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Latest developments in the synthesis of metal–organic frameworks and their hybrids for hydrogen storage†

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Metal-organic frameworks (MOFs) are promising materials for hydrogen (H_2) storage due to their versatile structures, high surface areas and substantial pore volumes. This paper provides a comprehensive review of MOF synthesis and characterization, as well as their practical applications for H_2 storage. We explore various MOF synthesis techniques, highlighting their impact on the nanopore structure and functionality. Special emphasis is placed on strategies for enhancing H_2 storage capacities by increasing specific surface areas, optimizing pore size distributions, and facilitating H_2 release by improving thermal conductivity. Key advances in MOF-based hybrids, such as MOFs combined with carbonaceous materials, metals or other inorganic materials, are discussed. This review also addresses the effectiveness of linker functionalization and the introduction of unsaturated metal centers to optimize H_2 storage under ambient conditions. We conclude that the development of competitive MOF-based hybrids, particularly those that incorporate carbons, offers significant potential for improving H_2 storage and recovery, enhancing thermal stability and increasing thermal conductivity. These advancements are in line with the US Department of Energy (DOE) specifications and pave the way for future research into the optimization of MOFs for practical H_2 storage applications.

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1. Introduction

Hydrogen (H_2) is a promising alternative energy carrier due to its potential to reduce greenhouse gas emissions when produced from renewable energy sources. However, efficient and safe storage of H_2 remains a major challenge.¹ Although H_2 has the highest specific energy density, $33.6 \text{ kW h kg}^{-1}$, it also has the lowest volumetric energy density, 0.0108 MJ L^{-1} , measured under standard conditions,² which is 3000 times less than that of gasoline.³ Hydrogen appears to be one of the most promising alternatives to achieve carbon neutrality, offering a clean energy source to replace fossil fuels in industries, transportation and power systems.⁴ Produced from renewables, it enables deep decarbonization and ensures a stable energy supply, driving the transition to a sustainable, low-carbon future.⁵

Storing H_2 at pressures above 70 MPa or at temperatures below $-253\text{ }^\circ\text{C}$ is a possible alternative for increasing H_2

density during transport and storage, but it requires harsh conditions and raises public safety concerns. Adsorption of H_2 at $-196^\circ C$, the boiling point of liquid nitrogen, enables H_2 to be stored at moderate pressures, of the order of 5 MPa, but requires high-surface area materials with a suitable pore size distribution (PSD) and high bulk density.

A wide range of carbon-based materials has been thoroughly studied for H₂ storage, showing that excess H₂ adsorption capacities at room temperature are lower, typically less than 2 wt%, compared with capacities observed at -196 °C, which remain generally below 7 wt%.⁶ For this reason, metal-organic frameworks (MOFs) have emerged as promising candidates for H₂ storage due to their tunable porosity, high surface area and the possibility of tailoring their properties to specific applications.⁷ Excess H₂ storage capacities in the range of 2.4 to 9.1 wt% have been obtained in MOFs with Brunauer-Emmett-Teller (BET) areas (A_{BET}) of up to 6000 m² g⁻¹. The highest H₂ storage capacity reported to date is 9.05 wt% at -196 °C and 7 MPa for NU100.⁸

Due to the limitations of the BET method, these very high A_{BET} values are more indicative of pore volume than the actual surface area. Indeed, when excess H_2 storage capacities at -196°C are plotted as a function of A_{BET} for a large number of MOFs, the observed trend does not follow Chahine's heuristic

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This review aims to provide a comprehensive overview of the current state of research in H₂ storage, using MOFs as materials of interest, focusing on the enhancement of the properties of MOF hybrids, the challenges faced and future prospects, including their potential applications in the energy industry.

MOFs or porous coordination polymers (PCPs) are materials containing metal ions connected by organic linkers to form a 3D network.¹⁴ The metal ions form primary building units (PBUs) with precise geometric structures, linked by secondary building units (SBUs).¹⁵ Commonly used metal ions include Cr^{3+} , Fe^{3+} , Co^{2+} and Zn^{2+} ,¹⁶ with coordination numbers from 2 to 7, yielding various geometries such as linear, T-shaped, tetrahedral, square planar, octahedral, *etc.*¹⁷ Organic linkers, such as carboxylates, phosphates, sulfonates, *etc.*, can form coordination bonds, with fumaric, succinic, and terephthalic acids being low-cost options. Other ligands such as peptides, carbohydrates, amino acids and cyclodextrins are also used.¹⁸ Different classes of MOFs exist, of which “MOFs” is the

- **Non-solvothermal synthesis** takes place at temperatures below the boiling point of the solvent under standard pressure, usually at room temperature.¹⁶ For instance, some widely used MOFs such as MOF-5, MOF-74, MOF-177, HKUST-1, IRMOF-0, MIL-53(Al), MOF-2 and ZIF-7 have been successfully synthesized under ambient conditions.^{24–28} The shape of the crystals obtained and the percentage of purity are strongly influenced by the reaction temperature.²⁹ Yields are also affected by

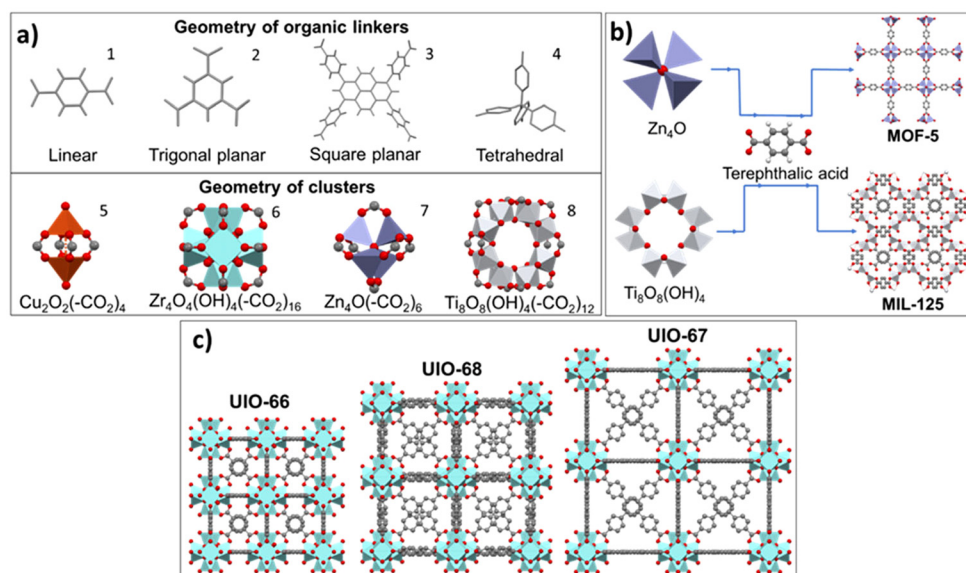


Fig. 1 (a) Geometry of some organic linkers (1: BDC; 2: BTC; 3: H4TBAPY and 4: tetraphenylmethane) (adapted from ref. 12 and 13), and geometry of some clusters; (b) assembly of two different clusters with the same organic linker to obtain two MOFs; (c) assembly of the same cluster ($\text{Zr}_4\text{O}_4(\text{OH})_4(-\text{CO}_2)_{16}$) with 3 linkers to obtain three different MOFs.

temperature, as shown by Lestari *et al.*,³⁰ who reported a 24% yield for HKUST-1 at room temperature *versus* 99% at 120 °C. However, by using ambient temperature, other synthetic routes emerge as alternatives, broadening the horizons for future research.

- **Sonochemical synthesis** uses ultrasound to create nanomaterials with the help of sound-wave-induced bubbles. The small bubbles promote interactions between particles up to 13 eV, leading to significant reactions. The bubble stages – formation, growth and collapse – induce chemical reactions in the synthesis of MOFs.^{31,32} Reaction time has a significant influence on crystal size in sonochemical synthesis. Qiu *et al.*³³ found that short runs (5–10 min) produced spherical nanocrystals of 50–100 nm, while longer runs (30–90 min) produced needle-shaped crystals of 700–900 nm. Vaitsis *et al.* concluded that ultrasound outperforms electrical and microwave heating due to its simplicity, faster reactions and improved energy efficiency, but with the use of organic solvents.³⁴

- **Electrochemical synthesis** was first used to synthesize HKUST-1 in 2005, paving the way for various electrochemical methods and materials design for MOFs, including MOF-5,³⁵ MIL-53,³⁶ MIL-100(Fe)³⁷ and ZIF-8.³⁸ Electrosynthesis is practical and cost-effective, as it operates under milder conditions and within shorter timescales. It offers advantages such as mild reactions, easy operation and efficient charge transfer, which promotes rapid MOF crystal growth.^{35,39} Antonio *et al.*⁴⁰ used electrosynthesis to prepare titanium(III)-based MOFs, namely Ti^{III} -MIL-101 and Ti^{III} -MIL-102, and extended it to other Ti^{III} -MIL structures using TiCl_4 . The materials produced by electrosynthesis showed similar characteristics to the more expensive TiCl_3 , demonstrating its cost-effectiveness. However, electrochemical synthesis often involves organic solvents,

which can potentially impact the surface area, pore volume and thermal stability.⁴¹

- **Microwave-assisted synthesis** is an effective method for high-throughput syntheses, as it heats the material uniformly due to molecular dipolarity and ionic conduction.⁴² Rapid microwave heating can generate hot spots that give rise to metastable materials.⁴³ However, after careful control of the synthesis conditions, this approach increases efficiency as crystals disperse throughout the solution, leading to faster and higher yields due to rapid consumption of reagents.⁴⁴ Although crystals are smaller than with traditional methods, microwave crystallization reduces synthesis time and material use while maintaining the surface area.^{45–47} Wu *et al.*⁴⁸ synthesized conductive, partially carbonized metal–organic frameworks with ruthenium nanoparticles using household microwave ovens. Among them, $\text{Ru}@p\text{-Co3HHTP2-3.2\%}$ exhibited excellent performance in the electrocatalytic H_2 evolution reaction. These studies highlight the potential of microwave-assisted methods for the efficient synthesis of advanced materials with enhanced H_2 -related properties, but they are generally associated with the use of organic solvents.

- **Ionothermal synthesis** uses ionic liquids (ILs) as solvents or templates, resulting in MOFs with a negatively charged skeleton structure. The IL cations are firmly integrated into the MOF framework.⁴⁹ ILs have properties that can be advantageous over traditional solvents, such as their extremely low vapor pressures. They can advantageously replace organic solvents such as *N,N*-dimethylformamide (DMF).⁵⁰ This synthesis can operate at lower temperatures such as 30 °C, consuming less energy than the solvothermal approach. Peng *et al.* synthesized mesoporous Cu-MOF nanoplates using ILs.⁵¹ The resulting material had high crystallinity and combined the pro-

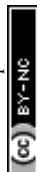
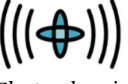


Table 1 Advantages and disadvantages of different MOF synthesis methodologies/strategies

Synthesis method	Advantages	Disadvantages
Solvothermal/hydrothermal 	○ High crystallinity ⁶³ ○ Control of morphology ^{64,65} ○ Control of particle size ⁶⁶	○ Long synthesis times ³⁰ ○ Use of organic solvents ⁶⁷
Non-solvothermal 	○ Energy saving by using room temperature ^{68,69}	○ Low yield ⁷⁰ ○ Use of organic solvents ²⁶
Sonochemical/ultrasound 	○ Control of crystal growth ³³ ○ High yield ^{71,72} ○ Short synthesis times ⁷³	○ Use of organic solvents ⁷⁴
Electrochemical 	○ Easy to scale ⁷⁵ ○ Short synthesis times ^{76,77}	○ Reduction in A_{BET} ^{39,41} ○ Use of organic solvents ⁷⁸
Microwave-assisted 	○ Short synthesis times ^{79,80}	○ Small crystal size ⁴⁴ ○ Use of organic solvents ²¹
Ionothermal 	○ Ionic liquids replace organic solvents ^{81,82}	○ Reduction in A_{BET} ⁸³
Mechanochemical 	○ Solvent-free ^{57,84} ○ Short synthesis times ⁸⁵	○ Difficult to control morphology and particle size ⁸⁶

properties of a mesoporous material with small particle sizes. In 2014, Liu *et al.* introduced an innovative approach for immobilizing ILs into ZIF-8 membranes. ZIF-8's inherent hydrophobicity and ability to act as a template with an ionic liquid effectively confined the IL within the membranes and reduced leaching when exposed to water.⁵²

- **Mechanochemical synthesis** uses mechanical energy, such as compression, shear or friction, to facilitate chemical transformations. This technique is particularly relevant to green chemistry, as it eliminates or reduces the need for solvents.⁵³ Mechanochemical synthesis is a promising method for the large-scale production of MOFs due to its advantages, such as solvent-free reactions at room temperature and relatively short reaction times of 10 to 60 min. Ball milling is the primary process used to crush precursors between balls, resulting in bond breakage, defects and increased reactivity.^{54,55} Over the past decade, mechanochemical synthesis of MOFs has performed well compared with conventional techniques, as shown in reviews⁵⁶ or book chapters.⁵⁷ Although ball milling is widely used, it has limitations such as sample damage and non-uniform mixing. Other methods, such as RAM, can overcome these problems. RAM uses low-frequency, high-intensity acoustic energy to gently mix materials without physical contact with balls.⁵⁸ Titi *et al.* demonstrated that the RAM

technique is more advantageous than ball milling for synthesizing ZIF-L, ZIF-8 and HKUST-1.⁵⁹ RAM enables larger batches to be synthesized while retaining control over product composition and particle size.

MOF formation, layout and shape are affected not only by the building blocks, but also by factors such as solvent, pH, temperature, reagent concentration, reaction time, molar ratios, counter ions and pressure. These factors fall into two categories (Fig. S3b†): (1) compositional parameters – solvent, pH, molar ratios, counter ions, and concentration; and (2) process parameters – pressure, time, and temperature.⁶⁰ In assembly processes, solvents coordinate with metal ions or integrate into the lattice.⁶¹ Although they do not integrate directly into the MOF, solvents play a role in structure orientation and crystal growth. The choice of solvent influences ligand deprotonation, which in turn has an impact on the MOF structure.⁶⁰ For instance, using different solvents, Banerjee *et al.* revealed various crystal structures in MOFs synthesized with magnesium and 3,5-pyridine dicarboxylic acid (PDC).⁶² Water coordinated best with magnesium, but the maximum A_{BET} value achieved was $52 \text{ m}^2 \text{ g}^{-1}$. Acidity/basicity has a significant influence on the crystallization and growth of inorganic–organic composite materials. pH has an impact on ligand deprotonation, strengthening the bond between ligands



and metal ions through pH adjustments.⁶⁰ Temperature also has a significant impact on MOF characteristics, as demonstrated by Biemmi *et al.*, who found that temperature variations (from 75 to 180 °C) altered the morphology and purity of HKUST-1.²⁹

Synthesis time has a significant effect on MOFs' crystal size, as shown by Xu *et al.* who synthesized MOF-808 at 120 °C using ZrCl_4/BTC (3:1 ratio) for 36–96 h.⁸⁷ During the first 36–72 h, A_{BET} and micropore volume increased from 1052 to 2177 $\text{m}^2 \text{g}^{-1}$ and from 0.30 to 0.72 $\text{cm}^3 \text{g}^{-1}$, respectively. After 72–96 h, A_{BET} and micropore volume decreased to 968 $\text{m}^2 \text{g}^{-1}$ and 0.28 $\text{cm}^3 \text{g}^{-1}$, respectively. Suresh *et al.*⁸⁸ studied various process parameters to optimize MOF synthesis for H_2 storage. The researchers investigated the effect of reagent concentration, temperature and reaction time on crystal size distribution. Shorter reactions (12–18 h) at higher temperatures (110–150 °C) produced cubic crystals with a wide size distribution (200–1300 μm), whereas longer reactions (24–72 h) at lower temperatures (60–90 °C) produced crystals with a narrower size distribution and with a 15% reduction in A_{BET} .

2.2. MOF characterization

Characterizing MOFs is a crucial step in understanding their structure and properties. The main techniques to characterize a MOF are as follows: X-ray diffraction (XRD), to identify the crystal structure and unit cell dimensions; scanning electron microscopy (SEM), which provides images of surface morphology and particle size distribution (Fig. 2a); thermogravimetric analysis (TGA), to determine thermal stability and weight loss behavior upon heating (Fig. 2c); gas sorption analysis, to determine pore volume, pore size distribution and the surface area (Fig. 2b); Fourier-transform infrared spectroscopy (FTIR), to identify functional groups present; and elemental analysis to find out the composition of the MOF, usually in terms of carbon, nitrogen and oxygen contents. These analyses provide valuable information on the physical and chemical properties of MOF materials. This information is crucial for understanding their potential applications.

Other promising but less explored techniques are described in Fig. 2. Confocal fluorescence microscopy has the unique ability to capture three-dimensional images at the level of individual crystals (Fig. 2e), while offering the sensitivity needed to investigate the initiation of defect formation. Raman spectroscopy provides detailed information on the molecular vibrations and vibrational modes present in a material, which can be useful for studying the structure, composition and properties of MOFs. Confocal laser scanning microscopy can be used to observe the stability of MOF hybrids if they contain a fluorescent component such as carbon dots (CDs). XPS spectra are used to analyze the elemental composition and chemical state of a material's surface, to confirm the doping of a MOF (Fig. 2d), and nuclear magnetic resonance (NMR) can be used to study the structure of organic components in MOFs and the interaction between organic molecules and metal ions (Fig. 2f).

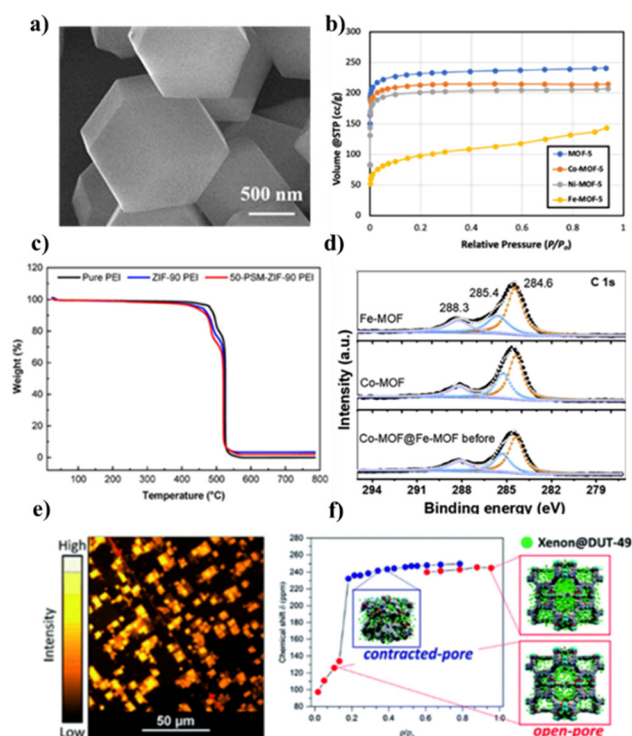


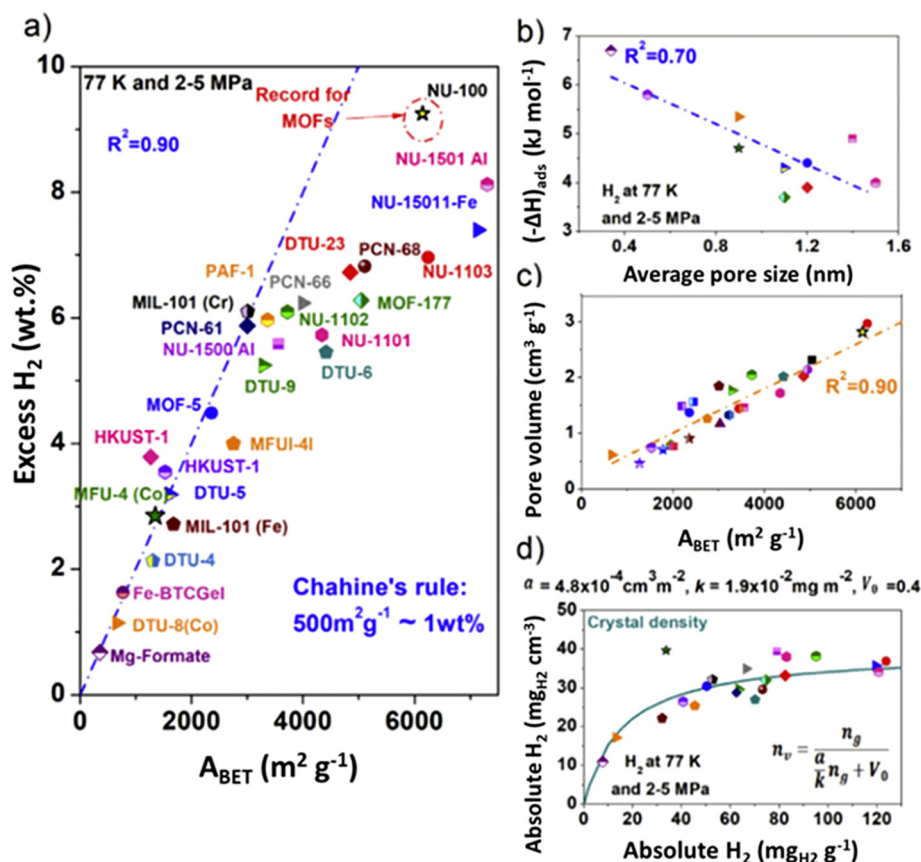
Fig. 2 Main MOF characterization techniques: (a) SEM images of ZIF-8 (reproduced from ref. 89 © 1996–2024 MDPI); (b) nitrogen adsorption isotherms at -196 °C of MOF-5 and doped MOF-5 (reproduced from ref. 90 © 1996–2024 MDPI); (c) TGA of pure PEI, ZIF-90 PEI and 50-PSM-ZIF-90 PEI membranes (reproduced from ref. 91 © 1996–2024 MDPI); (d) XPS spectra of Fe-MOF, Co-MOF, Co-MOF@Fe-MOF, and the hybrid MOF (reprinted with permission from ref. 92; Copyright © 2024 with permission from Elsevier. Also Lancet special credit, reprinted from The Lancet from ref. 92; Copyright © 2024 with permission from Elsevier); (e) confocal fluorescence imaging of defects in a MOF-5 single-crystal (reproduced from ref. 93 © 1999–2024 John Wiley & Sons, Inc. or related companies); (f) chemical shift of xenon adsorbed in DUT-49 at -73 °C measured during the adsorption experiment (red symbols indicate DUT-49op signals; blue symbols indicate DUT-49cp signals) (reprinted with permission from ref. 94; Copyright(2017) American Chemical Society).

3. Fundamental properties and performance of MOFs for hydrogen storage

The characteristics required to design the ideal MOF for H_2 sorption have been reported in several studies.^{15,95,96} In general, MOFs must have a high surface area and a large number of relatively small, interconnected pores to maximize H_2 adsorption. Low-density MOFs are disadvantageous as they can lead to weak H_2 – H_2 interactions in the channels, reducing adsorption capacity. Additionally, volumetric H_2 storage capacities are also reduced. When used near room temperature, the inner surface of MOFs must feature local polar groups to enhance interactions between MOFs and H_2 molecules, and this requirement relates specifically



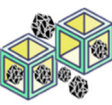
Fig. 3c illustrates a linear relationship between SSA and pore volume for different MOF families. This behavior was previously reported by Gómez-Gualdrón *et al.*, who calculated the A_{BET} of microporous and mesoporous MOFs.⁹⁹ In Fig. 3d, absolute volumetric H_2 adsorption is plotted against absolute gravimetric H_2 , showing that for MOFs with high BET areas, a plateau in H_2 uptake on a volumetric basis is reached. The latter was determined using the following equation, deduced



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Table 2 Advantages and disadvantages of different MOF hybrids

Hybrids	Advantages	Disadvantages
Interpenetrated MOFs (IMOFs) 	○ Improved framework stability¹⁵⁴ ○ Larger adsorption selectivity¹⁵⁵	○ Surface area potentially decreased¹⁵⁶
MOF-on-MOF 	○ Properties of different MOFs combined¹⁵⁷	○ Difficult synthesis¹¹
MOF/carbon-based materials 	○ Increased A_{BET}¹⁵⁸ ○ Increased H_2 adsorption ($-196\text{ }^\circ\text{C}$)¹⁵⁹ ○ Increased thermal conductivity¹⁴³	○ Decreased crystallinity¹⁵⁹
MOF/metal particles and ions 	○ Increased H_2 adsorption ($25\text{ }^\circ\text{C}$)¹⁶⁰ ○ Enhanced adsorption enthalpy¹⁶¹	○ Decreased surface area¹⁶²

4.1. MOF@MOF hybrids for hydrogen adsorption

MOF@MOF hybrids refer to materials composed of two MOFs combined into a single system. By combining two MOFs, it is possible to achieve various advantages aimed at increasing H_2 adsorption capacity, such as reducing pore size, increasing gas selectivity and improving MOF stability.^{168,169} Fig. 5 shows the influence of combining two MOFs on H_2 adsorption at $-196\text{ }^\circ\text{C}$ and $25\text{ }^\circ\text{C}$. Combining MOFs by interpenetration can have a reducing effect on the SSA of the resultant hybrids. However, all samples show an increase in H_2 adsorption.

4.1.1. Interpenetrated MOFs (IMOFs). The presence of large pore spaces in the MOF system can be associated with instability and subsequent collapse of the structure. To solve this problem, interpenetration (also called catenation or interweaving) can be used, as it allows the entanglement of two identical MOFs (homo IMOFs) or two different MOFs (hetero IMOFs) that are not directly connected but cannot be separated without breaking bonds^{154,170–172} (Fig. 4). Interpenetration minimizes vacant zones and has the potential to significantly improve framework stability. It allows empty spaces to be occupied and generates repulsive forces that prevent individual networks from collapsing. Consequently, the synthesis of MOFs with adjustable pore sizes using elongated organic linkers poses considerable challenges, as the formation of interwoven frameworks should be preferred to improve stability.¹⁷³ Catenation can be used to produce materials with fine pores and enhance adsorption heat by increasing the overlap of attractive potential between opposing pore walls. As a result, the interpenetrated framework shows a significant reduction in pore size, resulting in stronger interaction with H_2 molecules.¹⁰⁰

Ma *et al.* (2007) investigated the effect of interpenetration on H_2 adsorption in PCN-6, a porous coordination network. The N_2 adsorption isotherm at $-196\text{ }^\circ\text{C}$ shows that the non-

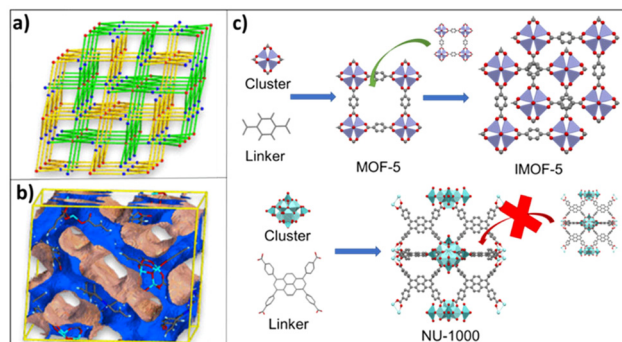


Fig. 4 (a) Topological representations of interpenetration along the *a*-axis; (b) the 1D channel viewed along the *a*-axis (a) and (b) reproduced from ref. 174, with these figures having been published in *CCS Chem.* [2022]; [Ultrahigh hydrogen uptake in an interpenetrated Zn_4O -based metal-organic framework] is available online at <https://10.31635/ccschem.021.202000738>; (c) simplified topology of an interpenetrated MOF-5 and the impossibility of NU-1000 interpenetration.

interpenetrated material has a Langmuir surface area of $2700\text{ m}^2\text{ g}^{-1}$, while the interpenetrated material has a Langmuir surface area of $3800\text{ m}^2\text{ g}^{-1}$, representing a 41% increase. Interpenetration resulted in a 133% increase in volumetric H_2 uptake (3.94 kg m^{-3} for non-interpenetrated frameworks vs. 9.19 kg m^{-3} for interpenetrated frameworks) and a 29% increase in gravimetric H_2 uptake (1.35 wt% for non-interpenetrated frameworks and 1.9 wt% for interpenetrated frameworks).¹⁸⁵

Jiang *et al.* also used a MOFMC for H_2 storage, an interpenetrated MOF-5@Multi-Walled Carbon Nanotubes (MWCNTs), called Int-MOFMC-meso.¹⁷⁵ The latter was able to store 2.02 wt% H_2 at $-196\text{ }^\circ\text{C}$ under 1 bar. This value is higher than those obtained for the aforementioned MOFMC materials and indicates better thermal and moisture stability. However, the



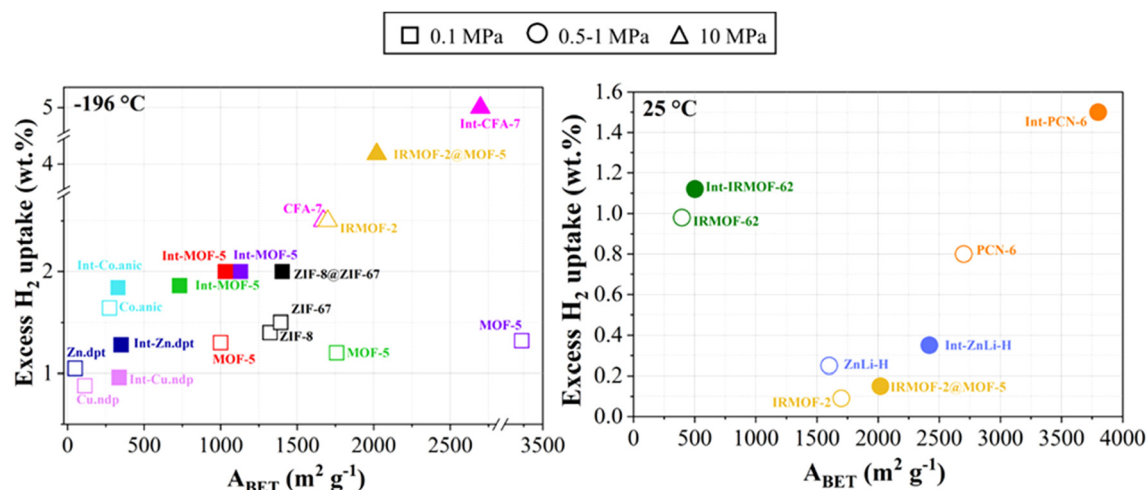


Fig. 5 Excess H_2 storage capacities of MOFs and their MOF@MOF hybrids at -196 °C (left) and 25 °C (right). (□, ■ ref. 175); (□, ■ ref. 176); (□, ■ ref. 177); (□, ■ ref. 178); (□, ■ ref. 174); (□, ■ ref. 100); (○, ●, △ ref. 179); (□, ■ ref. 180); (□, ■ ref. 181); (○, ● ref. 182); (○, ● ref. 183); (○, ● ref. 184).

A_{BET} was significantly lower than that of previous MOFMCs: $805 \text{ m}^2 \text{ g}^{-1}$. According to the authors, the pores were not filled with zinc species or solvent, but it was the presence of an interpenetrated structure and the unsaturated metal site present on the mesopore surface that improved H_2 storage performance, even with a lower A_{BET} .¹⁷⁵

4.1.2. MOF-on-MOF. Extensive studies on MOFs have led to the development of a promising class of hybrid materials known as MOF-on-MOF, as shown in Fig. 6a. The left-hand side of the figure shows the original MOF seed, while the right-hand side displays the MOF grown as a secondary layer. This demonstrates how two or more MOF units are combined to create a new hybrid material.¹⁸⁶ This approach results in unique properties that can be customized for specific appli-

cations. This method enables the distinct properties of different MOFs to be combined, such as high porosity, specific functionality or catalytic activity, and can also improve the stability and mechanical properties of the resulting material.¹⁸⁷

In general, there are two main approaches for synthesizing MOF-on-MOF structures. The first approach involves a two-step process, with pre-synthesized host MOFs used as seeds in the first step, and guest MOFs are grown on them in the second step to form MOF-on-MOF structures. The second approach involves a one-pot process that controls the nucleation and growth kinetics of both host and guest MOFs.¹¹

The growth of guest MOFs can occur *via* five mechanisms, namely: epitaxial, heteroepitaxial, surfactant-assisted, nucleation kinetic-guided, and ligand/metal ion-exchange growth.^{11,190} However, current MOF-on-MOF systems mainly focus on compositions consisting of two or more components¹⁸⁸ (Fig. 6a and b). For example, Ikigaki *et al.* reported a ternary MOF-on-MOF copper structure,¹⁹¹ composed of an oriented MOF-on-MOF film, with lower and upper MOF layers. The films were created by epitaxially matching the interface and “one-pot” and liquid-phase epitaxy methods for the layers with copper-based reactants.

To assess the interaction between MOFs involved in MOF-on-MOF hybrids, their structures can be studied using SEM images, and element mapping enables their structures to be investigated through morphology analysis of two or more MOF varieties (see Fig. 6c–f). By integrating the aforementioned properties of various MOFs into MOF-on-MOF systems, it is possible to control gas adsorption capacity and selectivity while improving adsorbent stability.¹¹

Li *et al.* developed a MOF-on-MOF structure specifically designed for gas adsorption. The structure comprised a core composed of a mixture of bio-MOF-11 and bio-MOF-14, while a bio-MOF-14 shell encapsulated the core. Water stability testing confirmed that the hydrophobic bio-MOF-14 shell pro-

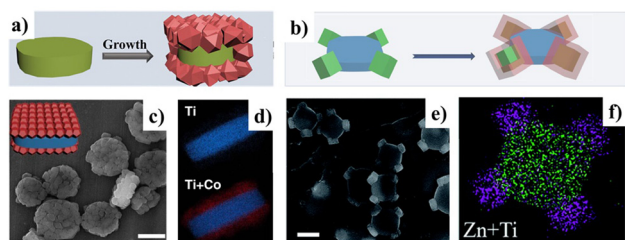


Fig. 6 (a) Scheme of a binary MOF-on-MOF heterostructure (reproduced from ref. 157; Copyright © 1999–2024 John Wiley & Sons, Inc. or related companies); (b) scheme of a ternary MOF-on-MOF heterostructure (ref. 188, reprinted with permission as indicated in the Terms and Conditions of the license); (c) SEM image of MOF MIL-125@ZIF-67 (ref. 188, reprinted with permission as indicated in the Terms and Conditions of the license); (d) element mapping image of MIL-125@ZIF-67 (reproduced from ref. 188, reprinted with permission as indicated in the Terms and Conditions of the license); (e) SEM image of MIL-125@ZIF-8 (reproduced from ref. 189 with permission from the Royal Society of Chemistry); (f) elemental mapping image of MIL-125@ZIF-8 (reproduced from ref. 189 with permission from the Royal Society of Chemistry).

4.2. MOF hybrids with carbon-based materials or metals

Fig. 7 shows the various possible synthesis approaches for obtaining a MOF hybrid, including covalent modification at metal nodes (Fig. 7a) or organic ligands (Fig. 7b), encapsulation (Fig. 7c), layer-by-layer deposition (Fig. 7d), or nucleation in the presence of other materials (Fig. 7e).¹⁹⁶

MOF hybrids can be synthesized by various methods, such as *in situ* growth, post-synthetic modification and physical mixing.^{180,197,198}

- ***In situ* growth:** In this approach, carbon-based materials or metals are incorporated into the MOF structure during MOF synthesis. These materials can therefore serve as nucleation sites for MOF crystal growth, and their presence can influence the morphology, structure and properties of the resulting MOF hybrid. The designation for this approach is MOF@A, with “A” being another material that forms a non-covalent interaction between the two components. Alfe *et al.* used graphene-like (GL) materials to prepare HKUST-1@GL, MIL-96(Al)@GL and MIL-101(Fe)@GL by *in situ* growth. The materials obtained achieved good selectivity for CO₂ over CH₄ using MOF@GL

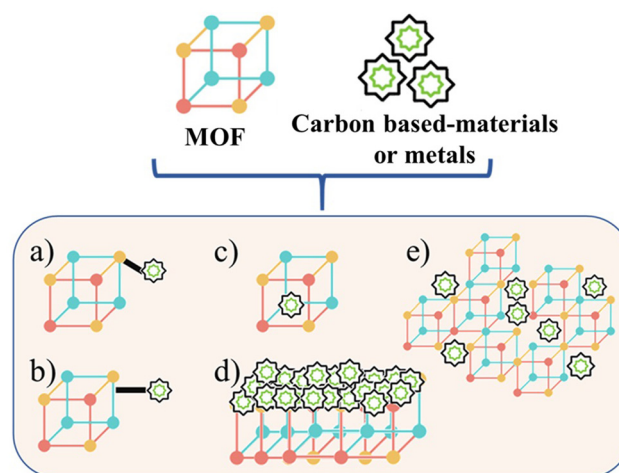


Fig. 7 Scheme of hybrid materials based on MOFs and carbons or metals: (a) covalent modification at metal nodes; (b) covalent modification at organic ligands; (c) encapsulation; (d) layer-by-layer deposition; and (e) nucleation in the presence of other materials (adapted from ref. 196).

hybrids.¹⁹⁹ Pt and Au nanoparticles were used as nucleation sites during ZIF-8 synthesis, enabling Pt and Au nanoparticles to be encapsulated.²⁰⁰ He *et al.* synthesized MOF-5@Au²⁰¹ and Liu *et al.* synthesized UIO-66@Pt using a one-pot method in which the nanoparticles and MOFs were synthesized simultaneously.²⁰²

- **Post-synthetic modification:** In this approach, pre-synthesized MOFs are modified by introducing carbon-based materials or metals onto the MOF surface or into its pores once MOF synthesis has been completed. Post-synthetic modification methods allow other materials with specific properties or functionalities to be introduced into MOFs without altering the MOF structure.²⁰³

Covalent modifications encompass both coordinated covalent modifications of metal clusters and covalent modifications of ligands. By employing covalent modification techniques, it is possible to synthesize MOF hybrids with small molecules, metals/metal clusters, covalent organic frameworks (COFs), polymers and graphene.^{196,203} Rao *et al.* developed a composite membrane combining graphene oxide (GO) and UiO-66-NH₂ by tethering UiO-66-NH₂ to GO surfaces. The covalent attachment of UiO-66-NH₂ with GO enabled the creation of a continuous proton transfer channel, contributing to the high performance of the composite membrane.²¹⁵

Post-synthetic modification also includes techniques such as coating, layering and other methods that do not rely on the formation of covalent bonds. For instance, Chen *et al.* developed a material comprising perovskite quantum dots (QDs) encapsulated in HKUST-1 by immersing HKUST-1 thin films in solutions containing QD precursors. QDs of 1.5–2 nm matched the pore size of HKUST-1 and the resulting material improved its stability under 70% relative humidity, whereas QDs alone decomposed under the same conditions.²¹⁶ Villajos *et al.* obtained a ZIF-8@Pd hybrid by synthesizing Pd nano-

particles in the presence of commercial ZIF-8²¹² and Hu *et al.* followed a similar route to obtain HKUST-1@Pd.²⁰⁹

- **Physical mixing:** This approach involves simply mixing MOFs and carbon-based or inorganic materials without any covalent or coordination bonds between them. This approach is relatively simple and straightforward but may result in phase separation or weak interactions between MOFs and other materials. Otal *et al.* stated that the inherent characteristics of MOFs, including crystallinity, structure and porosity, were maintained even after the modification of pre-synthesized MOFs.²¹⁷ Some studies confirm a significant improvement in H₂ sorption capacities when MOFs are mixed with carbon-based materials.^{163,218} Prasanth *et al.* clearly demonstrated a substantial improvement in the H₂ sorption capacities of MIL-101 samples through the incorporation of Single-Walled Carbon Nanotubes (SWCNTs). H₂ sorption capacities increased from 6.4 to 9.2 wt% at −196 °C and 6 MPa and from 0.2 to 0.6 wt% at 25 °C and 6 MPa.²¹⁸ In their feature article, Szczeniński *et al.* studied the incorporation of GO into different MOF matrices such as HKUST-1 and MIL-101(Cr). They observed that the presence of GO can significantly increase their surface area and influence their morphology and structure. The dense atomic structure of GO contributes to stronger dispersion interactions and a greater number of unsaturated coordination bonds when combined with MOFs, which is crucial for improving adsorption properties.¹⁶³

4.2.1. MOF hybrids with metal particles and ions for hydrogen storage. One of the most attractive structural features of some MOFs is coordinative unsaturation, which can be achieved by introducing additional terminal ligands bound to metal clusters.²¹⁹ Fig. 8 shows the influence of ion and metal particle doping on H₂ adsorption. The addition of ions or nanoparticles often reduces the SSA of the hybrid, calling into question the reliability of using the BET area as an indicator of

H₂ storage capacities in MOFs and MOF-derived materials. However, all samples show an increase in H₂ adsorption, especially at room temperature (25 °C). To improve H₂ storage, it is thus crucial to design novel MOF materials that not only have customized pore sizes and substantial void volumes, but also contain highly efficient adsorption sites. Among these sites are exposed metal ions, whose binding enthalpy lies between −20 and −30 kJ mol^{−1}.¹⁶¹

- **Metal ion doping of MOFs:** Metal ions can be introduced into the MOF matrix by ion exchange procedures as well as by chemical reduction methods, with the aim of increasing the adsorption enthalpy. Peedikakkal *et al.* showed that metal-exchanged MOF-5@Ni and MOF-5@Co exhibit slightly higher H₂ uptake (about 5 wt%) compared with the parent MOF-5.⁹⁰ Adsorption results by Prabhakaran and Deschamps revealed a substantial increase in the H₂ uptake capacity of MIL-101 thanks to the synergistic modification involving activated carbon and lithium doping (at both −196 °C and 25 °C). The H₂ storage capacity (−196 °C, 1 bar) of the doped MOF (MIL-101@AC-Li) showed an H₂ uptake of 1.60 wt% compared with 1.20 wt% in undoped MIL-101.²⁰⁴ Prabhakaran *et al.* demonstrated that Li⁺ doping (830 ppm) of MIL-101@SWCNTs improved H₂ uptake by more than twofold (4.96–10.43 mg g^{−1}) at 25 °C and 90 bar.¹⁶⁰

- **Metal nanoparticles on MOFs:** The synthesis of MOF hybrids with metal nanoparticles involves incorporating the latter into the MOF structure using template methods or pre-synthesis strategies. This introduction effectively increases the number of adsorption sites, boosts adsorption enthalpy and enables synergistic physical–chemical H₂ adsorption. In particular, MOF@Pd hybrids have received considerable attention because Pd can absorb large amounts of H₂ at ambient temperature and pressure. Cheon *et al.* reported that H₂ sorption capacity was increased to 1.48 wt% at −196 °C and 1 atm, com-

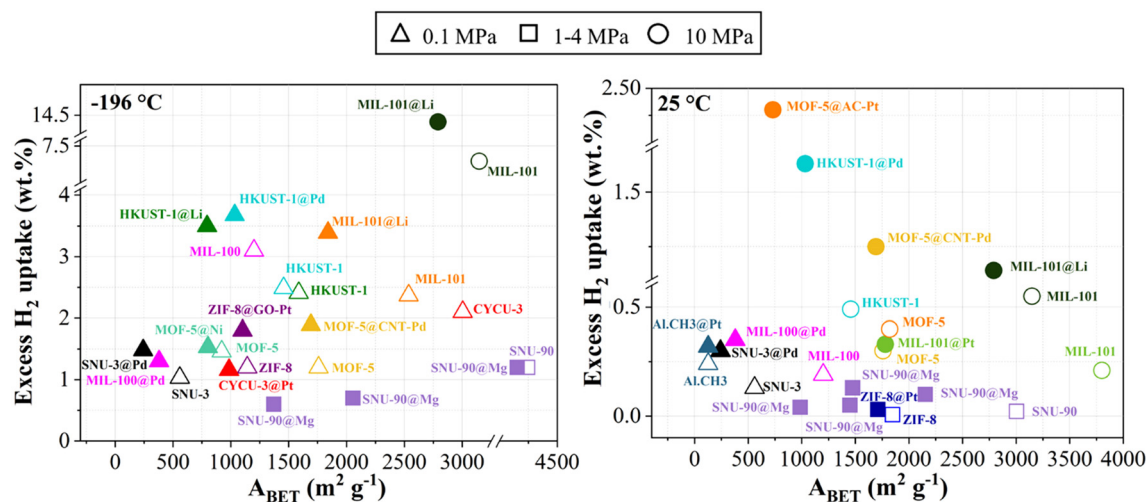


Fig. 8 Influence of adding metal particles into MOFs on the H₂ storage capacities of the resultant hybrid materials (●○ ref. 204); (△, ▲, △ ref. 205); (△, ▲ ref. 206); (△, ▲, ○ ref. 207); (○, ●, △ ref. 90); (□, ▲ ref. 208); (○, ●, △ ref. 209); (△, ▲ ref. 210); (○, ● ref. 211); (□, ▲ ref. 212); (△, ▲ ref. 213); (△, ▲ ref. 214).

pared to 1.03 wt% for pure SNU-3 MOF (despite a 43% decrease in the surface area).¹⁶² Zlotea *et al.* showed that the MIL-100(Al)@Pd hybrid doubled H₂ uptake compared with the original MOF at room temperature.²⁰⁶ Yang *et al.* loaded Pt into MOF-5@CNT hybrids to further increase H₂ storage capacity. The hybrid was prepared by *in situ* incorporation of the as-prepared Pt-loaded MWCNTs into MOF-5 crystals. Four materials were evaluated in terms of H₂ uptake: MWCNTs ($A_{\text{BET}} = 147 \text{ m}^2 \text{ g}^{-1}$), MWCNTs-Pt ($A_{\text{BET}} = 124 \text{ m}^2 \text{ g}^{-1}$), MOF-5 ($A_{\text{BET}} = 1758 \text{ m}^2 \text{ g}^{-1}$) and MOF@MWCNT-Pt ($A_{\text{BET}} = 1692 \text{ m}^2 \text{ g}^{-1}$). The authors studied H₂ uptake at -196°C and 1 bar, as well as 25°C and 100 bar. The highest H₂ uptake (-196°C and 1 bar) was observed for MOF@MWCNT-Pt with 1.89 wt%, followed by MOF-5 with 1.20 wt%. At 25°C and 100 bar, MOF@MWCNT-Pt showed much higher H₂ uptake values compared to the other materials, reaching 1.25 wt%.²⁰⁷

Prabhakaran and Deschamps synthesized a hybrid MOF by incorporating an AC, namely NORIT-RB3, during the synthesis of MIL-101, as well as lithium at different concentrations. H₂ adsorption capacities were evaluated at -196°C and 25°C , using pressures up to 100 bar. The highest H₂ uptakes were obtained for the MIL-101-B@AC-Li material, with 14.4 wt% at -196°C and 1.1 wt% at 25°C , both at 100 bars. Although the A_{BET} of the MIL-101-B@AC-Li material was much lower, $2791 \text{ m}^2 \text{ g}^{-1}$ than those of MIL-101, $3148 \text{ m}^2 \text{ g}^{-1}$, and MIL-101@AC, $3458 \text{ m}^2 \text{ g}^{-1}$, and slightly lower than that of MIL-101-A@AC-Li, $2958 \text{ m}^2 \text{ g}^{-1}$, all of these hybrids provided H₂ uptake capacities $>100 \text{ mg g}^{-1}$ (10 wt%) at -196°C . However, the significantly lower A_{BET} value of MIL-101-C@AC-Li ($1868 \text{ m}^2 \text{ g}^{-1}$) compromised higher H₂ uptakes, reaching a maximum of 87.70 mg g^{-1} at -196°C .²⁰⁴

4.2.2. MOF hybrids with carbon materials for hydrogen storage. In this section, we examine how the addition of carbon materials improves the properties relevant to H₂ storage described in section 3.

- Increase in surface area: The addition of carbon-based materials to the MOF matrix often increases the SSA of the resulting MOF hybrid, enhancing its adsorption capacity at cryogenic and near-ambient temperatures.^{199,204,220–222,226,227}

Fig. 9 shows the effect of the BET area on H₂ adsorption for pure MOFs and for MOF hybrids with carbon-based materials at different storage pressures.

Yang *et al.* prepared MOF-5@MWCNT hybrids using acid-treated MWCNTs and MOF-5. The resultant materials exhibited a higher Langmuir specific surface area, from 2160 to $3550 \text{ m}^2 \text{ g}^{-1}$, resulting in an approximately 50% increase in H₂ storage capacity at 25°C and 95 bar (from 0.3 to 0.6 wt%) and a 25% increase in H₂ storage capacity at -196°C and 1 bar (from 1.2 to 1.5 wt%). Furthermore, these hybrids demonstrated significantly improved stability in the presence of ambient moisture.¹³¹ Petit *et al.* synthesized copper-based MOF@graphite oxide hybrids, and four materials were evaluated for H₂ adsorption: HKUST-1, HKUST-1@GO (5 wt%), HKUST-1@GO (9 wt%), and HKUST-1@GO (18 wt%). A_{BET} and H₂ uptake were $990 \text{ m}^2 \text{ g}^{-1}$ and 2.2 wt% for HKUST-1, $989 \text{ m}^2 \text{ g}^{-1}$ and 2.4 wt% for HKUST-1@GO (5 wt%), $1002 \text{ m}^2 \text{ g}^{-1}$ and 2.2 wt% for HKUST-1@GO (9 wt%), and $996 \text{ m}^2 \text{ g}^{-1}$ and 2.0 wt% for HKUST-1@GO (18 wt%), respectively. The authors attributed the improved uptake to the formation of new small pores for the hybrids.²²¹

Prasanth *et al.* incorporated SWCNTs into MIL-101, and the best-performing material, incorporating 8 wt% of SWCNTs, presented H₂ sorption capacities of 9.2 wt% (at -196°C and 6 MPa) and 0.6 wt% (at 25°C and 6 MPa) compared with 6.4 wt% and 0.2 wt%, respectively, for the pristine MIL-101. Although this material has a slightly lower SSA, the authors ascribed these higher H₂ sorption capacities to the reduction in pore size and the increase in micropore volume in the hybrid due to the incorporation of SWCNTs.²¹⁸ Liu *et al.* hybridized Cu-MOFs with graphene oxide (GO) and achieved about

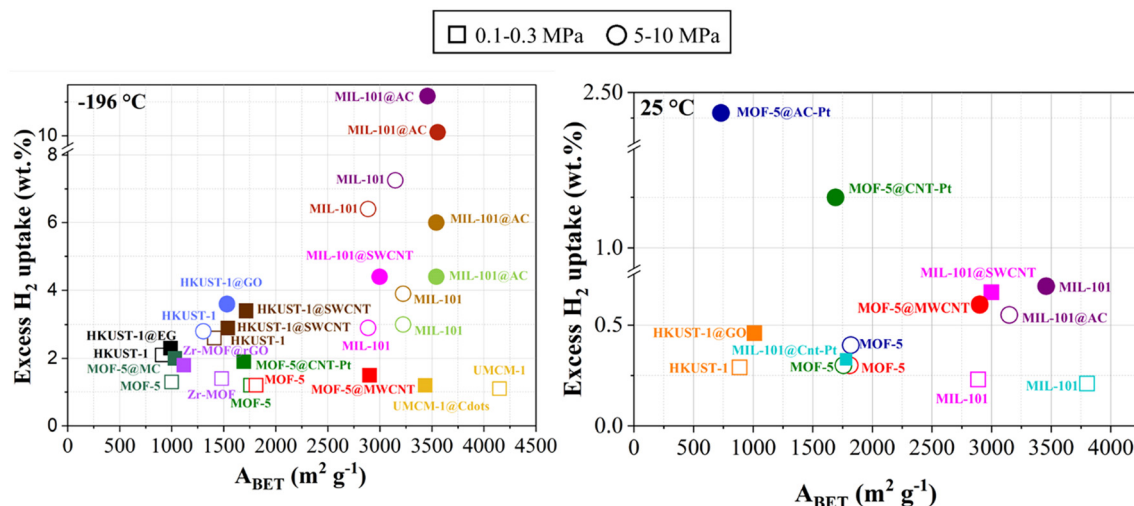


Fig. 9 Excess H₂ uptake of MOF hybrids reported in recent studies at -196°C (left) and 25°C (right) (○● ref. 220); (□■ ref. 221); (□■ ref. 222); (□■ ref. 223); (○●, □■ ref. 131); (□■, ● ref. 207); (□■ ref. 175); (○● ref. 224); (□■ ref. 214); (○●, ● ref. 158); (○●, □■ ref. 218); (○●, □■ ref. 159); (○● ref. 204); (□■ ref. 225).



- **Increase in thermal stability:** The presence of a carbon-based material can also increase the thermal stability of the hybrid.^{175,222} Policicchio *et al.* provided an overview of the thermal stability of hybrids obtained after the incorporation of

4.2.3. MOF hybrids with other inorganic materials. Hybrids with MOFs have been used for various applications, such as CO₂ capture, and can include alternative materials such as zeolites, cellulose and clays.²³⁵ MOFs@clay hybrids include feedstock materials such as attapulgite, amino-clay, cordierite, kaolin and bentonite. Wang *et al.* studied the influence of introducing diatomite (Da) into the MIL-101 (Cr) matrix. Their study evaluated the H₂ storage capacity of the Cr-MOF@Da hybrid at 25 °C and 1 bar. The H₂ adsorption isotherms showed a linear increase as the wt% of diatomite increased, obtaining 0.022 wt% for Cr-MIL-101@Da-4. The hybrids also showed improved thermal stability.²³⁶

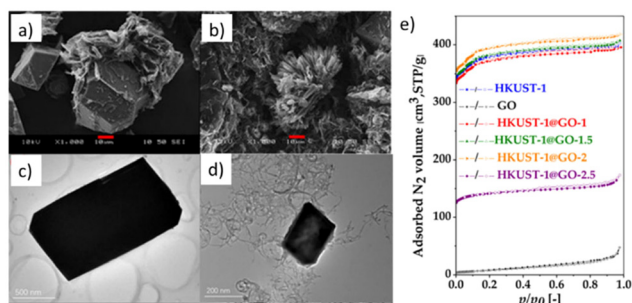


Fig. 10 (a) SEM images of HKUST-1@1qg L⁻¹ GO; (b) SEM images of HKUST-1@2.5 g L⁻¹ GO. Scale bar is 10 μm (reproduced from ref. 228 © 1996–2024 MDPI); (c) TEM images of Co-bpdc (cobalt benzene-1,4-dicarboxylate) as a pure MOF; (d) TEM images of Co-bpdc@MWCNTs as a hybrid (reproduced from ref. 229 © 1996–2024 MDPI); (e) N₂ adsorption–desorption isotherms (–196 °C) of pristine GO, HKUST-1 and hybrid materials with different GO contents (reproduced from ref. 228 © 1996–2024 MDPI).

MOF@clays have been the subject of research interest, especially for the development of complex geometries of MOFs using 3D printing.²³⁷ MOFs@zeolite hybrids combine the high SSA of MOFs with the high mechanical strength of zeolites. By selecting the type of synthesis, a core-shell structure can be obtained that may offer certain advantages, such as gas separation, hydrophobicity, *etc.*²³⁸ For instance, Musyoka *et al.* fabricated a MIL-101(Cr)@zeolite-templated carbon (ZTC) hybrid for H₂ storage applications. H₂ adsorption measurements were carried out at −196 °C up to 1 bar. The hybrid material was compared with the individual materials and showed an increased surface area and H₂ uptake capacity of 2957 m² g^{−1} and 2.55 wt%, respectively. These results are significantly better than those obtained with MIL-101 (2552 m² g^{−1}, 2.39 wt%) and ZTC (2577 m² g^{−1}, 2.39 wt%).²³⁹

5. Conclusions

The development of MOF-based hybrid adsorbents, combining MOFs with a variety of other materials and nanostructures, has attracted considerable interest in recent times. This approach aims to improve the performance and scalability of MOFs, opening up possibilities for future materials.

MOFs alone, due to their versatile structures, high surface areas and substantial pore volumes, are already considered promising materials for H₂ storage, as evidenced by NU100, which reaches 9.05 wt% at 7 MPa and −196 °C. Moreover, a variety of synthesis methods enables the nanopore structure of MOFs to be controlled, which is essential for their applicability in adsorption. Our review covered different synthesis techniques, delineating their respective advantages and drawbacks in controlling MOF parameters, as well as characterizing MOFs and their hybrids. By recognizing the potential of MOFs, increasing the SSA and optimizing pore size distribution should make it possible to increase H₂ storage capacities in line with the DOE specifications.

To optimize hydrogen storage under ambient conditions, strategies such as linker functionalization and the introduction of unsaturated metal centers are highly effective. A notable example is that of exposed metal ions, which often have binding enthalpies ranging from −20 to −30 kJ mol^{−1}. Other advances concern the creation of competitive MOF hybrids, especially through the incorporation of carbon materials, which show promise in increasing adsorption capacity, improving thermal stability and enhancing thermal conductivity. To improve the selectivity and stability of MOFs, MOF@MOF hybrids offer a promising approach. By integrating the characteristics of two distinct MOFs into a single, unified material, this method effectively combines their advantages. Combinations such as MOF@carbon-based materials preserve the advantages of MOFs while improving thermal conductivity, surface area and ease of shaping.

In conclusion, MOF-based hybrids represent a promising approach for improving H₂ storage capabilities, offering significant potential to meet the demanding standards set by the

US DOE. Key areas of future research should focus on increasing the volumetric capacity of these materials, as their gravimetric performance is already outstanding, but volumetric improvements are essential for practical applications such as transportation and portable energy systems. These developments will play a decisive role in optimizing the performance of MOF hybrids and advancing their viability for commercial hydrogen storage applications.

Abbreviation

(−ΔH) _{ads}	Adsorption enthalpy
A _{BET}	Brunauer–Emmett–Teller area
BDC	1,4-Benzenedicarboxylic acid
BET	Brunauer–Emmett–Teller
BPDC	Biphenyldicarboxylate
BTC	Benzene-1,3,5-Tricarboxylic acid
CDs	Carbon dots
Co-bpdc	Cobalt benzene-1,4-dicarboxylate
COFs	Covalent organic frameworks
DMF	<i>N,N</i> -Dimethylformamide
DOE	U.S. Department of Energy
FTIR	Fourier transform infrared spectroscopy
GL	Graphene-like
GO	Graphene oxide
H ₂	Hydrogen
ILs	Ionic liquids
IMOFs	Interpenetrated MOFs
MIL	Materials of Institut Lavoisier
MOFs	Metal organic frameworks
MWCNTs	Multi-walled carbon nanotubes
nGr	Nano graphite
NMR	Nuclear magnetic resonance
NU	Northwestern University
PBUs	Primary building units
PCPs	Porous coordination polymers
PDC	3,5-Pyridine dicarboxylic acid
PSD	Pore size distribution
PTFE	Polytetrafluoroethylene
QDs	Quantum dots
RAM	Resonant acoustic mixing
SBUs	Secondary building units
SEM	Scanning electron microscopy
SSA	Specific surface area
SWCNT	Single-walled carbon nanotubes
TGA	Thermogravimetric analysis
UIO	Universitetet i Oslo
XRD	X-ray diffraction analysis
ZTC	Zeolite-templated carbon

Author contributions

L.J.-L.: writing – original draft and formal analysis; R.M.-O.: review & editing, formal analysis, and supervision; L.G. A.:



writing – original draft and formal analysis; A.C.: review & editing and supervision; V.F. review & editing, supervision, project administration, and formal analysis.

Data availability

The data supporting this article have been included as part of the ESI.†

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Conflicts of interest

There are no conflicts to declare.

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