric mixture of metal precursor and the organic ligand in an adequate organic solvent, in a hermetically sealed container (autoclave). If the used solvent is water, the method is called hydrothermal. The container is then heated in an oven at a certain temperature for a period of time. Under these conditions the formation of MOFs crystals occurs. This procedure has the advantage of being a single step method obtaining good yields. One of its disadvantages is its difficult to scale for large size synthesis, since the method considers many variables that must be parameterized, in addition to the use of large amounts of organic solvents and long synthesis times⁴¹. On the other hand, the microwave method is similar to the solvothermal method, but the energy source for the MOF's formation is microwave radiation. Microwave radiation helps to obtain MOFs in a shorter synthesis time compared to the solvothermal method, in addition to obtaining crystals with controllable particle sizes. However, currently this method is not scalable, due to the size of the required reactor and the requirement of large amounts of electricity⁴². Current synthesis methods seek to provide solutions to these problems of scalability in MOF and have the characteristics of being easy and cheap to execute, such as spray drying method⁴³. The spray drying technique is a highly efficient method for synthesizing MOFs with precisely controlled particle sizes. This process involves atomizing a precursor solution into nano-sized droplets, which are then rapidly dried by a stream of hot gas. As the solvent evaporates, MOF particles begin to form, resulting in a uniform and well-defined morphology. One of the major advantages of this method is its ability to produce MOFs with



consistent particle sizes, ensuring homogeneity in the final material⁴⁴. Additionally, spray drying offers short preparation times, making it a time-efficient approach compared to traditional MOF synthesis methods. Furthermore, this technique is highly scalable, allowing to produce large quantities of MOFs, which is crucial for industrial and commercial applications. A key factor in the success of spray drying is the proper formulation of the precursor solution. All necessary species, including metal salts and organic linkers, must be fully dissolved and well-mixed to ensure uniform nucleation and particle formation. Careful optimization of solvent composition, temperature, and drying parameters is essential to achieve high-quality MOF structures with desirable properties for specific applications^{44,45}. Another method is flow chemistry which specializes in having a constant inflow and outflow of reactants and products^{46,47}, where the inflow contains the precursors, and the outflow contains the MOF that is formed inside the reactor. This method uses different continuous flow reactors, such as stirred tank reactors or plug flow reactor. The great advantages of this method are the easy control of the reaction parameters, where the concentration of the precursors, agitation of the reactor, and speed of the flows must be controlled since the necessary time must be given for the MOF formation to occur. This precise control also allows controlling the size of the particles, in addition to its scalability to obtain large quantities of MOF. Since there are several MOFs that have shown promising applications as H₂ storage, it is essential to develop synthesis methodologies to obtain large quantities and test these MOFs in H₂ storage systems on a larger scale, therefore methods such as spray drying or flow reactors are good options for scalability of the MOFs, but there are no reports of MOF synthesis by spray drying and flow reactors methods applied to H₂ adsorption.

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Open Metal Sites (OMS). Among the most promising strategies to enhance the affinity of MOFs for H_2 , the incorporation of open metal sites (OMS) stands out due to the strong interactions that OMS provide with H_2 molecules. MOFs exhibit varying degrees of metal center coordination, which can be either fully coordinated or unsaturated, leading to structural defects such as missing organic linkers^{48–50}. These OMS enable the design of new binding sites (see Figure 4), significantly expanding the range of applications for these materials, including catalysis, gas storage, and separation^{51–54}. The generation of reactive OMSs in MOFs is one of the most attractive strategies, as they can create local environments similar to those of homogeneous catalysts. Moreover, the presence of OMSs in these porous materials enhances sorbent selectivity^{55,56}.

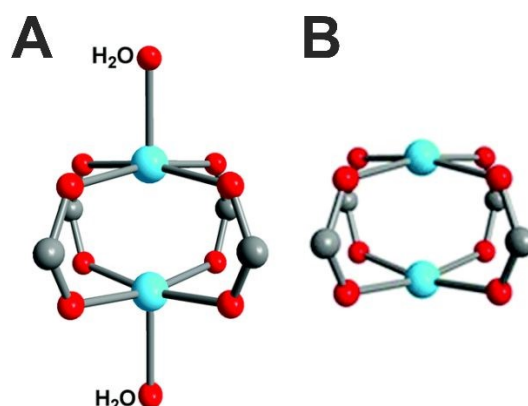


Figure 4. SBU of HKUST-1. (A) HKUST-1 with water molecules after activation and (B) HKUST-1 activated with loss of water molecules giving rise to OMS. Reproduced from ref.⁵⁷. Copyright 2024 Advanced Energy Materials.

By modifying the coordination of metal ions in the SBU of the material, the crystallinity and porosity of the structure must be maintained. During the synthesis of MOFs, vacant



coordination sites are usually occupied by solvent molecules (labile ligands), which stabilize the structure by saturating the coordination sphere.

To generate OMS, it is necessary to remove a labile terminal ligand, which usually are synthesis molecule such as DMF, water, or alcohols⁵⁸. Thus, different strategies are used for the generation of OMS:

a) **Solvent exchange and thermal activation:** For example, a high-boiling solvent (DMF) is replaced by a more volatile solvent (acetone). Acetone molecules are then removed by thermal activation at low temperatures and high vacuum pressures^{59,60}.

b) **Chemical activation:** This method consists of washing the MOF with volatile solvents, which are subsequently removed by air drying at room temperature^{61,62}.

c) **Photothermal activation:** This method is applied to kinetically stable metal ions and uses UV-Vis radiation to induce a photoactive excited state, facilitating the removal of ligands⁶³.

Furthermore, once the OMS are obtained, it is possible to quantify the percentage obtained in each material. The techniques used are gas adsorption techniques, temperature programmed desorption (TPD), and infrared spectroscopy using probe molecules such as H₂, CO₂, CO, and water^{64–66}.

The presence of OMS in MOFs allows the design of materials with specific interactions, which expands their functionality. Additionally, the stronger binding sites presented within the OMS-MOF structures enhance the interactions between H₂ and the material. On the contrary, has been demonstrated that when the metal centers is fully coordinated (defect-free materials), the material have a low performance on H₂ adsorption and production⁶⁷. This turn OMS-MOF as a highly promising material for H₂ separation and storage.



The most commonly used secondary building units (SBUs) to generate open metal sites are bimetallic, where the solvent coordination at the available sites is in axial positions. There are different bimetallic materials used for H₂ production, such as MOF-74 with divalent OMS. A isostructural MOF-74-M (M₂(dobdc), where M= Co, Cu, Mg, Mn, Ni and dobdc= 2,5-dioxide-1,4-benzenedicarboxylate). This MOF has the highest known OMS volumetric density. MOF-74-Ni exhibits low thermal stability, so the incorporation of bimetallic OMS with Mg is necessary to stabilize the structure. In this case it has been shown that materials with (Ni_xMg_{1-x})-MOF-74 (where "x" corresponds to the fraction of each metal) increase the H₂ production⁶⁸. In 2015, Orcajo et al. studied the capacity of the bimetallic MOF-74 for H₂ adsorption in the presence of OMS. In this case, the highest adsorption capacity was attributed to materials containing bimetallic OMS of Co and Ni. This was compared with monometallic MOF-74-Cu, which had a lower adsorption capacity due to its lower affinity for H₂⁶⁹.

Open metal sites have been generated in HKUST-1, through syntheses method, which increases the available surface area and intensifies the interaction between the gas and the material⁷⁰. However, the storage capacity of this material can vary significantly depending on the activation method and sample handling in the presence of open metal sites^{71–73}.

On the other hand, Suh and his group compared the H₂ storage capacity in structural materials with and without OMS, using MOFs with different amounts of these available sites (SNU-4, SNU-5, and SNU-5'). SNU-5 (SNU: Seoul National University) which presents open metal sites, showed a higher adsorption capacity⁷⁴.

In every case the OMS produces an increase in the H₂ storage capability, as the generated interaction, often described as electrostatic attraction, results in a stronger binding strength compared to conventional MOFs (MOFs which do not possess the OMS). The presence of



OMSs boosts the adsorption capacity of MOFs, allowing them to store more H₂ gas. This enhanced adsorption is attributed to the increased interaction strength between the metal sites and the H₂ molecules. Thus the generation of new MOFs with the possibility of having more OMS is a current topic in research for adsorption materials⁷⁴.

Linkers modifications for H₂ affinity. The organic linker is essential to the MOF structure since they contribute to determine the topology of the material, and by consequence, they play an important role in the properties and applications of MOFs. For H₂ industry applications, surface area is directly related with gas adsorption capacity, thus the development of new MOFs with ultra-high surface area is being studied. One of the simplest ways to increase the surface area is to incorporate longer linkers to form isorecticular MOF, this approach allows to synthesize MOFs with similar crystalline structure but with different compositions⁷⁵. However, there are two difficulties, (1) the large void generated could cause the interpenetration of the crystal frameworks as a form of structural stabilization (but occluding each other's pores) and (2) the incorporation of longer linkers decreases the crystal framework stability like the case of PCN-610 were the crystal structure collapsed after the removal of the solvent guest molecules^{76–81}

Zhou et al.⁸¹ worked with a family of isorecticular MOFs based on dendritic hexacarboxylic acids with different lengths. The MOFs PCN-61; -66; -68 and -610 exhibited a BET surface area that increased with the linker's length from 3000 m² g⁻¹ to 5109 m² g⁻¹ in the case of PCN-68. However, the structure of PCN-610 completely collapsed during the activation process. On the other hand, Hupp et al.⁸² synthesized NU-100 (the same as PCN-610, but NU-100 was successfully activated) with a BET surface area of 6143 m² g⁻¹. The effect of a high surface area over the gas adsorption capacities for H₂ were studied for the mentioned



PCN and NU MOFs. The H₂ uptake showed that in the low-pressure region the sorption capacities are dominated by H₂ affinity, where PCN-61 had the highest isosteric heat due to its reduced pore volume. The high pressure range is controlled by surface area and pore volume, so NU-100 exhibited a total gravimetric H₂ uptake 164 mg g⁻¹ at 70 bar and 77 K, and PCN-68 exhibited a total gravimetric H₂ uptake of 130 mg g⁻¹, followed by PCN-66 with an uptake of 110 mg g⁻¹ and finally 90 mg g⁻¹ for PCN-61 at 100 bar and 77K. This trend gets inverted when calculating the volumetric H₂ uptake capacities, where the MOFs exhibited a total volumetric uptake of approximately 48, 50 and 52 g L⁻¹ at 100 bar and 77 K for PCN-66, PCN-68 and PCN-61, respectively. The inversion in trend is due to the volumetric capacities are dominated by the densities of the crystal framework.

These works highlight the effect of elongating the linker on the H₂ uptake performance. As could be noted, the increase in surface area weakens the crystal structure and lowers the volumetric uptake. This hinders the application of MOFs for H₂ transportation where a balance between gravimetric and volumetric uptake is needed.⁸³

On the other hand,⁸⁰ the use of two linkers to yield two new MOFs (MOF-180, MOF-200) with high surface areas was studied by Yaghi *et al.*⁸⁰, the mixing of 4,4',4''-benzene-1,3,5-triyl-tribenzoate (BTB)/2,6-naphthalenedicarboxylate(NDC) and 4,4',4''-(benzene-1,3,5-triyl-tris(ethyne-2,1-diyl))tribenzoate (BTE)/biphenyl-4,4'-dicarboxylate (BPDC) linkers yielded MOF-205 and MOF-210, respectively. MOF-205 and MOF-210 exhibited a surface area of 4460 and 6240 m² g⁻¹ and a total gravimetric H₂ uptake of 123 and 176 mg g⁻¹ at ~60 bar and 77 K, respectively, see Table 1⁷⁶Moreover, the influence of the di- and tritopic linker length ratio (L_D/L_T) and mole fraction to yield UMCM-1; -2; -3; -4 and -5 was analyzed⁷⁶. The mixture of different linkers has effects over the reactivity which requires a modification of the mole fraction in the synthetic feed, where tritopic linkers are consumed



in the reaction statistically 1.5 times faster than ditopic linker due to the presence of more carboxylic groups. So, there is needed an excess of the ditopic linker (compared with its presence in the framework) to produce a pure copolymerization of the MOF. The UMCM-X series were successfully synthesized in a mole ratio between 8:2 and 5:5. On the other hand, changes in L_D/L_T influence the connectivity of the linker to the cluster, constructing new structure types in some cases. According to known MOFs, the linker length ratio to generate a stable structure lies within a region from 0,44 to 0,66⁸⁴.

⁸⁵The improvement in surface area of MOFs via linker elongation implies the framework debilitation, were a gentle activation with supercritical CO₂ helps to maintain the integrity of the crystal structure^{82,85}. Linker elongation also increases the susceptibility of self-interpenetration, which is given on many cubic and tetrahedral networks, thus a topology selection or other techniques to avoid interpenetration could be considered^{80,85,86}. Despite this difficulties, MOFs are near to achieve the on-board H₂ storage proposed by the U.S. Department of Energy for 2020 (4,5 wt%, 30 g L⁻¹, -40 to 60 °C, 5 – 12 bar) and for 2025 (5.5 wt%, 40 g L⁻¹, -40 to 60 °C, 5 – 12 bar)⁸⁷.

Table 1. Summary of MOFs with high H₂ adsorption capacities.

MOF	Linker	Molecular Formula	BET surface Area [m ² g ⁻¹]	Total H ₂ gravimetric uptake at 77 K [mg g ⁻¹]	Total H ₂ volumetric uptake at 77 K [L g ⁻¹]	Topology	Synthesis Method	Ref.
PCN-61	H ₆ BTEI	Cu ₃ (BTEI)(H ₂ O) ₃	3000	90 ^a	52 ^a	rht	Solvothermal	81,88, 89
PCN-66	H ₆ NTEI	Cu ₃ (NTEI)(H ₂ O) ₃	4000	110 ^a	48 ^a	rht	Solvothermal	81,88, 89
PCN-68	H ₆ PTEI	Cu ₃ (PTEI)(H ₂ O) ₃	5109	130 ^a	50 ^a	rht	Solvothermal	81,89

NU-100/PCN-610	H ₆ TTEI	Cu ₃ (TTEI)(H ₂ O) ₃	6143	164 ^c	-	rht	Solvothermal	81,82,89
MOF-200	H ₃ BBC	Zn ₄ O(BBC) ₂ (H ₂ O) ₃	4530	163 ^b	36 ^b	qom	Solvothermal	80
MOF-205	H ₃ BTB, H ₂ NDC	Zn ₄ O(BTB) _{4/3} (NDC)	4460	120 ^b	46 ^b	ith-d		
MOF-210	H ₃ BTE, H ₂ BPD C	Zn ₄ O(BTE) _{4/3} (BPDC)	6240	176 ^b	44 ^b	toz		
MOF-5	H ₂ BDC	Zn ₄ O(BDC) ₃	3800	110 ^a	66 ^a	pcu	Solvothermal	80,90
MOF-177	H ₃ BTB	Zn ₄ O(BTB) ₂	4750	110 ^c	47 ^c	pyr	Solvothermal	91,92
DUT-32	H ₂ BPD C, H ₃ BTB TB	Zn ₄ O(BPDC)(BTB) _{4/3}	6411	166 ^b	-	umt	Solvothermal	93
NOT-112	H ₆ L	Cu ₃ (L)(H ₂ O) ₃	3800	100 ^c	50 ^c	rht	Solvothermal	94,95
DUT-49	H ₄ BBC DC	Cu ₂ (BBCDC)	5476	165 ^a	-	fcu	Solvothermal	96
NU-1500-Al	H ₆ PET	Al ₃ (μ ₃ -O)(H ₂ O) ₂ (OH)(PET)	3560	89 ^a	44.6 ^a	acs	Solvothermal	83
NU-1501-Al	H ₆ PET-2	Al ₃ (μ ₃ -O)(H ₂ O) ₂ (OH)(PET-2)	7310	170 ^a	47.9 ^a	acs		
NU-1501-Fe	H ₆ PET-2	Fe ₃ (μ ₃ -O)(H ₂ O) ₂ (OH)(PET-2)	7140	152 ^a	45.4 ^a	acs		
DUT-23(Co)	H ₃ BTB, BIPY	[Co ₂ (BIPY)] ₃ (BTB) ₄	4850	~178 ^a	40 ^a	pto	Solvothermal	97
UMC M-2	H ₂ T ² D C, H ₃ BTB	Zn ₄ O(T ² DC)(BTB) _{4/3}	5200	68.8	-	umt	Solvothermal	98

^aAt 100 bar K ^bAt 80 bar ^c70 bar. H₆BTEI: 5,5',5''-benzene-1,3,5-triyltris(1-ethynyl-2-isophthalic acid); H₆NTEI: 5,5',5''-(4,4',4''-nitrilotris(benzene-4,1-diyl)tris(ethyne-2,1-diyl))trisophthalic acid; H₆PTEI: 5,5'-((5'-(4-((3,5-dicarboxyphenyl)ethynyl)phenyl)-[1,1':3',1''-terphenyl]-4,4''-diyl)-bis(ethyne-2,1-diyl))diisophthalic acid; H₆TTEI: 5,5',5''-(((benzene-1,3,5-triyltris(ethyne-2,1-diyl))tris(benzene-4,1-diyl))tris(ethyne-2,1-diyl))trisophthalic acid; H₃BBC: 4,4',4''-[benzene-1,3,5-triyl-tris(benzene-4,1-diyl)]tribenzoic acid; H₃BTB: 4,4',4''-benzene-1,3,5-triyl-tribenzoic acid; H₂NDC: 2,6-naphthalenedicarboxylic acid; H₃BTE: 4,4',4''-[benzene-1,3,5-triyltris(ethyne-2,1-diyl)]tribenzoic acid; H₂BPDC: biphenyl-



4,4'-dicarboxylic acid; H2BDC: 1,4-benzenedicarboxylic acid H3BTCTB: 4,4',4''-[benzene-1,3,5-triyltris-(carbonylimino)]trisbenzoic acid; H6L: 1,3,5-tris(3',5'-dicarboxy[1,1'-biphenyl]-4-yl)benzene; H4BBCDC: 9,9'-([1,1'-biphenyl]-4,4'-diyl)bis(9H-carbazole-3,6-dicarboxylic acid); H6PET: See ref.⁹⁹; H6PET-2: See ref.¹⁰⁰; BIPY: 4,4'-bipyridine; H2T2DC: thieno[3,2-b]thiophene-2,5-dicarboxylate

Another application of MOF in H₂ industry is their use as molecular sieves to purify H₂^{101,102}. In this context, Ghalei et al.¹⁰³ evaluated the effect of the bulkiness or functionality of organic linkers on the H₂ separation performance of isorecticular series of UiO-66 MOFs utilizing terephthalic acid (H₂BDC) 1,4-naphthalenedicarboxylic acid (H₂NDC), 9,10-anthracenedicarboxylic acid (H₂ADC), 2-amino-terephthalic acid (H₂BDC-NH₂) and 2-bromoterephthalic acid (H₂BDC-Br). In this work it was observed that the bulkier organic ligands (H₂NDC and H₂ADC) significantly enhanced the H₂/CO₂ selectivity of separation to 15.3 and 31.9. While for the H₂BDC linker (the less bulky linker) H₂/CO₂ selectivity was 4.7, so it was concluded that the enhanced separation selectivity was induced by molecular sieving. Furthermore, the incorporation of functional groups did not change the H₂ separation properties.

Production of H₂ in MOFs by electrocatalysis. In line with efforts to develop more sustainable energy technologies, MOFs have demonstrated significant potential for H₂ production through electrocatalytic processes. H₂ production through water electrolysis positions this process as a key candidate for the transition to cleaner energy systems¹⁰⁴. Electrolytic water splitting provides a viable and efficient method for alleviating energy shortages and reducing greenhouse gas emissions through a clean, safe, and straightforward process for H₂ production¹⁰⁵. This process involves two electrocatalytic reactions: the H₂ evolution reaction (HER) occurring at the cathode and the oxygen evolution



reaction (OER) taking place at the anode (see Figure 5), requiring a theoretical voltage of 1.23 V^{106–107}. The HER process is typically described as involving three steps: the Volmer step, where H₂O and an electron form H_{ad} and OH[−]; followed by the H₂ formation, which can occur via the Heyrovsky step, where H₂O, H_{ad}, and an electron yield H₂ and OH[−]; or through the Tafel step, where two H_{ad} combine to produce H₂^{108–110}.

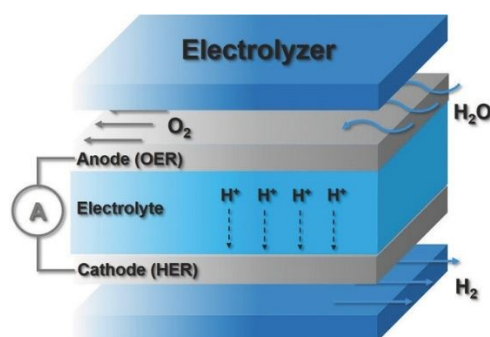


Figure 5. Schematic representation of a water electrolyzer for electrocatalytic water splitting. Reproduced from ref.¹⁰⁷ Copyright 2024 John Wiley & Sons.

The procedure is outlined in the equations below:



In recent decades, noble metals such as platinum (Pt), iridium (Ir), ruthenium (Ru), and rhodium (Rh), have been extensively studied as catalysts for the HER and OER. However, their high cost and limited availability pose significant barriers to widespread adoption in large-scale industrial applications^{111,112}. This challenge underscores the importance of developing affordable and highly efficient electrocatalysts to advance electrocatalytic water splitting, a sustainable process for H₂ production and a promising pathway for clean energy generation^{113,114}. MOFs are regarded as progress toward the practical use of solid catalysts in advanced industrial applications¹¹⁵. MOFs are distinguished by their unique electronic and



structural properties, making them highly promising materials for electrocatalytic applications¹¹⁶.

Naik Shreyanka et al. reported three TM-MOFs known as M–BTC MOF, where M represents Cu, Co, and Ni, and BTC refers to 1,3,5-benzenetricarboxylic acid, which showed improved electrocatalytic activity for water splitting¹¹⁷. Among these, the Co-BTC MOF demonstrated a H₂ production rate of approximately 332.9 μmol/h, highlighting its effectiveness as a catalyst for practical applications in sustainable fuel generation. X-ray photoelectron spectroscopy (XPS) analysis evidence a mixed oxidation states of Co, Co²⁺ (781.30 eV) and Co³⁺ (783.08 eV). This performance of Co-BTC is primarily attributed to its structural properties, featuring unsaturated coordination sites. However, recent studies highlight metal node engineering as a highly effective approach for enhancing the electrocatalytic properties of MOF-based catalysts. Xudong Wen and Jingqi Guan¹¹⁸ emphasize that integrating polymetallic components into MOFs represents a robust approach for electrocatalytic development of MOF-derived materials, a similar approach was used in other metal-based materials such as metallenes¹¹⁹. In this context, two main strategies have been explored: designing polymetallic MOFs composed of transition metal ions (TM-MOFs) and strategically doping TM-MOFs with noble metal species to achieve specific synergistic effects at the metal-centered active sites ^{120,121}

Lin Yang *et al.*,¹²² reported a Fe-doped Ni-MOF, which showed efficiency and durability as an electrocatalyst for oxidizing water in alkaline medium. The Fe-Ni-MOF (labelled as Fe0.1-Ni-MOF/NF) showed an effectiveness for oxygen evolution reaction (OER) in basic medium (1.0 M KOH solution), requiring low overpotentials of 243 and 263 mV to reach 50 and 100 mA cm⁻², respectively. It maintained its catalytic performance for over 20 hours at a high current density of 150 mA cm⁻². Additionally, it achieved high turnover frequency (TOF)



values of 0.018 and 0.086 O₂ s⁻¹ at overpotentials of 250 and 300 mV, respectively. The XPS spectrum showed the existence of the elements Fe, Ni, C, and O, indicating that Fe exists as Fe³⁺ and Ni as Ni²⁺, respectively. This result suggests that MOF based on Ni and Fe shows potential as a viable material to generate an electrode catalyst for water-splitting devices in alkaline conditions for large-scale H₂ production. This mixed-metal strategy within MOFs was also employed by Peng Cheng *et al.*¹²³ to synthesize a bimetallic family of Ni-NKU-101 MOFs. The isostructural bimetallic series, denoted as M_xNi_{1-x}-NKU-101 (X= 0.15; 0.19; 0.22 and 0.24), was prepared by partially substituting Ni centers with Mn, Co, Cu, or Zn ions. Among this series, the Cu/Ni-based systems exhibited the best HER performance. This work demonstrated that the metal ratio significantly influences the electrocatalytic HER activity. The XPS analysis revealed that the inclusions of Cu in Ni-NKU-101 induced an upshift of the electron density around the Cu centers due to their strong tendency to draw electrons from O and Ni atoms. This electron redistribution enhances the adsorption capacity of H₃O⁺, thereby improving HER performance.¹²³ Moreover, from this report it is suggested that the enhanced catalytic performance observed in bimetallic Cu-Ni MOFs can be further attributed to several synergistic factors. These include optimized H₂ binding sites resulting from the combined presence of Cu and Ni, tunable electronic properties achieved by varying the Cu-Ni ratio, and significantly increased surface area facilitated by Cu²⁺ ion exchange. These findings collectively highlight the potential of bimetallic MOFs as promising catalysts for various applications. In this context, Zhang *et al.*¹²⁴ synthesized a series of MOF-74-type frameworks based on Ce, Fe and Ni with organic ligand 2,5-dihydroxyterephthalic acid (DHTA) labeled as Ce_xFeNi-MOF-74 (X=0.50; 0.75; 0.86 and 0.90). These MOFs can be directly used as a working electrode. Among these materials, Ce_{0.9}FeNi-MOF-74 exhibited superior electrocatalytic activity and stability towards both the HER and OER. XPS analysis



revealed the presence of multiple oxidation states of the metals, suggesting synergistic interactions that contribute to the observed catalytic activity. This material achieved overpotentials of 257 mV and 262 mV at a current density of 100 mA cm⁻² for OER and HER, respectively. The reported performance can be considered as an excellent performance for this reaction. Moreover, Ce_{0.9}FeNi-MOF-74 demonstrated excellent stability with negligible voltage decay during a 60-hour continuous operation. This study demonstrates a novel approach for the rational design and synthesis of efficient water splitting polymetallic MOF-based electrocatalysts.

Along these lines, Yilin Wang et al.¹²⁵ report that the incorporation of noble metals into bimetallic MOFs can profoundly modify their local electronic structure. This modification enhances the availability of active sites, refines the electronic configuration, and synergistically facilitates the adsorption and dissociation of intermediates, thereby significantly boosting the catalytic performance of the materials. The development of bimetallic MOFs is therefore needed to enhance the catalytic activity involved in both the HER and OER.

Jianrong Chen *et al.*¹²⁶, synthesized a FeCo-MOF doped with Ru, which showed a good performance in water electrolysis under alkaline conditions. XPS analysis confirmed the successful formations Ru/FeCo-MOF catalysts. The author points out that doping of FeCo-MOF with Ru enhanced the catalytic performance of the material. The inclusion of Ru introduces new active sites and tunes the electronic structure through interactions with Fe and Co. The Ru_{0.04}/FeCo-MOF configuration demonstrated superior activity, achieving a current density of 10 mA cm⁻² with a voltage of only 1.498 V, surpassing RuO₂-based systems. This catalyst also exhibited excellent stability, maintaining 88.9% conversion after 8000 cycles. Notably, the nanosheet-stacked array structure provided a large active surface



area and efficient ion exchange, leading to exceptional performance in both OER (309 mV at 50 mA cm⁻²) and HER (180 mV at 10 mA cm⁻²) under alkaline conditions. Furthermore, the high surface capacitance of 8600 mF cm⁻² underscores its potential in energy storage. These findings highlight a promising strategy for tailoring morphology and electronic structure to develop advanced catalysts for energy conversion and storage applications.

Gugtapeh et.al.¹²⁷ reported a composite material based on a bimetallic MOF (NiCo-MOF) combined with N-doped graphene quantum dots (NGQDs). The NGQD/NiCo-MOF composite was synthesized via a controlled electrodeposition strategy, resulting in a non-noble metal catalyst for alkaline water splitting. The synergy between Ni and Co ions enabled tuning of the electronic structure and an increase in active sites, while the uniform incorporation of NGQDs into the porous NiCo-MOF matrix enhanced local electrical conductivity. The composite exhibited outstanding electrochemical stability, sustaining HER and OER activities for more than 150 hours in 1 M KOH. Additionally, the two-electrode electrolyzer achieved overall water splitting with a low driving voltage of 1.62 V at a current density of 10 mA·cm⁻². These exceptional electrochemical characteristics underscore the promise of NGQD/NiCo-MOF as an efficient MOF-based electrode material for H₂ electrocatalyst. Recent reports by Bin Zhao et al.¹²⁸ have introduced another class of MOF-based heterostructures, combining MXenes with TM-MOFs, resulting in efficient electrocatalysts for the OER. The composite electrocatalyst, obtained from Ni-doped Co-MOF-74 and Ti₃C₂T_x MXene (denoted as CoNi-MOF-74/MXene/NF). This material exhibited exceptional performance for the OER, achieving a current density of 100 mA/cm² at a low overpotential of just 256 mV, accompanied by a Tafel slope of 40.21 mV/dec. In HER catalysis, the CoNi-MOF-74/MXene/NF achieved a current density of 10 mA/cm² at a remarkably low overpotential of 102 mV. Furthermore, a two-electrode electrolyzer utilizing CoNi-MOF-74/MXene/NF as



both the cathode and anode required only 1.49 V to achieve a current density of 10 mA/cm². These results highlight a promising approach for the development of high-performance bimetallic MOF-based electrocatalysts.

Wen Gu *et al.*¹²⁹ explored the catalytic performance of layered double hydroxides (LDHs) integrated with MOFs for the OER. They synthesized a FeNi LDH/MOF heterostructure via a two-step solvothermal method using Fe-soc-MOF as the substrate, followed by Ru doping through a hydrothermal process. The incorporation of Ru was shown to significantly enhance electrochemical activity by modulating the electronic structure and facilitating electron transfer. The resulting material exhibited excellent performance, achieving a low overpotential of 242 mV at a current density of 10 mA cm⁻² and demonstrating stable operation for 48 hours of continuous electrolysis. The high OER efficiency stems from the FeNi LDH/MOF heterostructure exposure of more active sites, with additional new active sites generated through Ru doping.

On the other hand, it is important to highlight that the working conditions could affect material stability. From the mentioned material it was reported that the pH of the working condition used to test co-BTC affects the integrity of the material. However, NiCo-UMOFN¹³⁰, NiMn-MOF¹³¹, Ru@FeNi LDH/MOF, NGQD/NiCo MOF, FeCoMOF¹³², Ce_{0.9}FeNi-MOF-74 does not present any perceptible change on their structure and catalytic capacity under working condition. The above mentioned works demonstrated that the tunability of MOF is a huge advantage to improve the catalytic performance through the modulation of electronic interactions. The insights gained into bimetal non-noble metal MOFs underscore their versatility and promise for the next generation electrocatalysts in energy conversion applications. In addition, it underscores the potential of MOF-based composite materials as versatile platforms for catalytic applications, where their tunable structure and ability to



integrate with diverse components enable the design of high-performance electrocatalysts for efficient and sustainable energy conversion processes.

Production of H₂ in MOFs by photocatalysis. The photocatalytic production of H₂ has been studied since the discovery of the water-splitting reaction in 1972. In this report, the water molecule broke into molecular H₂ and molecular oxygen in the presence of a TiO₂ electrode exposed to ultraviolet radiation¹³³. This method of H₂ production has the advantage of using solar energy, making the process environmentally friendly^{134,135}. However, this represents a limitation because most of the sunlight corresponds to the visible range of light. Consequently, the band gap of the semiconductor, used as photocatalyst, must be narrow enough to absorb solar light efficiently¹³⁶.

In general, the photocatalytic process to obtain H₂ has three main steps. The first one is the absorption of sunlight by the light-irradiated photocatalyst that generates the electronic excitation of the material, causing the transition of electrons from the valence band to the conduction band and the formation of holes in the valence band (known as the electron-hole pairs), which correspond to charge carriers^{135,137}. The second step corresponds to the electron-hole pairs separation and its independent migration to the photocatalyst's surface. The third step of this process consists of the reduction reaction of the electrons in the photocatalyst surface with water to produce H₂. Simultaneously, in the surface, the oxidation reactions occur between the holes and water or sacrificial reagents, denominated scavengers, improving the separation of the charge carriers¹³⁷. Initially, some compounds, such as ZnO, TiO₂, ZnIn₂S₄, Zn₂Ga₂O₄, and CdS, were used as conventional photocatalysts in H₂ production. However, these materials have disadvantages, such as low solar energy harvest due to a large band gap and an insufficient transport capacity of the photogenerated



charge carriers, which cause fast recombination of electron-hole pairs and generates a photocatalytic process with low H₂ production. For this reason, it has been necessary to develop new semiconductor materials with efficient photocatalytic activity in H₂ production capable of overcoming the drawbacks mentioned above^{134,138}. Thus, MOFs gain relevance due to the semiconductor characteristics of their structure, as the organic linkers act as an antenna able to absorb sunlight and transmit it to the metal clusters, where the redox reaction can occur^{139,140}. Despite the advantages of the MOF structures, these materials present the inconvenience of having large band gap value, thus showing absorption of light in the ultraviolet wavelength range.

According to the semiconductor character of the MOFs, it is possible to determine their band gap value by knowing the energy difference between the frontier molecular orbitals of the molecule. Specifically, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO)⁷⁵. Thus, the tunability of the MOF structure plays an important role because, through the incorporation of electronic donor groups, such as amino (-NH₂) or hydroxyl (-OH) in the linker, it's possible to decrease the energy gap between the HOMO and the LUMO. Consequently, the band gap is shifted to lower values, which is associated to the absorption in the visible range of the solar spectrum. This band gap reduction helps MOFs to reach more efficient photocatalyst for H₂ production^{75,141}. An example of the improvement in the photocatalytic properties of MOFs with the incorporation of linkers with electronic donor groups is the case of UiO-66 and UiO-66-NH₂. The first material (UiO-66) is known for showing no activity for the photocatalytic H₂ production in the visible range of light¹⁴². Meanwhile, UiO-66-NH₂ proved to be an active material for H₂ photocatalytic production with a mean production rate of 0.210 μ mol/gh in the visible range of light¹³⁶. Another example is the incorporation of fluor to the linker used to synthesize a



Cu-NH₂ MOF. This approach demonstrated that the incorporation of fluor to the linker structure improve the photocatalytic performance of the material¹⁴³.

Another employed methodology to achieve efficient H₂ production is by avoiding the recombination of electron-hole pairs through the generation of heterojunctions with MOFs.

A heterojunction is the interface result of the union between two different semiconductor materials that can generate a band alignment, due to the similarity of the distinct band structure of each material¹³⁵ (see Figure 6). Thus, a heterojunction resultant of the semiconductor materials combination improves the separation of the charge carriers in the system, diminishing their recombination rate¹⁴⁴. Focused on this topic, several studies have been conducted on the different types of heterojunctions that involve MOF structures.

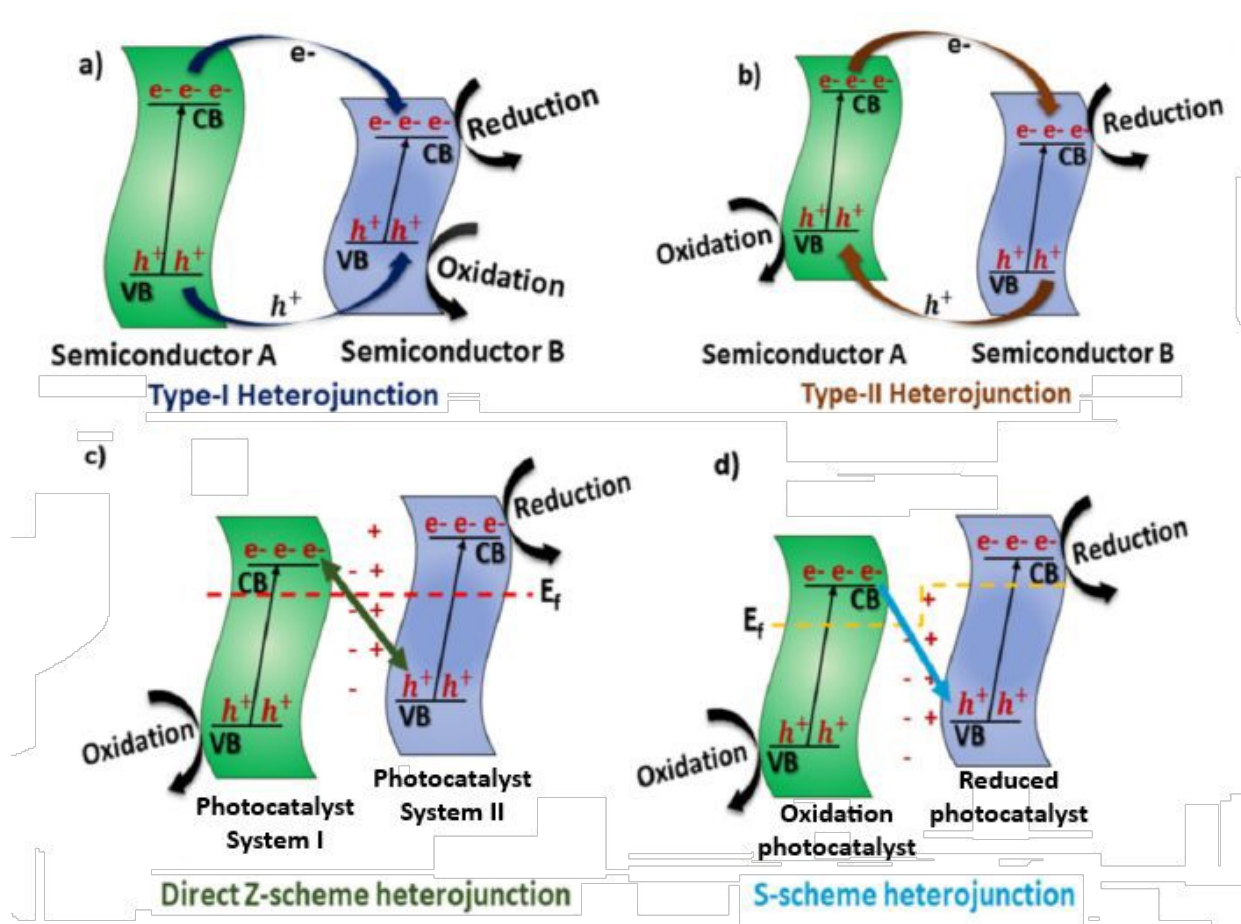


Figure 6: Schematic representations of different types of heterojunctions. a) Type I

heterojunction, b) Type II heterojunction, c) Direct Z-scheme heterojunction and d) S-scheme heterojunction. Modified from¹⁴⁵. Copyright 2024 Elsevier.

One of the band structures in the photocatalyst studied for H₂ production is the type II heterojunctions, where the valence and conduction bands of both semiconductors are staggered. Thus, the photogenerated holes are transferred to the conduction band that has the less positive energy value, while the electrons are transferred to the conduction band with the less negative energy value¹⁴⁶. An example of this type of material is the work realized by Chen et al., which generated a semiconductor with a Type II heterojunction between ZnIn₂S₄ and a MOF with copper metal centers, which was able to produce H₂ with a rate of 0.300 mmol/gh¹⁴⁷. Also, the CdS/UiO-66-NH₂ heterojunction exhibited a H₂ evolution rate of 0.640 mmol/gh¹³⁵. Meanwhile, the heterojunction formed between CuInZnS quantum dots and a nickel-based MOF developed by Deng et al. was able to generate H₂ with a rate of 2.642 mmol/gh.

Alternatives to the type II heterojunctions are the Z-Scheme and S-Scheme. These two heterojunctions solve the low redox capacity of the type II heterojunctions by retaining the electrons in the conduction band^{146,148}. In case of the Z-Scheme, it has been developed materials that include a porphyrin MOF combined with protonated carbon nitride¹⁴⁹ or ZnIn₂S₄¹³⁹. Those combinations generated semiconductor materials with photocatalytic H₂ production rate of 0.200 mmol/gh and 0.284 mmol/gh, respectively. In case of the S-Scheme, different studies have reported materials with heterojunctions, for example, some formed by ZnCdS/MOF-545Co¹⁵⁰ and Cu-MOF/Cd_{0.5}Zn_{0.5}S¹⁵¹, showing a H₂ production rate of 0.148 mmol/h and 18.986 mmol/gh, respectively.



Furthermore, the design of a ternary heterojunction has been studied. An example is the reported by Bi *et. al.* who generated the photocatalytic composite NiS/CdS@DUT-67 with a H₂ production rate of 9.618 mmol/gh¹⁵². In this material, NiS and DUT-67 manage the electron flow direction in the heterojunction and the charge carrier's separation during the photocatalysis, thus, they work as dual cocatalysts of CdS^{141,152}. Besides, an engaging topic is the assembly of heterojunctions between MOFs, denominated MOF/MOF heterojunctions. This was studied using a semiconductor material formed by MIL-167/MIL-125-NH₂ heterojunction. This material shows photocatalytic activity to produce H₂ with a rate of 0.455 mmol/gh that is a better performance than its single components (0.8 and 51.2 μ mol/gh for MIL-167 and MIL-125-NH₂, respectively). To achieve this material, the authors used MOFs with comparable light absorption behavior and ensured the growth of one MOF in the presence of the other previously synthesized MOF to assure the correct electronic contact between the MOFs to generate the heterojunction¹⁵³. Considering the concept of MOF/MOF heterojunctions, Ma *et al.* worked to generate a heterojunction made by two 2D-MOF. Specifically, the material with Ni-BDC/NiTCPP-3 heterojunction shows a photocatalytic H₂ production rate of 0.428 mmol/g¹⁵⁴. It is worth mentioning that the stability of the material is a topic that needs to be more explored in the mentioned works. From these it is mentioned that the presence of TEOA (triethanolamine) as scavenger affects the stability or activity of the material after long-term reactions.

Another interesting way to generate different types of heterojunctions is the use of MOFs as a sacrificial template, that means, generate semiconductors by calcinating MOFs. Some examples of this methodology to obtain photocatalyst for H₂ production are the generation of a carbon-coated nickel phosphide (C-Ni₅P₄) by calcinating a Ni-MOF combined with C-Ni₅P₄/CdS semiconductor and the calcination of ZIF-9 to origin CoP by phosphating method



to generate CoP/In₂O₃ composite. The first one shows a H₂ production rate of 12.283 mmol/gh¹⁵⁵, while the CoP/In₂O₃ composite presents a total production of 0.251 mmol of H₂ in five hours¹³⁷. Moreover, Ouyang et al. have reported the calcination of Co-MOF-74 to produce Co₃O₄/CoO/Co₂P ternary heterojunction with a photocatalytic H₂ production rate of 6 mmol/gh¹⁵⁶. Also, Musa et al. develop doped TiO₂ materials by calcinating MIL-125-NH₂ obtaining a dual photocatalyst capable of producing H₂ with a rate of 0.329 mmol/gh and, at the same time, degrading pollutants in water as herbicides¹⁵⁷.

MOF used for H₂ storage. H₂ storage is the limiting step toward the application of H₂-powered fuel-cell vehicles and their global commercialization¹⁵⁸. The current application of H₂ relies on compressed gas or liquified gas, and both systems require the use of carbon fiber-reinforced tanks that are expensive and potentially unsafe¹⁵⁹. To overcome these limitations the current development of H₂ storage is guided by the directive of US Department of Energy (DOE) which encourages the production of material that can storage 6.5 wt% and 50 g/L under operation conditions which are established as high pressure (5-100 bar) and low temperature (77-160 K). These conditions allow the utilization of an all-metal tank which are safety and practically inexpensive compared with the carbon fiber-reinforced tank¹⁶⁰. Additionally, this condition allows a range of work where the H₂ can be adsorbed by the material at 100 bars and 77 K and desorbed at 5 bars and 160 K, generating a work window which represents the deliverable capacity of the developed material.

Until today several groups have studied the development of material that can store H₂¹⁶¹⁻¹⁶³. MOFs are highlighted in this field due to their high porosity, malleability, and stability. Considering the structure of the MOF, topology, pore size, pore structure and metal composition (open metal sites) are the mayor aspect that impact their capacity to store H₂. In a previous work where the form of the pore was compared, it was demonstrated that the



cage like form presents higher interactions between the material and the H₂ molecule than channel-like pores¹⁶⁴. The size and form of the pore can be studied deeply through reticular chemistry. Reticular chemistry has been a key discipline to develop new MOF material with improved H₂ adsorption capacity^{3,160}. In this sense, the development of NU-1501 was achieved considering a rational design for the topology using an **acs**-a topology to obtain a material with a surface area of 7310 m² g⁻¹. This material presents a H₂ gravimetric adsorption capacity of 14 wt% and a volumetric working capacity of 46.2 g L⁻¹⁸⁹. Furthermore, the application of reticular chemistry has guided different studies to explore different topologies in silico to identify possible material that can store H₂ under the described working condition. Through this theoretical approach a study was conducted to analyze how the variation of their building blocks affects H₂ adsorption of the **rht**-type MOF. From this approach the authors identified the material PCN-61 which has a pore volume and volumetric surface area like MOF-5¹⁶⁵, which is the best performance MOF material for H₂ storage described until today.

On the other hand, the variation of open metal sites has been studied. In a report that used experimental and theoretical approaches to evaluate MOF-74 using Ni²⁺, Co²⁺ and Mg²⁺, it was determined that Ni²⁺ presents the highest volumetric H₂ delivery capacity with 10.74 g L⁻¹. It is important to mention that MOF materials present low interaction capacity with the H₂ molecule at room temperature, due to the low polarizability of the H₂ molecule. To overcome this, the open metal sites in MOFs can be changed by a metal that increases the charge density in the OMS, thus can strongly polarize the H₂ molecule. The ideal range of isosteric heat of adsorption (Q_{st}) of H₂ in MOF is estimated to be between -15 and -25 kJ mol⁻¹¹⁶⁰. One example of the material developed to store H₂ at room temperature is the NU-2100 prepared using Cu⁺¹ which presents a delivery capacity of 10.4 g L⁻¹ under 233 K/100



bar to 296 K/5 bar¹⁶⁶ with a Q_{st} of $-15.7 \text{ kJ mol}^{-1}$. Another example is the $V_2Cl_2(btdd)$ which presents a Q_{st} of $-20.9 \text{ kJ mol}^{-1}$ and a delivery capacity of 26 g L^{-1} at 198 K/250 bar to 313 K/5 bar¹⁶⁷. Finally, the CuIZn-MFU-4l presents a Q_{st} of -33.4 kJ/mol and a delivery capacity of 8.2 g L^{-1} at 298 K/100 bar to 298K/ 5 bar¹⁶⁸. Despite the different developments to improve the H_2 storage capacity and deliverability performance of MOF remains a large way to reach the application of these materials in the H_2 storage system required for light H_2 -powered vehicles. One of the decisive factors is the scalability to reproduce the MOF with the best performance and reach working conditions that adjust to the desirable respect to delivery capacity at room temperature^{169,170}.

Future of MOFs in the real life H_2 storage. As it has been shown in the previous sections, MOFs have shown significant promise in H_2 storage applications due to their high surface areas, tunable pore sizes, and chemical functionalities. There are recent applications of MOFs in H_2 storage devices. As of now, there are limited commercial devices that utilize MOFs for this purpose. However, several notable recent developments highlight progress in this field. In this sense, H_2 MOF is a startup Co-founded in 2021 by Nobel laureate Sir Fraser Stoddart, along with Samer Taha and Omar Yaghi¹⁷¹. H_2 MOF is a California-based startup dedicated to addressing challenges associated with H_2 storage and transportation using MOFs. The company focuses on developing MOF-based solutions to enhance H_2 storage efficiency. Specifically, the company aims to tackle challenges associated with H_2 storage and transportation by leveraging MOFs' ability to store H_2 at lower pressures and higher densities compared to conventional methods like compressed gas cylinders. Their approach focuses on designing next-generation MOFs that improve H_2 uptake efficiency, ensuring safer and more cost-effective storage. The startup's work aligns with global efforts to enhance H_2 infrastructure for fuel cell vehicles and industrial applications. Australian startup



Rux Energy, in collaboration with the University of Sydney, is scaling up the manufacturing of advanced MOF materials for H₂ storage¹⁷². Their focus is on creating highly absorbent, nanoporous MOFs that can significantly increase H₂ storage capacity in tanks. The project aims to develop field trial prototypes for use in heavy trucking and H₂ hubs, addressing the challenges of efficient H₂ storage in large-scale applications. This initiative represents a critical step toward practical, high-capacity H₂ storage solutions necessary for the widespread adoption of H₂ as a zero-carbon fuel. On the other hand, a program focused on engineering MOF composites aims to deliver densely packed, hierarchically porous materials with enhanced H₂ binding sites. These composites are designed to improve workable H₂ storage capacity and are processable through advanced manufacturing techniques for prototype development. The initiative includes testing H₂ storage capacity and resistance to embrittlement, with the goal of identifying promising materials for practical applications. Furthermore, there have been computational advancements in MOF design, where recent studies employing Grand Canonical Monte Carlo simulations have evaluated the H₂ storage capacities of novel Al-nia MOFs at room temperature¹⁷³. These simulations indicate that certain MOFs can achieve the Department of Energy's (DOE) H₂ storage targets, suggesting potential for future practical applications, which need to be experimentally supported. However, the ability to computationally predict MOF performance before synthesis accelerates material discovery, reducing the cost and time needed for experimental testing. There have been also developments of other multi-binding site covalent-organic frameworks (COFs). In this sense, research into COFs with multiple binding sites has shown promises for H₂ storage and delivery at room temperature¹⁷⁴. These materials, related to MOFs, offer tunable structures that can be optimized for enhanced H₂ uptake, presenting a viable pathway toward efficient H₂ storage solutions. This breakthrough suggests that COFs, when



optimized, could provide an alternative pathway to efficient H₂ storage for fuel cells and portable energy applications.

While these developments highlight significant progress, MOF-based H₂ storage solutions still face challenges related to cost, scalability, and long-term stability. However, ongoing research continues to push these materials toward commercial viability. With improvements in material synthesis, computational modeling, and industrial collaboration, MOFs could soon play a critical role in sustainable H₂ storage for transportation, aerospace, and grid energy applications.

Future research should prioritize a deeper understanding of MOF materials for hydrogen storage at ambient temperatures, as current MOFs exhibit very low hydrogen uptake capacities. Additionally, greater emphasis is needed on exploring cost-effective solvents and elucidating the catalytic mechanisms involved. Comprehensive analyses comparing the investment costs and economic feasibility of various hydrogen storage methods are also lacking and need further investigation. Advanced modeling studies that accurately reflect real-world conditions and complexities should be employed to enhance predictive capabilities. Despite progress, the discovery of stable, recyclable, and efficient MOF-based catalysts for low-cost water splitting remains a significant challenge. Therefore, continued research is essential before these technologies can be commercially deployed.

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The data supporting this article have been included as part of the Supplementary Information.

