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UiO-type metal–organic frameworks as a platform for hydrogen storage studies

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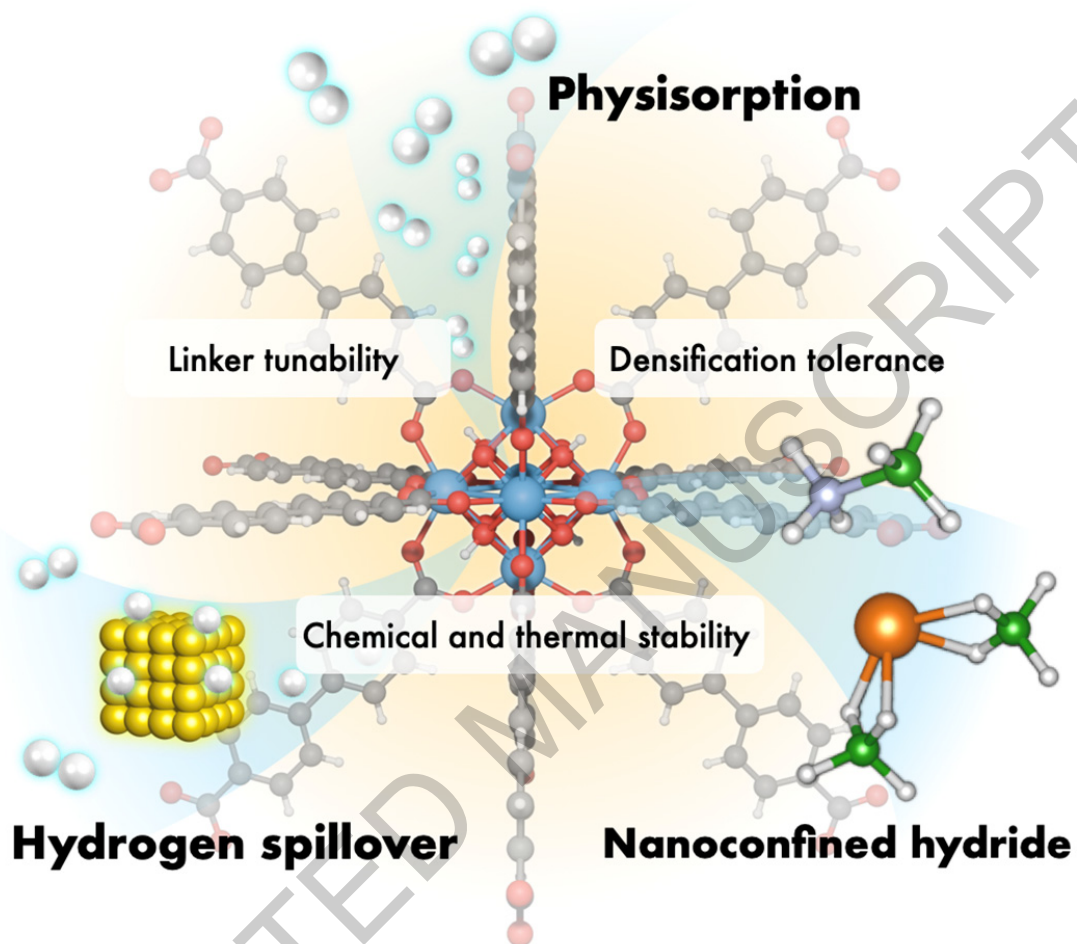
UiO-type metal–organic frameworks as a platform for hydrogen storage studies

Hydrogen has attracted significant attention as a clean energy carrier due to its high gravimetric energy density and zero-carbon emissions at the point of use. However, its low volumetric energy density poses major challenges for safe and efficient storage. In this context, porous materials, particularly metal–organic frameworks (MOFs), have been extensively investigated as promising hydrogen-storage media because of their high surface areas, tunable pore environments, and structural diversity. Among them, Zr-based Universitetet i Oslo (UiO)-type MOFs have emerged as important platforms for hydrogen storage studies because of their exceptional framework stability, high synthetic versatility, and compatibility with the incorporation of functional species such as metal nanoparticles and hydrides. This review focuses on recent advances in hydrogen storage studies using UiO-type MOFs. First, the fundamental synthesis strategies and structural characteristics of UiO frameworks are outlined. Subsequently, key concepts of physisorption-based hydrogen storage, including adsorption mechanisms and evaluation metrics, are introduced. The hydrogen storage performance of pristine, functionalized, and densified UiO-type MOFs is then discussed, highlighting the influence of pore structure, linker functionality, and framework densification on hydrogen uptake. Beyond physisorption, chemisorption-related approaches, including spillover-assisted hydrogen storage and nanoconfinement of hydride species within UiO-type MOFs, are also highlighted. These studies demonstrate that UiO-type MOFs not only function as effective hydrogen adsorbents but also serve as versatile platforms for tuning hydrogen interactions. Finally, current challenges and future perspectives are discussed, providing insights into the development of next-generation hydrogen storage materials.

Keywords: hydrogen storage; metal–organic frameworks; UiO-type MOFs; physisorption; densification; hydrogen spillover; nanoconfinement

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Graphical abstract



UiO-type MOFs as a versatile platform for hydrogen storage via physisorption, spillover, and nanoconfinement strategies.

1 Introduction

Hydrogen has attracted considerable attention as an environmentally friendly energy carrier because of its exceptionally high gravimetric energy density and absence of carbon dioxide emissions at the point of use [1–5]. On a mass basis, hydrogen stores approximately 120 MJ kg⁻¹, which is nearly three times higher than gasoline (44 MJ kg⁻¹) [1]. However, hydrogen has a very low volumetric energy density, making its storage and transportation challenging. Therefore, hydrogen is stored mainly as compressed gas or liquefied hydrogen. Compressed hydrogen storage requires high-pressure tanks typically operated at 35 or 70 MPa, whereas liquid hydrogen storage relies on cryogenic cooling to 20 K [6]. Although these technologies are already being implemented, both approaches have practical drawbacks, including the high energy cost of compression or liquefaction, strict requirements for storage and transport infrastructure, and safety concerns associated with high-pressure or cryogenic operations [4,7]. Therefore, extensive research has been devoted to developing alternative hydrogen storage technologies.

To overcome these limitations, alternative hydrogen-storage strategies based on solid-state materials have attracted increasing attention [8–11]. Among various hydrogen storage approaches, porous materials have been extensively studied because of their ability to accommodate hydrogen mainly through physisorption within internal pore structures, as well as through chemisorption- or spillover-related processes when metal species or catalytic components are incorporated [12–16]. In particular, metal-organic frameworks (MOFs) are regarded as one of the most versatile classes of porous materials [17–21]. Since the early 2000s, pioneering studies on MOF-5 [22], HKUST-1 [23], and related high-surface-area MOFs [24] have stimulated extensive research on hydrogen storage in MOFs. These early studies highlighted the importance of high surface area, pore structure, and accessible adsorption sites for hydrogen uptake. However, some early MOFs also suffered from limited chemical, thermal, or moisture stability, which restricted their use under practical and experimental conditions.

Against this background, Zr-based Universitetet i Oslo (UiO)-type frameworks have emerged as particularly attractive MOFs because of their exceptional chemical and thermal stability [25]. In addition to their robustness, their synthetic versatility and functional group tunability make UiO-type MOFs useful platforms for investigating structure-property relationships in various fields, including catalysis [26–35], photocatalysis [36–44], gas storage [45–55], water harvesting [56–59], water purification [60–63], membrane [64–68], D₂/H₂ separation [69], energy storage [70–73], chiral separation [74–76], uranium extraction [77–82], biomedical [83–87], and sensing [88–93] applications. For hydrogen storage, these characteristics make UiO-MOFs suitable for correlating synthetic design, framework stability, and hydrogen storage behavior. Therefore, UiO-MOFs should be regarded not simply as durable MOFs but also as versatile model systems for investigating structure-property relationships in hydrogen storage and guiding the rational design of next-generation solid-state hydrogen storage materials. To clarify the position of UiO-type MOFs within the broader landscape of hydrogen storage materials, Table 1 summarizes selected state-of-the-art solid-

state and carrier-based hydrogen storage materials with different storage/release mechanisms [94–107].

In this review, we focus on UiO-type MOFs as a versatile platform for hydrogen storage studies rather than providing a broad comparison across different MOF families. We summarize recent progress in both physisorption- and chemisorption-related hydrogen storage approaches within the UiO-MOF family and discuss how structural design, linker functionalization, material densification, spillover, and nanoconfined hydrides influence hydrogen storage behavior. First, the fundamental synthetic strategies and structural characteristics of UiO-type frameworks are outlined. Second, we introduce the key parameters governing hydrogen storage through physisorption mechanisms, providing a foundation for evaluating storage capacity. We then review hydrogen physisorption studies of prototypical, functionalized, and densified UiO-type MOFs, focusing on the influence of structural modifications on their hydrogen storage performance. Third, we discuss key strategies for chemisorption-assisted hydrogen storage, highlighting the role of metal composites in enhancing storage capacity. Subsequently, recent developments in spillover-assisted hydrogen storage and the nanoconfinement of hydride species within UiO-type MOFs are explored. Finally, the current challenges and future perspectives for the design of UiO-based hydrogen storage materials are summarized. Through this platform-oriented perspective, this review aims to clarify how UiO-type MOFs can serve not only as hydrogen adsorbents but also as model systems for understanding structure–property relationships and guiding the rational design of solid-state hydrogen storage materials.

2 Synthesis and structural features of UiO-type MOFs

The synthesis chemistry of MOFs plays a central role in determining their crystallinity, structural stability, defect formation, and adsorption-related properties. Therefore, before discussing hydrogen storage in detail, it is useful to briefly outline the fundamental synthetic strategies for UiO-type MOFs as a basis for understanding their structural features. Detailed discussions on the synthesis of UiO-type MOFs can be found in several comprehensive reviews [108,109]. Herein, we briefly summarize the key aspects of their synthesis.

2.1. Synthesis of prototypical UiO-type MOFs

Cavka et al. [25] first reported the solvothermal synthesis of prototypical UiO-66, UiO-67, and UiO-68 compounds in 2008 (Figure 1a) [25]. These UiO-type frameworks are constructed from $\text{Zr}_6\text{O}_4(\text{OH})_4$ clusters and linear dicarboxylate linkers. In the $\text{Zr}_6\text{O}_4(\text{OH})_4$ cluster, six Zr atoms form an octahedral core, with the triangular faces of the Zr_6 octahedron capped by μ_3 -OH or μ_3 -O groups, where μ_3 indicates that each oxo or hydroxo group bridges three Zr atoms (Figure 1b). These frameworks are typically prepared by reacting Zr precursors with dicarboxylate linkers in polar aprotic solvents. For instance, UiO-66 was synthesized from ZrCl_4 and terephthalic acid (H_2BDC) in *N,N*-dimethylformamide (DMF) containing a controlled amount of water under solvothermal conditions, typically with a reaction time of around 24 h (Figure 1c). During solvothermal heating, the Zr precursor undergoes hydrolysis and condensation to generate the $\text{Zr}_6\text{O}_4(\text{OH})_4$ clusters, followed by coordination with

terephthalate linkers to form the UiO-66 framework. Similarly, the authors synthesized a series of isorecticular frameworks with increasing linker lengths, including UiO-67 (4,4'-biphenyldicarboxylic acid (H₂BPDC)) and UiO-68 (4,4''-terphenyldicarboxylic acid (H₂TPDC)). The exceptional chemical and thermal stabilities of UiO-type MOFs are generally attributed to the highly connected Zr₆-based framework topology, together with the strong Zr–O bonds [110–114]. The bond dissociation energy of the Zr–O bond is estimated to be approximately 760 kJ mol⁻¹, which is significantly higher than those of the Al–O (~512 kJ mol⁻¹), Cu–O (~343 kJ mol⁻¹), and Zn–O (~284 kJ mol⁻¹) bonds found in representative MOFs [115], such as MIL-100 (Al–O bond), HKUST-1 (Cu–O bond), and MOF-5 (Zn–O bond). Furthermore, Zr₆O₄(OH)₄ features a 12-coordinated node, which imparts high structural stability. These characteristics are reflected in the remarkable thermal stability of UiO-66 (475 °C), which is significantly higher than those of other common MOFs such as Al-MIL-100 (400 °C) and HKUST-1 (300 °C) [116]. UiO-66 also exhibits exceptional mechanical stability, with a minimum shear modulus of 13.7 GPa, significantly higher than those of other benchmark MOFs, including MOF-5 (1.4 GPa) and HKUST-1 (1.04 GPa) [117]. These characteristics contribute to make UiO-type MOFs an outstanding platform for a wide range of hydrogen-related studies. Compared with UiO-66 and UiO-67, pristine UiO-68 has been investigated less extensively. This may partly reflect the limited solubility of H₂TPDC in common organic solvents, which makes its synthesis more sensitive to the reaction conditions. Nevertheless, UiO-68-type frameworks can be obtained more readily when functionalized linkers are employed [118,119].

In addition to typical solvothermal synthesis, alternative synthetic strategies, including microwave-assisted synthesis [120–123], aqueous solution-based production [124,125], mechanochemical synthesis [126–129], and flow synthesis [130–133] have also been explored for UiO-type MOFs. These methods have considerable potential to reduce production costs and improve scalability. Based on laboratory-scale solvothermal synthesis, the material cost of UiO-66 has been estimated to be approximately 503.9 USD kg⁻¹ [134]. This cost is comparable to, or even lower than, those of other widely studied MOFs, such as MOF-5 (527.3 USD kg⁻¹) and Ni-MOF-74 (886.7 USD kg⁻¹), indicating that UiO-type MOFs are already cost-competitive for laboratory-scale studies. However, further cost reduction is necessary for practical applications to achieve target production costs as low as 10–15 USD kg⁻¹ [135,136]. In this context, a techno-economic assessment based on hypothetical pilot-scale production of amine-functionalized UiO-66 suggested that aqueous solution-based synthesis could reduce the production cost to approximately 15.8 USD kg⁻¹ [137]. This result indicates that substantial cost reductions may be achievable for UiO-type MOFs through solvent replacement, improved yields, and process scale-up.

2.2 Acid-modulated synthesis and defect engineering

The crystallinity and structural defects of MOFs are strongly related to their gas sorption applications [138–140]. From the first report of the prototypical UiO series, the addition of a modulator in the synthesis has been shown to improve the reproducibility and crystallinity, as well as being useful for controlling the particle size and density of defects [141,142].

Representative studies on the acid-modulated synthesis and defect engineering of UiO-type MOFs are summarized below.

2.2.1 Acid modulation

Early synthetic studies on UiO-type MOFs revealed that achieving highly crystalline products is not always straightforward. In 2011, Schaate et al. [143] reported that although the original procedure reproducibly produced highly crystalline UiO-66, the synthesis of UiO-67 often led to poorly crystalline products, and attempts to synthesize UiO-68 were unsuccessful [143]. They found that acid-modulated synthesis using monocarboxylic acids such as benzoic acid and acetic acid markedly improved the crystallinity and reproducibility of UiO-66 and UiO-67, while also enabling control over the crystal size over a wide range, from nanosized particles to single crystals. The mechanism was proposed to involve the competitive coordination of monocarboxylic acids with the dicarboxylate linker at the Zr_6 clusters, thereby slowing nucleation and crystal growth and improving crystallinity and reproducibility.

Since then, the use of acid modulators has become a widely adopted strategy in the synthesis of UiO-type MOFs for controlling crystallization behavior [144–148]. Zhao et al. [149] further developed an acid/base co-modulation strategy in which acetic acid and triethylamine (TEA) were used to control crystal growth and nucleation, enabling the large-scale synthesis of monodisperse UiO-66 crystals with tunable sizes and defect densities (Figure 2) [149]. In terms of structural defects, modulation has also been recognized as strongly related to defect formation in UiO-type frameworks, as discussed in Section 2.2.2.

2.2.2 Structural defects

Structural defects have attracted considerable attention in UiO-type MOFs because they can significantly alter the local structure and thus influence the physicochemical properties of the framework [150–152]. Valenzano et al. [153] first reported missing linker defects in UiO-66 based on thermogravimetric analysis [153]. Their analysis suggested that approximately one in 12 terephthalate linkers coordinated to each Zr_6 node was missing. Subsequently, Wu et al. [154] provided the first direct structural evidence of missing linker defects in UiO-66 using high-resolution neutron diffraction [154]. They demonstrated that the concentration of missing-linker defects could be systematically tuned by varying the amount of acetic acid used as a modulator and the synthesis time. Gutov et al. [155] reported that formic acid modulation introduced modulator-capped defects in UiO-67, which were primarily discussed in the context of missing-linker defects [155]. However, Shearer et al. [156] later showed that, under typical monocarboxylic-acid-modulated synthesis conditions, defective UiO-66 samples are often dominated by missing-cluster defects [156] (Figure 3a). Furthermore, Bueken et al. [157] developed a mixed-linker strategy to selectively introduce missing-linker defects in UiO-66 [157]. They incorporated a thermally labile linker, trans-1,4-cyclohexane-dicarboxylate, together with the conventional terephthalate linker during UiO-66 synthesis. Upon subsequent thermolysis, the labile linker was selectively removed from the framework,

generating missing-linker defects without relying on conventional modulator-induced defect formation. In contrast to these approaches for generating missing-linker defects, Feng et al. [158] reported a post-synthetic strategy for creating missing-cluster defects in UiO-66 [158]. They first synthesized bimetallic (Zn, Zr)-UiO-66 samples with different Zn/Zr ratios and then applied a mild acid-washing treatment (Figure 3b). Because Zn nodes are less stable than Zr nodes under acidic conditions, the Zn species could be selectively removed while preserving the UiO-66 framework, resulting in well-defined missing-cluster defects.

Separately, using high-resolution transmission electron microscopy (HRTEM), atomic-scale visualization studies have provided further insight into the spatial arrangement of defects in UiO-type frameworks [159,160]. For example, Liu et al. directly visualized ordered missing-linker and missing-cluster defects in UiO-66 at sub-unit-cell resolution. In their study, defective UiO-66 was synthesized using formic acid as a modulator, and HRTEM revealed that ordered missing-linker regions were widely distributed, whereas missing-cluster defects appeared as smaller nanoscale domains. Three-dimensional reconstruction further showed that the missing-linker structure consisted of 8-connected Zr_6 clusters capped by terminal formate ligands, providing direct real-space evidence for the local ordering and termination of linker vacancies [159].

A broader overview of defect engineering in UiO-66, including various types of defects and their formation, characterization, and effects on the physicochemical properties, has been comprehensively summarized in another review [161,162]. Because hydrogen adsorption in porous materials strongly depends on the accessible surface area and pore structure, defect engineering in UiO-type frameworks has attracted considerable attention as a strategy for tuning adsorption properties.

2.3. Structural diversity in functionalized UiO-type MOFs

In addition to defect engineering, another important strategy for tuning the properties of UiO-type MOFs is the introduction of functional groups into the organic linkers. Because the UiO framework can accommodate a wide variety of dicarboxylate ligands while maintaining the same Zr-cluster node and topology, numerous functionalized derivatives have been developed [109,118,119,163,164]. Such functionalization can significantly alter the pore environment, including the pore size, polarity, and distribution of adsorption sites. Consequently, functionalized UiO-type MOFs exhibit considerable structural diversity and offer opportunities to tailor their physicochemical properties.

An early example is UiO-66-NH₂, in which amino-substituted terephthalate linkers are incorporated while preserving the UiO-66 framework [165]. The presence of amino groups provides additional chemical functionality, making this material an important platform for catalysis and post-synthetic modification [28,38–41,43,44,51,58,62,66,67,76,81,83,90]. Another important class is the pyridine-containing UiO-67 derivatives, such as frameworks constructed from bipyridine-based dicarboxylate linkers. These materials introduce coordination-capable nitrogen sites into the framework and are, therefore, useful for further metalation and catalytic applications [30,68,164]. Furthermore, variations in the organic

linker allow reproducible synthetic access to members of the UiO-68 family [118,119], even though the pristine UiO-68 framework is comparatively difficult to prepare reproducibly. Importantly, these functionalization strategies have been explored in the context of hydrogen storage. Their specific roles in tuning the hydrogen adsorption behavior and expanding the design versatility of UiO-type frameworks are discussed in Section 3.

3 UiO-type MOFs as hydrogen adsorption media

Owing to their high chemical and thermal stabilities, structural tunability, and synthetic versatility, UiO-type MOFs represent one of the most extensively studied Zr-based MOF families. These characteristics render these materials useful platforms for systematically elucidating the design principles of physisorption-based H₂ storage. In this section, we first summarize the fundamental parameters relevant to physisorption-based hydrogen storage and then review previous studies on H₂ storage in prototypical, functionalized, and densified UiO-type MOFs.

3.1. Fundamental parameters for physisorption-based hydrogen storage

Before discussing hydrogen storage studies on UiO-type MOFs, this section briefly summarizes the fundamental concepts, terminology, and evaluation parameters relevant to physisorption-based hydrogen storage. To provide a consistent basis for the following discussion, the definitions and evaluation criteria are outlined below.

3.1.1 Physisorption

Hydrogen storage in porous materials typically relies on physisorption [166,167]. Physisorption refers to the adsorption of molecules onto a material surface via weak intermolecular interactions, primarily van der Waals forces. In general, physisorption does not significantly alter the chemical structures of either the adsorbate or the adsorbent. In the case of H₂, owing to its relatively weak interaction strength, typically corresponding to an adsorption enthalpy (ΔH) of around -4 to -7 kJ mol⁻¹, physisorption enables reversible H₂ adsorption and desorption through temperature and pressure swings. In other words, the intrinsically weak H₂...adsorbent interaction requires rational material design to enhance hydrogen storage performance through strategies such as tuning the pore size, increasing the surface area, and optimizing the adsorption enthalpy.

We note that although pressures of 35–70 MPa are typically employed in practical hydrogen storage systems, a pressure range of 10–20 MPa is commonly used for high-pressure hydrogen adsorption measurements in laboratory-scale studies. This range is often adopted to benchmark the performance of porous materials because it is compatible with the upper pressure limits of commercially available hydrogen storage tanks. Achieving higher pressures requires additional compression equipment and more stringent safety protocols. Thus, this pressure range serves primarily as a reference condition for experimental evaluation rather than as a direct target for practical hydrogen storage applications.

3.1.2 Excess and total H₂ uptake

The amount of hydrogen stored in adsorbents is generally evaluated in terms of excess and total adsorption. Excess adsorption represents the amount of hydrogen present in excess of that in the free gas phase within the same volume, whereas the total hydrogen uptake includes both the excess adsorbed H₂ and compressed H₂ gas present in the pores (Figure 4). Experimentally, H₂ adsorption is typically evaluated using volumetric or gravimetric pressure–composition–temperature (PCT) measurements. In the volumetric method, the amount of adsorbed H₂ is calculated from the gas pressure drop in the measurement system using a gas-state equation, whereas the gravimetric method is based on directly monitoring the weight change of a sample upon gas adsorption using a highly sensitive microbalance.

In these measurements, the directly obtained values correspond to the excess gravimetric H₂ adsorption (N_{ex}) (e.g., g H₂ per gram of adsorbent). The total gravimetric H₂ uptake, N_{tot} , is calculated by accounting for the contribution of compressed gas to the pore volume (V_p) (Eq. 1).

$$N_{\text{tot}} = N_{\text{ex}} + d_{\text{H}_2} \times V_p \quad (1)$$

Here, d_{H_2} (g cm⁻³) is the density of compressed H₂ at a given temperature and pressure. V_p (cm³ g⁻¹) is generally determined from N₂ sorption isotherms, usually considering the amount of N₂ adsorbed at $P/P_0 \approx 0.95$ based on the Gurney rule. However, this value should be interpreted carefully because capillary condensation in the interparticle macropores can lead to an overestimation of V_p . The volumetric H₂ uptake (e.g., grams of H₂ per liter of adsorbent) can be estimated from the gravimetric uptake using the adsorbent density. Because this conversion is highly sensitive to the definition of density, including the crystal, bulk, and tap densities, volumetric capacities should be treated with caution.

In the field of MOF-based hydrogen storage, deliverable capacity in terms of both gravimetric and volumetric performance is widely regarded as the most important metric. The U.S. Department of Energy (DOE) has established system-level targets of 5.5 wt% (40 g L⁻¹) for 2025 and an ultimate target of 6.5 wt% (50 g L⁻¹) for onboard H₂ storage systems. These targets include the weight contributions of the storage tank, storage material, and auxiliary system components[168]. Direct comparison should therefore be interpreted cautiously. Although MOF powders alone do not represent complete storage systems, material-level capacities that approach or exceed these system-level targets are generally considered strong indicators of promising adsorbents. high-performing MOFs often achieve gravimetric deliverable capacities of 5–9 wt% and volumetric deliverable capacities of 40–50 g L⁻¹ under defined pressure- and temperature-swing conditions (e.g., 10 MPa at 77 K to 0.5 MPa at 160 K) [19,95,97,168,169], highlighting their potential to contribute significantly toward practical hydrogen storage applications (Figure 5).

3.1.3 Specific surface area

Because physisorption occurs on the internal surfaces of porous materials, the specific surface area is a major parameter that governs the hydrogen storage capacity. The empirical correlation between cryogenic gravimetric H₂ uptake and specific surface area is commonly referred to as the Chahine rule (i.e., 1 wt% excess H₂ uptake for every 500 m² g⁻¹ of surface area) (Figure 6) [170]. At ambient temperatures, this relationship becomes less universal, as H₂ uptake depends more strongly on additional factors such as adsorption enthalpy, pore size, and the nature of the adsorption sites. A comprehensive discussion of the correlation between the surface area and H₂ uptake can be found in previous reviews [18].

The specific surface areas of porous materials are generally determined from the N₂ adsorption isotherms measured at 77 K. Because the calculated surface area depends on the adsorption model used for the analysis, the obtained values are typically expressed as either Brunauer–Emmett–Teller (BET) [171–173] or Langmuir surface areas [174,175]. In hydrogen storage studies of MOFs, the BET surface area (S_{BET}), which takes into account multilayer adsorption on the surface, is more commonly used as the standard descriptor. This is because the Langmuir model, which is based on an ideal monolayer adsorption assumption, often overestimates the surface area of microporous adsorbents.

3.2 H₂ storage in prototypical UiO-MOFs

In 2012, Chavan et al. [176] first reported high-pressure H₂ adsorption using UiO-66 and UiO-67 [176]. UiO-66 and UiO-67 were synthesized using a typical solvothermal method in the presence of a small amount of water (95 °C for 100 h). N₂ sorption measurements at 77 K showed that UiO-66 and UiO-67 exhibited S_{BET} values of 969 and 1877 m² g⁻¹, respectively, with corresponding V_p values of 0.43 and 0.85 cm³ g⁻¹. The H₂ adsorption isotherms at 77 K showed fully reversible behavior for both UiO-66 and UiO-67, as shown in Figure 7a. The maximum gravimetric excess uptake reached 2.4 wt% at 0.32 MPa for UiO-66 and 4.6 wt% at 0.38 MPa for UiO-67. Although the H₂ uptake of UiO-67 was among the highest reported at that time, its superior chemical and thermal stability highlighted its potential advantages.

Variable-temperature Fourier transform infrared (VT-FTIR) spectroscopy was conducted (15–300 K under an H₂ pressure of 4.5–5.0 × 10⁻³ MPa) to elucidate the nature of the H₂ adsorption sites (Figure 7b). Notably, free H₂ is essentially infrared (IR)-inactive and, therefore, is not directly observable in conventional IR spectroscopy. By contrast, H₂ molecules become polarized upon adsorption on cationic or anionic surface sites, making the $\nu(\text{H-H})$ stretching vibrational mode IR-active. The $\nu(\text{H-H})$ bands appeared in the temperature range of 100–115 K and were red-shifted from the gas-phase Raman value (4160 cm⁻¹). For band assignment, the VT-FTIR spectra of hydroxylated UiO-67 and its dehydroxylated counterpart were compared, with dehydroxylated UiO-66 used as a reference. The most strongly perturbed component was located at 4108 cm⁻¹ ($\Delta\nu = -52$ cm⁻¹), which was assigned to H₂ interacting with the $\mu_3\text{-OH}$ groups of the Zr₆O₄(OH)₄ node as this band markedly decreased upon dehydroxylation. By contrast, a band at 4116 cm⁻¹ ($\Delta\nu = -44$ cm⁻¹) became

dominant after dehydroxylation, suggesting adsorption on μ_3 -O sites. At higher coverage, additional features in the 4120–4145 cm^{-1} region were observed, which were associated with interactions with the organic linker and/or condensed H_2 in the pores. These assignments suggest that preserving the μ_3 -OH sites is beneficial for H_2 adsorption.

At around the same time, Abid et al. [177] reported nanosized UiO-66 as a hydrogen adsorbent after optimizing the activation procedure through solvent exchange, yielding an SBET of 1434 $\text{m}^2 \text{g}^{-1}$ and a H_2 uptake of 4.2 wt% at 77 K and 6.0 MPa [177]. The authors also evaluated the isosteric heat of adsorption (Q_{st}) from temperature-dependent H_2 isotherms. The Q_{st} value was 11.9 kJ mol^{-1} at low loading and gradually decreased to 5.8 kJ mol^{-1} with increasing H_2 surface coverage, indicating a typical physisorption behavior. The initial value of 11.9 kJ mol^{-1} indicates relatively strong H_2 –framework interactions and approaches the range often considered favorable for adsorption-based H_2 storage (approximately 10–15 kJ mol^{-1} or higher[178]). However, the decrease to 5.8 kJ mol^{-1} with increasing H_2 coverage indicates that these stronger interactions are limited to the primary high-affinity adsorption sites, whereas subsequent adsorption occurs at weaker physisorption sites. This trend highlights the challenge of maintaining sufficiently strong H_2 –framework interactions over a broad loading range, particularly for practical storage under near-ambient-temperature conditions.

Zhao et al. [179] focused on optimizing the solvent to improve the H_2 uptake of UiO-66. UiO-66 [179]. Systematic synthesis using different solvents revealed that DMF plays a crucial role in obtaining phase-pure UiO-66. This solvent effect may be related to the ability of DMF to solvate both the amphiphilic dicarboxylate linker and polar Zr precursor species, thereby promoting the controlled assembly of Zr_6 nodes and BDC linkers. In contrast, solvents with less suitable polarity and precursor-solvation ability resulted in amorphous products or UiO-66 contaminated with residual or polymerized H_2BDC . UiO-66 synthesized in DMF at 50 $^\circ\text{C}$ exhibited high crystallinity, with an S_{BET} of 1358 $\text{m}^2 \text{g}^{-1}$ and a V_p of 0.43 $\text{cm}^3 \text{g}^{-1}$, and achieved a H_2 uptake of 3.35 wt% at 77 K and 1.8 MPa. Furthermore, grand canonical Monte Carlo simulations suggested that H_2 molecules preferentially adsorb near the phenyl rings of the BDC linker rather than exclusively at the inorganic node, highlighting the contribution of the BDC linker to the local adsorption environment for H_2 molecules. Ren et al. [180] reported a formic acid-modulated synthesis of UiO-66 to improve its crystallinity and H_2 uptake [180]. Upon increasing the amount of formic acid, the S_{BET} value increased from 241 to 1367 $\text{m}^2 \text{g}^{-1}$, while the H_2 uptake increased from 0.35 to 1.5 wt% at 77 K and 0.1 MPa.

García-Holley et al. [97] reported a benchmark study of H_2 storage in 14 representative MOFs under standardized temperature- and pressure-swing conditions to assess the H_2 storage performance under tank-relevant operating conditions [97]. In this dataset, the temperature-dependent H_2 uptake of UiO-67 at 77, 160, and 296 K was reported. UiO-67 was prepared using an optimized procedure. The obtained UiO-67 exhibited an S_{BET} value of 2360 $\text{m}^2 \text{g}^{-1}$ with $V_p = 0.91 \text{ cm}^3 \text{g}^{-1}$. Temperature-dependent H_2 adsorption and desorption studies showed a fully reversible behavior. Approximate maximum excess H_2 uptakes were estimated by digitizing the reported plots, giving 22 mmol g^{-1} (4.4 wt%) at 77 K ($\sim 3 \text{ MPa}$), 9 mmol g^{-1} (1.8 wt%) at 160 K (11 MPa), and 2.5 mmol g^{-1} (0.5 wt%) at 296 K (11 MPa) (Figure 8a).

Meanwhile, the corresponding total uptakes at 10 MPa, accounting for the contribution of compressed H₂ in the V_p , were 31.14 mmol g⁻¹ (6.28 wt%), 29.29 mmol g⁻¹ (5.90 wt%), and 5.74 mmol g⁻¹ (1.16 wt%) at 77, 160, and 296 K, respectively (Figure 8b). The authors further calculated the deliverable capacity, which is defined as the difference between the total H₂ uptake at 77 K and 10 MPa (charging) and that at 160 K and 0.5 MPa (discharging), in accordance with the tank design criteria. Under these conditions, UiO-67 delivered 6.0 wt% H₂. On a volumetric basis, UiO-67 delivered 41 g L⁻¹, corresponding to a mid-range value within the studied MOFs. It must be noted that the volumetric capacities were calculated the using monolithic density ($\rho = 0.688$ g cm⁻³) of UiO-67. Therefore, the practical performance may be lower, depending on the achievable packing density in a real tank system.

Notably, unlike UiO-66 and UiO-67, systematic H₂ adsorption data for pristine UiO-68 remain scarce, although simulation studies have been reported [181]. One possible reason originates from the synthetic challenges, as the extended linker of UiO-68 (TPDC) often exhibits limited solubility in conventional solvothermal media. This may have hindered the reproducible crystal growth of UiO-68.

3.3 H₂ storage in functionalized UiO-MOFs

Functional group engineering in MOFs has proven to be a powerful paradigm for modulating the interactions with H₂. Recently, Wang et al. [182] systematically investigated the impact of linker functionalization on the hydrogen storage performance of UiO-66 derivatives [182]. Seven UiO-66-X frameworks (X = H, CH₃, NH₂, OH, F, Br, and NO₂) were synthesized via a solvothermal method using X-substituted BDC linkers (Figure 9a). N₂ sorption measurements showed that functionalization generally reduced S_{BET} and V_p compared with pristine UiO-66 (1386 m² g⁻¹ and 0.56 cm³ g⁻¹, respectively) due to steric occupation of pore spaces. Consequently, all the derivatives exhibited lower H₂ uptake than pristine UiO-66 (2.11 wt%) at 77 K and 5 MPa. However, under ambient conditions (298 K and 10 MPa), UiO-66-F showed the highest uptake of 0.27 wt%, corresponding to a 22% enhancement over pristine UiO-66 (0.22 wt%), whereas the other derivatives showed an inferior performance. As shown in Figure 9b, the H₂ uptake generally correlates with the magnitude of the average electrostatic potential-derived charge of the functional group ($|Q_R|$), suggesting that the extent of charge redistribution plays a key role in modulating the interaction between the framework and H₂. In this context, a larger $|Q_R|$ generally corresponds to higher H₂ uptake, although $|Q_R|$ alone does not fully account for the behavior of the NO₂-substituted derivative, indicating that additional factors such as the size of the functional group should also be considered. Therefore, $|Q_R|$ should be regarded as useful, albeit simplified, indicator of the electronic effect, while the overall adsorption behavior is still influenced by the detailed local electronic environment of each substituent.

Building on ligand functionalization, Su et al. [183] systematically investigated how ligand length, types of functional groups, and metal node variations affect H₂ storage performance in the UiO-type MOFs [183]. They synthesized UiO-66, UiO-67, a bipyridine-

functionalized UiO-67 analog (UiO-67bpy), and a Ti-substituted UiO-67bpy (UiO-67-bpy-Ti/Zr- n) following a reported procedure with minor modifications (Figure 9c). For UiO-67-bpy-Ti/Zr- n , n denotes the molar fraction of Ti relative to Zr in the metal nodes, quantified using inductively coupled plasma optical emission spectrometry (ICP-OES), and $n = 0.3, 0.6$, or 0.9 . H₂ adsorption measurements revealed clear structure–property trends across these three values (Figure 9d). Specifically at 298 K and 10 MPa, extending the linker from UiO-66 to UiO-67 increased excess H₂ uptake from 0.23 to 0.28 wt%, consistent with the enlarged porosity associated with the longer ligand. Compared with UiO-67, UiO-67-bpy exhibited improved H₂ storage from 0.28 to 0.32 wt%, despite its lower surface area. This result highlights the contribution of nitrogen-containing functional groups to enhanced H₂ physisorption. Furthermore, UiO-67-bpy-Ti/Zr-0.6 exhibited the highest excess H₂ uptake of 0.40 wt%. X-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) analyses suggested that Ti doping induces a local “strong-Zr, weak-Ti, negative-O” potential gradient that enhances H₂ polarization and stabilizes physisorption.

It is important to note that although functional-group engineering has made ΔH more negative, reaching values of approximately -15 to -20 kJ mol⁻¹, this does not necessarily translate into higher adsorption capacity. The entropic penalty, which is often overlooked, plays a significant role. [184]. As H₂ molecules become more strongly bound to functional sites, the loss of translational and rotational freedom can offset the enthalpic benefits at 298 K. Consequently, a more negative ΔH is often accompanied by a significant entropy-driven compensation (enthalpy–entropy compensation) effect, and the net thermodynamic driving force should be evaluated in terms of the Gibbs free energy, $\Delta G = \Delta H - T\Delta S$. Future research should therefore evaluate ΔH , ΔS , and ΔG together to provide a more complete thermodynamic understanding of hydrogen adsorption in functionalized MOFs.

Beyond simple linker substitution, various modification strategies, including cross-linking [185,186], mixed-ligand design [187], and composite formation [188–190], have been explored in UiO-66 to tune its hydrogen adsorption properties. Collectively, these results demonstrate that synergistic tuning of the linker length, functional groups, and metal-node composition enables the optimization of H₂ physisorption beyond simple surface-area effects.

3.4 H₂ storage in compressed UiO-66 and UiO-67

Considering potential applications, MOF powders must be packed into confined tank volumes, making the volumetric H₂ capacity as critical as the gravimetric capacity. However, their inherently low bulk density typically imposes a significant limitation on the volumetric H₂ capacity. Bambalaza et al. [94] reported the effects of high-pressure compaction on the gravimetric and volumetric H₂ uptake of UiO-66 [94]. The prepared UiO-66 was systematically compacted into pellets under pressures up to 665 MPa. Remarkably, powder XRD (PXRD) analysis confirmed that the UiO-66 framework essentially retained its crystal structure upon compaction. N₂ sorption measurements showed that the S_{BET} value of the compacted UiO-66 pellet was 1707 m² g⁻¹, which was approximately 98% of its original S_{BET} , with a modest reduction in V_p owing to the elimination of interparticle voids. At 77 K and 10 MPa, the total

gravimetric H₂ uptake of the compacted UiO-66 pellet reached 5.1 wt%, which is essentially identical to that of the powder form (5.0 wt%). This result is in clear contrast to most reports on MOF compaction, which often causes surface area loss and reduces gravimetric uptake. The authors concluded that this mechanical robustness arises from the high minimum shear modulus of UiO-66 (~13.7 GPa), which is significantly higher than those of typical MOFs, such as ZIF-8 (~2.7 GPa) and MIL-53(Ga) (~0.16 GPa). Moreover, the packing density dramatically increased from ~0.57 to 1.45 g cm⁻³ upon compaction, resulting in a substantial enhancement in volumetric H₂ capacity. For instance, at 77 K and 10 MPa, the total volumetric H₂ capacity calculated using the packing density (1.45 g cm⁻³) reached 74 g L⁻¹, which was more than two-fold higher than that of the powder form (29 g L⁻¹). Later, the same authors further demonstrated that retention of hydroxylated Zr₆O₄(OH)₄ nodes is important not only for enhancing H₂ uptake, in agreement with the findings of Chavan et al. [184], but also for preserving the mechanical robustness of UiO-66 under high-pressure compaction[191].

As an alternative densification approach to enhance the H₂ volumetric capacity, Murugavel et al. [95] reported the densification of UiO-67 into binder-free monolithic structures via a sol-gel synthesis approach. Unlike conventional mechanical compaction, this strategy enabled the formation of high-density monolithic structures while preserving the intrinsic porosity of the framework. To yield high-density monolithic UiO-67 (monoUiO-67) and the powder form UiO-67 (powdUiO-67), the as-synthesized and washed UiO-67 gel-like product was divided into two portions: one portion was dried at room temperature to yield monoUiO-67 , whereas the other was directly thermally activated to produce powdUiO-67 (Figure 10a). The resulting monoUiO-67 exhibited a bulk density (ρ_{bulk}) of 0.68 g cm⁻³, which is significantly higher than that of powdUiO-67 ($\rho_{\text{bulk}} = 0.155 \text{ g cm}^{-3}$). Despite this large difference in ρ_{bulk} , monoUiO-67 retained most of the textural and structural features of the powder form, showing only a modest decrease in S_{BET} from 2513 to 2303 m² g⁻¹ and in V_p from 0.81 to 0.73 cm³ g⁻¹. H₂ adsorption measurements revealed that the gravimetric uptake of monoUiO-67 slightly decreased upon densification, owing to a modest reduction in the surface area. By contrast, the volumetric uptake increased to ~48 g L⁻¹ at 77 K and 10 MPa, compared with ~37 g L⁻¹ for powdUiO-67 . This enhancement was mainly attributed to the marked increase in ρ_{bulk} and the resulting increase in the volumetric surface area of the monolithic sample. Furthermore, under temperature-pressure swing (TPS) conditions (charging at 77 K and 10 MPa, discharging at 160 K and 0.5 MPa), the delivered capacity of monoUiO-67 reached approximately 44 g L⁻¹, exceeding that of powdUiO-67 (36 g L⁻¹) (Figure 10b,c). These results highlight that densification into monolithic architectures is an effective strategy for enhancing the practical volumetric hydrogen storage of UiO-type MOFs, even when a slight reduction in gravimetric uptake occurs.

4 UiO-type MOFs as chemisorption-assisted hydrogen storage

While physisorption in UiO-type MOFs provides a reversible adsorption mechanism, its practical hydrogen storage performance is fundamentally limited by the weak H₂-MOF interaction ($\Delta H \approx -5 \text{ kJ mol}^{-1}$). Volumetric and gravimetric uptake data indicate that these materials are already approaching their maximum storage capacities under typical high-

pressure measurement conditions, particularly at room temperature. These limitations highlight the need for alternative or complementary strategies, such as spillover-assisted storage, chemisorption-assisted storage, and nanoconfined hydride storage, to further enhance hydrogen storage performance. In this section, we first summarize the fundamental concepts of spillover-assisted and hydride-based hydrogen storage, along with representative studies using UiO-type MOFs.

4.1 Spillover-assisted hydrogen storage on UiO-type MOFs

4.1.1 Hydrogen spillover

Hydrogen spillover, where H_2 dissociates into atomic hydrogen and migrates onto the host surface, has attracted significant attention as a strategy for generating and delivering reactive hydrogen species. Historically, hydrogen spillover has been primarily discussed in the context of heterogeneous catalysis since the 1960s [192–196], whereas its extension to hydrogen storage in porous materials has been developed more recently [197–201]. Hydrogen spillover typically requires a dissociation catalyst such as Pt- or Pd-based nanoparticles. Accordingly, MOFs serve as ideal model platforms for spillover studies, enabling the controlled placement of dissociation catalysts while offering hydrogen-accepting surfaces and transport pathways. Although hydrogen spillover has been widely investigated, its quantitative contribution to hydrogen storage remains controversial because of reproducibility issues and the difficulty of directly identifying mobile hydrogen species [202]. Among the various MOFs, UiO-type MOFs are robust hosts that can tolerate postsynthetic modifications and nanoparticle incorporation. Based on this background, this section summarizes the recent progress of spillover-assisted hydrogen storage in UiO-type MOFs.

4.1.2 Room-temperature hydrogen storage using noble metal nanoparticles

Although room-temperature hydrogen uptake is essential for practical hydrogen-storage applications, the physisorption of H_2 onto porous adsorbents is typically weak at ambient temperatures. Kang et al. [203] addressed this limitation using a spillover strategy in UiO-66 and its amino-functionalized analog (UiO-66-NH₂) as the host framework [203]. The UiO-66-NH₂ samples were synthesized with different acid modulators (AcOH or HCl) and denoted as UiO-66_{AcOH}-NH₂ and UiO-66_{HCl}-NH₂, respectively. Pt decoration was carried out through the methanol-phase impregnation of the MOFs (UiO-66, UiO-66_{AcOH}-NH₂, and UiO-66_{HCl}-NH₂) with an H_2PtCl_6 precursor, followed by drying and H_2 reduction to form Pt nanoparticles (150 °C, 1 h) (Figure 11a). The amino groups in UiO-66-NH₂ were expected to anchor Pt anions, thereby retaining the Pt species during reduction and leading to well-dispersed Pt nanoparticles (Figure 11b).

H_2 adsorption isotherms at 30 °C revealed that pristine UiO-66 and its amino-functionalized derivatives exhibited linear physisorption behavior, reaching around 0.06–0.18 wt% at 3.0 MPa and 30 °C. By contrast, Pt-decorated UiO-66-NH₂ (Pt/UiO-66_{AcOH}-NH₂ and Pt/UiO-66_{HCl}-NH₂) exhibited a pronounced enhancement in hydrogen uptake (Figure 11c).

Among them, Pt/UiO-66_{HCl}-NH₂ showed the highest H₂ uptake, reaching 0.71 wt% at approximately 3.3 MPa and 30 °C. This enhancement was attributed to the hydrogen spillover effect, in which Pt nanoparticles catalytically dissociate H₂ molecules, and the resulting hydrogen species migrate onto the UiO-66-NH₂ framework. XPS analysis suggested that the spillover hydrogen species interact with, or hydrogenate, carboxylate groups within the framework. The modulator-controlled MOF particle size and Pt nanoparticle dispersion were also considered important factors facilitating the spillover process. Importantly, cycling measurements were conducted to evaluate reversibility under practical conditions. Cyclic tests of Pt/UiO-66_{HCl}-NH₂ at 30 °C showed that the initial uptake (0.71 wt% at ~3.3 MPa) gradually decreased to 0.36 wt% after five cycles (Figure 11d). TEM images indicated agglomeration of the Pt nanoparticles after cycling. Additionally, the O 1s XPS spectra showed an increased hydroxyl component, suggesting the partial loss or occupation of hydrogen-accepting sites.

Notably, such a significant decrease in hydrogen uptake over only a few cycles is not unique to this material. Rather, it reflects a broader limitation frequently observed in spillover-mediated hydrogen storage systems, in which repeated cycling can lead to degradation of active sites and a consequent reduction in storage capacity [202,204,205]. Although UiO-type MOFs generally maintain their stability under high-pressure hydrogen cycling, active hydrogen species generated during spillover may induce structural degradation at defect sites. Such processes may result in irreversible structural changes, including framework unzipping [206], particularly in regions containing a high concentration of defects.

Wang et al. [207] reported the enhancement of room-temperature hydrogen uptake by Pd-decorated UiO-66-NH₂ (Pd/UiO-66-NH₂) [207]. In their system, Pd nanoparticles were introduced via the chemical reduction of PdCl₂ using NaBH₄ in an aqueous UiO-66-NH₂ suspension. Hydrogen adsorption measured at 298 K showed a markedly increased uptake, reaching ~3.7 wt% at 20 MPa. Notably, the authors proposed that the ultrathin carbon layer observed at the Pd-MOF interface could lower the energy barrier for hydrogen migration. However, cyclability was not reported in this study, so the durability of the enhanced uptake remains unclear.

4.1.3 *Room-temperature hydrogen storage using non-noble metal nanoparticles*

In addition to noble metals, Liu et al. [208] demonstrated that inexpensive transition-metal nanoparticles can also induce an efficient spillover effect in UiO-66. Cu, Ni, or bimetallic CuNi nanoparticles were incorporated into UiO-66 via a double-solvent impregnation of UiO-66 in *n*-hexane with an aqueous solution of CuCl₂·2H₂O and/or NiCl₂·6H₂O, followed by NaBH₄ reduction, yielding Cu@UiO-66, Ni@UiO-66, and CuNi@UiO-66 (Figure 12a). Hydrogen adsorption isotherms at 298 K showed that pristine UiO-66 exhibited near-linear physisorption with a maximum uptake of 0.20 wt% at 6.0 MPa, whereas CuNi@UiO-66 displayed a pronounced enhancement, reaching 0.74 wt% at 6.0 MPa (Figure 12b). Notably, the authors concluded that the spillover efficiency of CuNi@UiO-66 was comparable to those of previously reported Pd- or Pt-modified MOFs. DFT calculations predicted that H₂ adsorbs

more favorably on the CuNi surface and that the energy barrier for H–H bond dissociation is lower than that on monometallic Cu or Ni, which supports the enhanced hydrogen uptake observed for CuNi@UiO-66. However, cycling performance was not reported in this study. In any case, an important challenge in spillover-based hydrogen storage is the design of systems that enable atomic hydrogen to recombine and desorb through associative desorption.

4.2 Tuning thermodynamics and kinetics of hydrides via nanoconfinement in UiO-type MOFs

4.2.1 Nanoconfinement

Hydrides, in which hydrogen is chemically bound to metal centers, are an important class of solid-state hydrogen carriers that offer high volumetric hydrogen density and inherent safety advantages [209–212]. However, bulk metal hydrides typically require elevated temperatures for dehydrogenation and high H₂ pressures for rehydrogenation, rendering onboard utilization and regeneration unfeasible. To address these limitations, reducing the size of the metal hydrides has become a well-established strategy for engineering the thermodynamics, kinetics, and reversibility of hydrogen chemisorption [168,213–215]. In this context, MOFs provide an attractive platform for hydride species because of their well-defined pore architectures and chemically tunable internal surfaces [216–218]. Herein, we focus on the use of UiO-type MOFs as host frameworks to probe the effects of nanoconfinement on hydride materials toward the development of practical hydrogen-storage systems.

4.2.2 Nanoconfined metal borohydride

Inside MOFs, metal hydrides can be stabilized as nanocrystals or nanoclusters, thereby inhibiting their agglomeration. To better understand the limitations and stabilization mechanisms of nanoclustering, Schneemann et al. [219] investigated metal hydride nanoconfinement using UiO-67 consisting of 2,2'-bipyridine-5,5'-dicarboxylate (UiO-67bpy) as a 3D-porous framework [219]. Owing to the electron-rich bipyridine nitrogen sites capable of anchoring electron-deficient metal species through donor–acceptor interactions, magnesium borohydride (Mg(BH₄)₂) was selected as a model hydride because of its high gravimetric hydrogen capacity (14.9 wt %)[220–223]. Mg(BH₄)₂ incorporated into UiO-67bpy (Mg(BH₄)₂@UiO-67bpy) was prepared using a facile solvent-impregnation method (Figure 13a). Structural and spectroscopic analyses revealed that Mg(BH₄)₂ was confined within the pores in a highly dispersed, nearly molecularly dispersed state rather than as bulk crystalline domains. Importantly, N K-edge X-ray absorption spectroscopy showed a blue shift in the absorption edge from 398.54 eV for UiO-67bpy to 398.85 eV for Mg(BH₄)₂@UiO-67bpy, indicating charge transfer from the bipyridine N atoms to Mg(II) upon coordination at the pyridinic nitrogen sites (Figure 13b). Hydrogen-release measurements further showed that Mg(BH₄)₂@UiO-67bpy begins to desorb H₂ at 120 °C, whereas bulk Mg(BH₄)₂ typically desorbs H₂ at 270–280 °C (Figure 13c). This behavior was attributed to confinement-induced electronic modulation that weakens the B–H bonds and facilitates hydrogen release. Variable-

temperature ^{11}B magic-angle spinning NMR (^{11}B MAS-NMR) further showed that $\text{Mg}(\text{BH}_4)_2$ confined within UiO-67bpy gradually decomposes upon heating, as the BH_4^- signal decreased while signals assigned to B–O species increased (Figure 13d). Rehydrogenation was unsuccessful, likely owing to the formation of stable B–O species that limit reversibility. Therefore, designing systems capable of reversible hydrogen uptake after H_2 release is of critical importance.

4.2.3 Nanoconfined metastable metal hydride

Furthermore, Shivanna et al. [224] extended this concept [219] to the stabilization of metastable metal hydrides (AlH_3) [225–227], within the same UiO-67bpy framework ($\text{AlH}_3@ \text{UiO-67bpy}$) (Figure 14a). Hydrogen release measurements showed that $\text{AlH}_3@ \text{UiO-67bpy}$ released H_2 corresponding to 1.10 wt% within 30 min at 250 °C, reaching 1.25 wt% after an additional 2 h (Figure 14b). Notably, rehydrogenation at 70 MPa H_2 and 60 °C for 72 h enabled partial reversibility, whereas an analogous composite prepared from the unfunctionalized UiO-67 framework ($\text{AlH}_3@ \text{UiO-67}$) showed no detectable reversibility under the same conditions. ^{27}Al magic angle spinning nuclear magnetic resonance (^{27}Al MAS NMR) spectroscopy showed three distinct Al chemical environments at 13 and 37 ppm, assigned to AlH_3 species, along with an additional signal at 66 ppm attributed to AlH_2 (Figure 14c). DFT calculations predicted that AlH_3 dissociates upon coordination to the bipyridine site and subsequently undergoes hydrogen spillover to the β -carbon of the linker, forming AlH_2 directly coordinated to the bipyridine sites (denoted as $^*\text{AlH}_2$). This dissociation process is derived from the nearly full electron ($0.82e^-$) transfer from AlH_3 to the bipyridine linker. Further calculations on the $\text{AlH}_2(\text{AlH}_3)_x$ cluster models qualitatively supported these assignments, suggesting that the 66-ppm resonance corresponds to $^*\text{AlH}_2$, while the signals at 13 and 37 ppm arise from the AlH_3 clusters anchored to $^*\text{AlH}_2$ (Figure 14d). Their findings provide a platform for tuning the thermodynamics and kinetics of metastable materials using UiO-67bpy.

4.2.4 Nanoconfined chemical hydride

This nanoconfinement strategy has also been applied to other chemical hydrides. Ammonia borane (AB: NH_3BH_3), which has a high hydrogen content (19.5 wt%) and is chemically stable at room temperature, has been extensively studied to lower its hydrogen-release temperature and suppress the formation of undesired byproducts [228–231]. Chung et al. [232] systematically studied the effect of nanoconfinement on AB using a series of MOFs, including UiO-66 and UiO-67, to elucidate the roles of pore size and porosity in hydrogen generation [232]. AB was incorporated into UiO-66 and UiO-67 using a solution-infiltration method, yielding $\text{AB}@ \text{UiO-66}$ and $\text{AB}@ \text{UiO-67}$, respectively. The PXRD pattern of $\text{AB}@ \text{UiO-66}$ was almost identical to that of the neat MOF, with no apparent diffraction peaks from AB, indicating that highly dispersed or amorphous AB was confined within the smaller pores. By contrast, $\text{AB}@ \text{UiO-67}$ exhibited weak additional diffraction signals attributable to AB, implying partial recrystallization in a larger pore environment than that of UiO-66.

Temperature-programmed desorption mass spectrometry (TPD-MS) revealed that hydrogen ($m/z = 2$) release from AB confined in MOFs shifted to significantly lower temperatures compared to neat AB (100 and 113 °C). The decomposition temperature of AB decreased as the AB domain size decreased. Consistent with this trend, AB@UiO-66, which had the smallest pore size among the studied MOFs, exhibited the lowest H₂ desorption temperatures (64 and 78 °C) (Figure 15).

5 Summary

This review summarized recent progress in hydrogen storage studies using UiO-type MOFs as robust and structurally tunable platforms. A summary of representative UiO-type MOFs and their reported H₂ uptake values is provided in Table 2. For hydrogen adsorption, an ideal MOF would combine several demanding requirements: facile and scalable synthesis, high accessible surface area, and high framework robustness. In this context, UiO-type MOFs occupy a distinct position because they already offer relatively accessible synthesis, exceptional chemical and thermal robustness, and broad structural tunability. Beyond their promising potential as hydrogen adsorbents, UiO-type MOFs also provide well-defined platforms for systematically examining key structural and chemical factors that govern hydrogen storage behavior, including surface area, pore structure, linker functionality, framework densification, metal nanoparticle incorporation, and nanoconfined hydride species. Thus, UiO-type MOFs should be regarded not only as hydrogen adsorbents but also as model systems for understanding the structure–property relationships that govern solid-state hydrogen storage materials.

For physisorption-based storage, the practical advantage of UiO-type MOFs becomes most apparent when their performance is evaluated under densification conditions. Many high-performing MOFs achieve large H₂ capacities through maximizing surface area and pore volume, but their low bulk density and structural fragility can limit their use in confined tank volumes. In contrast, the reported compaction of UiO-66 and monolithic processing of UiO-67 are particularly important because they demonstrate that UiO frameworks can improve volumetric H₂ capacity while largely preserving crystallinity, accessible porosity, and gravimetric uptake. As shown in Figure 5, for example, UiO-68-ANT shows a deliverable capacity close to that of MOF-177, indicating that extended-linker UiO frameworks can approach the volumetric deliverable performance of high-surface-area benchmark MOFs while offering the additional advantage of Zr-based framework robustness. In addition, monolithic UiO-67 exceeds monolithic HKUST-1, suggesting that open metal sites do not necessarily dominate high-pressure deliverable performance. Although open metal sites enhance H₂ binding at low coverage, the capacity under swing conditions is largely governed by accessible pore volume, framework density, and porosity retention after densification.

Functionalization can enhance the intrinsic H₂ adsorption ability of UiO-type MOFs, but its effect must be interpreted carefully. Polar functional groups, such as nitrogen-containing linkers and heterometallic nodes, can strengthen local H₂ interactions, particularly under near-ambient conditions. However, functional groups also occupy pore volume and

may reduce accessible surface area, which leads to reduce in total H₂ capacity. It is also important to note that stronger H₂ binding sites do not necessarily improve usable capacity at 298 K, because the entropic penalty associated with the localization of H₂ can offset the enthalpic gain. This highlights the importance of evaluating ΔH , ΔS , and ΔG together, using variable-temperature adsorption measurements to clarify whether newly introduced binding sites truly improve the thermodynamic driving force for H₂ adsorption.

Spillover-assisted storage and hydride nanoconfinement extend the role of UiO-type MOFs from passive adsorbents to platforms for controlling reactive hydrogen species. In both approaches, the central challenge is not simply to activate H₂ or lower the hydrogen-release temperature. The activated hydrogen species or dehydrogenated products must remain sufficiently reversible during desorption or rehydrogenation, rather than being irreversibly trapped at the framework. For spillover systems, hydrogen-accepting sites should promote migration without irreversibly trapping hydrogen. For nanoconfined hydrides, the hydride domain size and local hydride–framework interface must be controlled because excessive dispersion or direct contact with oxygen-rich Zr nodes may promote irreversible B–O, Al–O, or framework-bound species. These studies highlight the importance of controlling not only the size of reactive hydrogen-storage domains but also their spatial relationship with Zr₆ nodes, organic linkers, and metal nanoparticles.

Collectively, these findings show that UiO-type MOFs provide a robust and structurally tunable platform for studying hydrogen adsorption, spillover-assisted storage, and hydride nanoconfinement. Their hydrogen storage behavior is governed by multiple factors, including accessible porosity, framework density, adsorption-site chemistry, and the spatial arrangement of metal species or hydride domains within the framework.

6 Perspective

Future UiO-based hydrogen storage research should move toward spatially controlled framework engineering, taking advantage of the robustness and modular pore chemistry of UiO-type MOFs. For physisorption-based storage, a key design target is not simply to create stronger H₂-binding sites, but to optimize the number, distribution, and local environment of polar sites within accessible pores. In this regard, mixed-linker strategies provide a practical route to tune the density and spatial distribution of functional sites via the incorporation of a controlled fraction of linkers bearing polar groups or metal-coordination sites, while maintaining the overall UiO framework.

Building on this site-density control, highly dispersed Li⁺ sites represent an attractive example of spatially designed H₂-binding centers. Inspired by theoretical studies on alkali-metal-decorated porous materials [233–236], isolated Li⁺ sites could enhance H₂ affinity through charge-induced dipole interactions without requiring bulky functional groups. In UiO-type MOFs, oxygen-containing or anionic linkers, such as those bearing pendant carboxylate, sulfonate, or phenoxide groups, could be introduced through mixed-linker design and subsequently used as anchoring sites for Li⁺ ions. This approach could allow Li⁺ sites to be

spatially dispersed along the pore walls while preserving pore volume and molecular mobility. Importantly, the density of Li^+ sites should be optimized rather than simply maximized, because excessive polar sites may reduce pore volume, decrease pore accessibility, or overly restrict the motion of adsorbed H_2 molecules. Therefore, Li-decorated UiO frameworks should be evaluated in terms of the balance among adsorption enthalpy, adsorption entropy, Gibbs free energy, pore volume, molecular mobility, and deliverable capacity. At the same time, molecular-level binding-site design must be evaluated under practically relevant conditions. Densification tolerance alone is not sufficient for assessing the applicability of UiO-type MOFs as hydrogen adsorbents. Although UiO-type MOFs are widely recognized for their high chemical and thermal stability, repeated H_2 adsorption-desorption cyclability has rarely been systematically examined. Therefore, future studies should report cycle-dependent H_2 uptake, capacity-retention profiles, packing-density changes, and post-cycling structural and porosity characterization.

For chemisorption-related hydrogen storage, particularly spillover-assisted systems, future design should focus not only on H_2 dissociation but also on controlling the migration pathway of dissociated hydrogen species. Catalytic metal sites and hydrogen-accepting regions should be positioned so that dissociated hydrogen can migrate through the framework without being irreversibly trapped at oxygen-rich Zr_6 nodes or defect sites. In this regard, extended-linker structures, such as UiO-68-type frameworks, could be explored as future platforms for spatially separating catalytic metal sites from Zr-O/Zr-OH sites. Their larger pore spaces and longer linker regions may allow catalytic metal sites to be anchored on functionalized linkers, although such a design has not yet been systematically investigated for hydrogen storage. This spatial-design concept can also be extended to nanoconfined hydride systems. In these systems, future design should focus not just on confining hydride species within MOF pores, but on integrating confined hydride domains with nearby highly dispersed catalytic metal species in extended-linker UiO frameworks. For example, recent studies on borohydride-based nanocomposites have shown that nanoscale contact between hydride-derived domains and Ni catalytic clusters can substantially improve low-temperature hydrogenation and cycling reversibility [237,238]. These results suggest that hydride nanoconfinement should be coupled with spatially controlled catalytic H_2 activation rather than treated only as a size-reduction strategy.

Furthermore, UiO-based composite architectures could provide another route to introduce confined hydrogen-storage environments that are difficult to achieve in UiO frameworks alone. One possible direction is the incorporation of porous hydride frameworks into UiO-based matrices. Schneemann et al. demonstrated $\text{Mg}(\text{BH}_4)_2$ nanoconfinement in UiO-67bpy, establishing a precedent for combining UiO-type frameworks with borohydride-based hydrogen storage materials. Building on this work, exploring whether porous hydride phases, such as $\gamma\text{-Mg}(\text{BH}_4)_2$, can be incorporated while preserving their intrinsic microporosity would be an attractive future direction. Such a design is particularly interesting because $\gamma\text{-Mg}(\text{BH}_4)_2$ can accommodate densely packed molecular H_2 in its small pores, where H_2 is stabilized via directional $\text{B-H}^\delta\cdots\text{H}_2$ interactions with the hydridic pore surface [239,240]. If successful, this approach would expand hydride nanoconfinement beyond simple size reduction toward the

design of porous hydride domains within robust UiO matrices. Another possible direction is the construction of UiO/2D-material composites based on the nanopump effect reported for stacked two-dimensional materials [241,242]. In this concept, interlayer spaces with approximately 6–7 Å can increase the local density of H₂ through overlapping adsorption potentials from opposing two-dimensional surfaces. The role of UiO domains would be to serve as porous structural components that suppress dense restacking of the two-dimensional sheets and preserve H₂-accessible pathways to these confined spaces, thereby improving adsorption kinetics without eliminating the local confinement effect.

Finally, advances in computational materials science, including high-throughput screening, molecular simulations, and machine-learning-assisted materials design, are expected to accelerate the discovery of promising linker chemistries, defect configurations, and catalytic compositions. The combination of data-driven materials discovery with experimentally guided synthesis may enable the rational development of UiO-type MOFs possessing balanced adsorption thermodynamics, rapid hydrogen transport, excellent cycling durability, and scalable synthesis.

Overall, future UiO-type MOF research should move beyond optimizing individual properties and focus on designing where and how H₂-binding sites, catalytic metal species, and hydride domains are arranged within a robust porous framework. This direction is particularly suitable for UiO-type MOFs because their robust and modular frameworks allow physisorption-oriented binding-site design and chemisorption-related reactive-site design to be explored within the same structural platform. Such spatially controlled design will be essential for developing next-generation hydrogen storage materials that combine high usable capacity, reversibility, durability, and mechanistic tunability.

Disclosure statement

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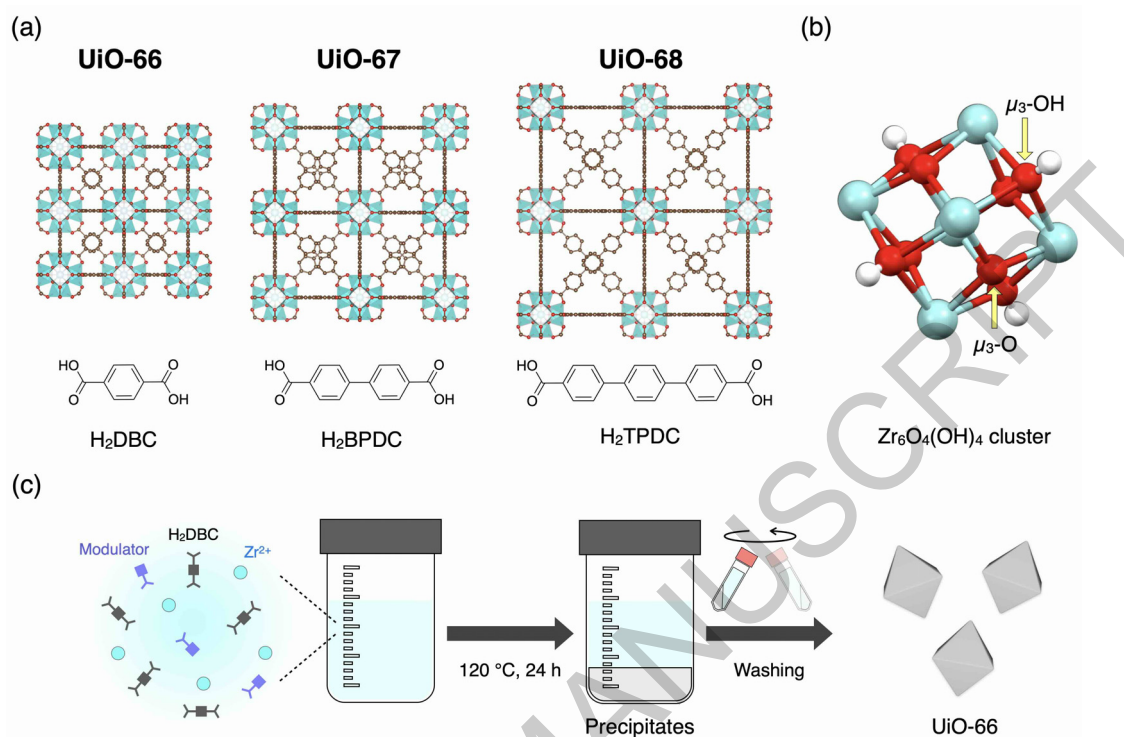


Figure 1. (a) Framework structures of UiO-66, UiO-67, and UiO-68 together with the corresponding organic linkers H₂BDC, H₂BPDC, and H₂TPDC, respectively. In panel (a), the framework is shown using polyhedral and ball-and-stick representations, where cyan, red, and brown denote Zr, O, and C atoms, respectively. Hydrogen atoms are omitted for clarity. (b) Schematic structure of a Zr₆O₄(OH)₄ cluster. The μ_3 -OH and μ_3 -O groups indicate that each hydroxo or oxo group bridges three Zr atoms. In panel (b), cyan, red, and white spheres represent Zr, O, and H atoms, respectively. (c) Schematic representation of a typical synthesis procedure of UiO-66. Monocarboxylic acids such as benzoic acid and acetic acid are often used as a modulator.

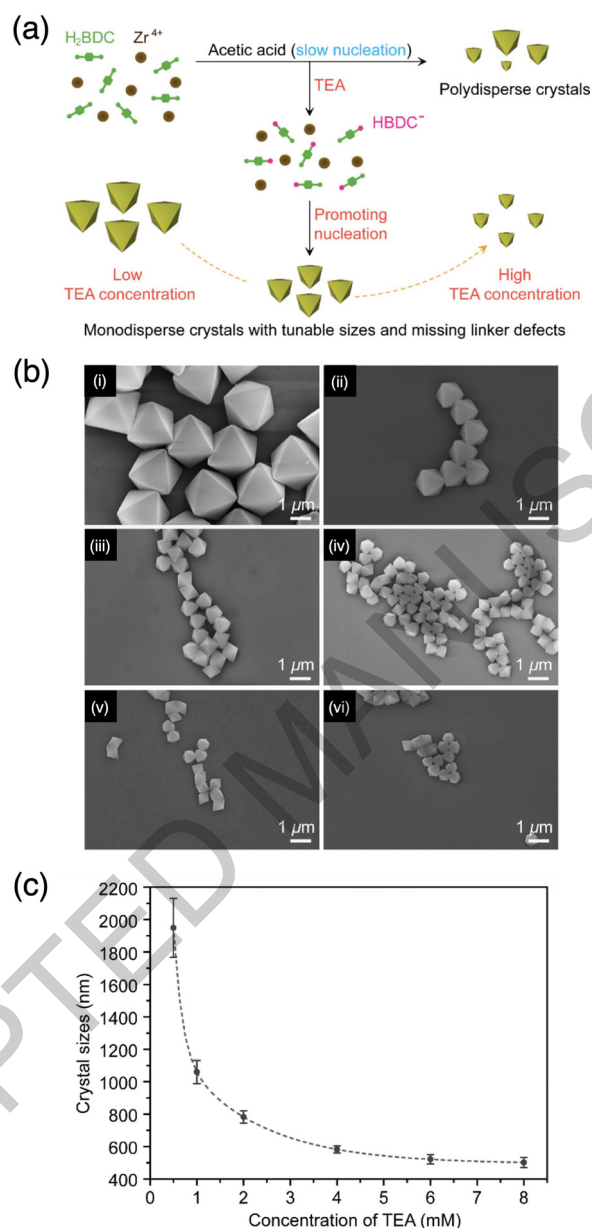


Figure 2. (a) Illustration of the acetic acid-modulated and acetic acid/triethylamine (TEA) comodulated syntheses of UiO-66 in large scale. (b) Scanning electron microscopy (SEM) images of UiO-66 crystals synthesized in the presence of 4 mM ZrCl_4 , 4 mM BDC, 2.4 M acetic acid, and TEA at concentrations of (i) 0.5, (ii) 1, (iii) 2, (iv) 4, (v) 6, and (vi) 8 mM, respectively. (c) Statistical average crystal sizes of samples obtained from four independent batches of reactions with the same experimental parameters versus TEA concentration. Reproduced with permission [149] 2017, American Chemical Society.

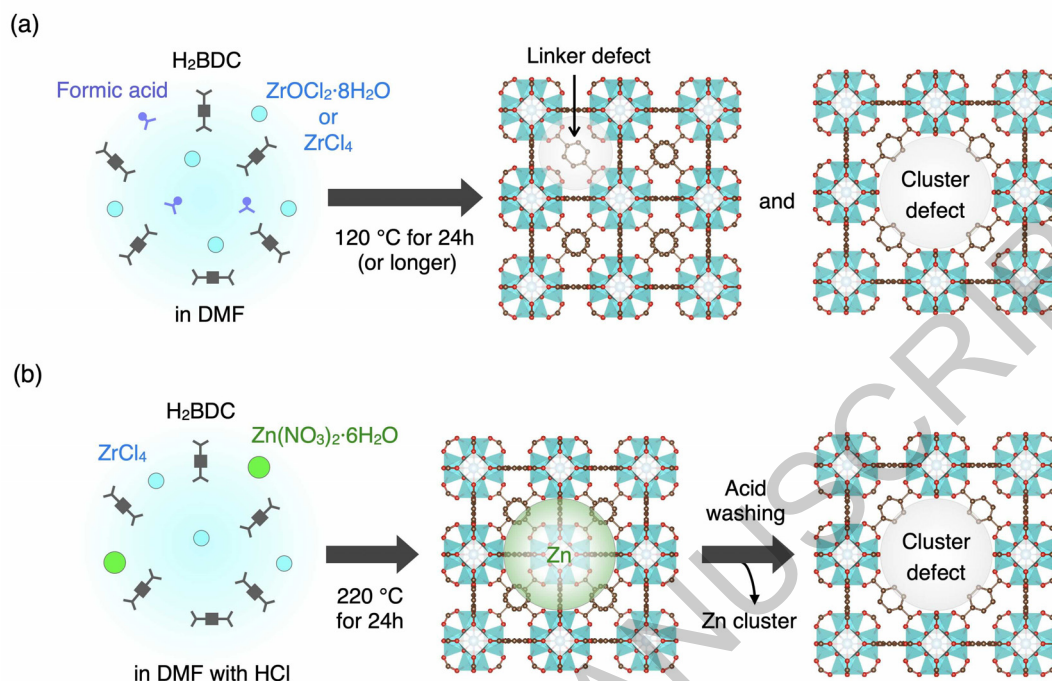


Figure 3. Schematic illustration of defect formation strategies in UiO-66. (a) Formic-acid-modulated synthesis of UiO-66, which can generate missing-linker and/or missing-cluster defects. (b) Post-synthetic creation of selective missing-cluster defects in mixed-metal (Zn, Zr)-UiO-66 by selective removal of acid-labile Zn species. The mixed-metal UiO-66 is first synthesized using a Zn precursor and subsequently treated by acid washing, resulting in missing-cluster-defective UiO-66. Cyan, red, gray, and white spheres represent Zr, O, C, and H atoms, respectively. Right: UiO-67 with a missing-cluster defect. Cyan, red, gray, and white spheres represent Zr, O, C, and H atoms, respectively.

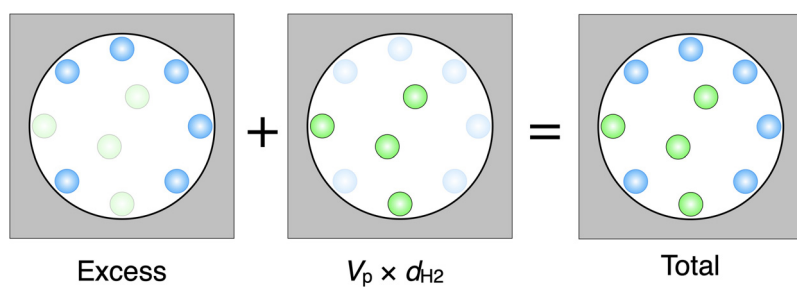


Figure 4. Schematic of the relationship between excess and total hydrogen adsorption in porous materials. The total uptake is expressed as the sum of the experimentally measured excess adsorption (shown as blue balls) and the contribution from the bulk gas (shown as green balls) within the pore volume ($V_p \times d_{H_2}$).

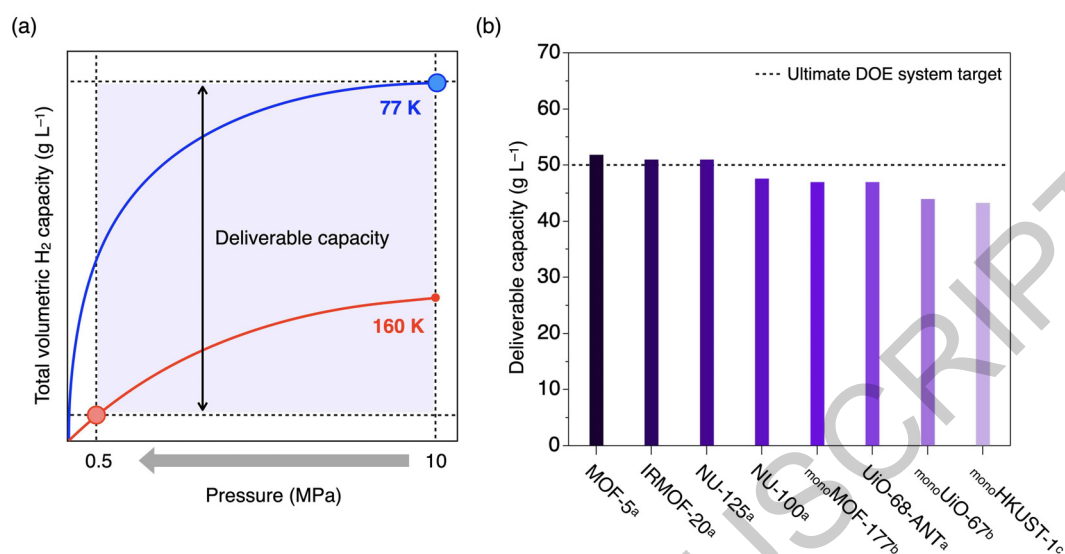
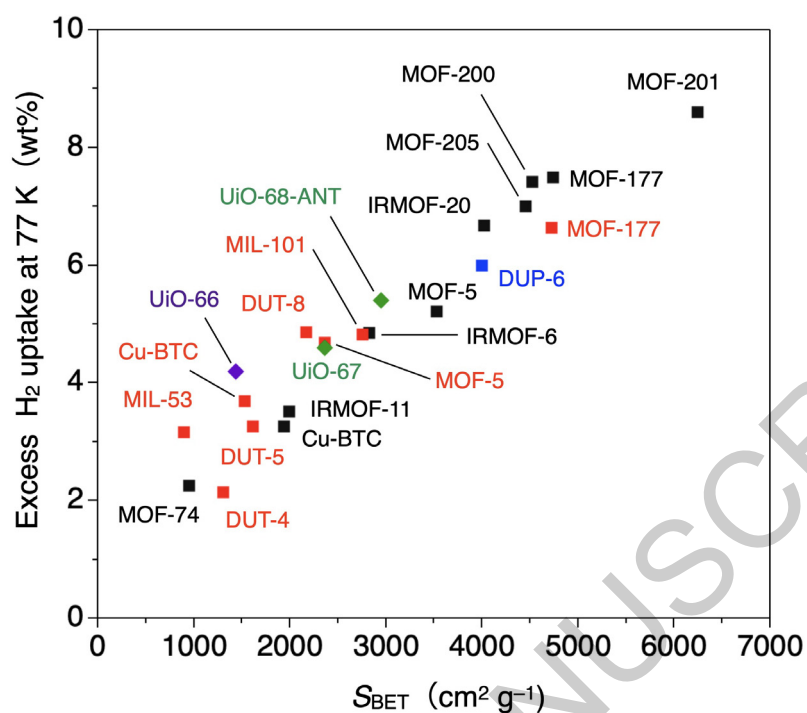


Figure 5. (a) Illustration of total volumetric hydrogen uptake as a function of pressure at 77 K (blue curve) and 160 K (red curve), showing the concept of deliverable capacity. (b) Comparison of volumetric deliverable H₂ capacities for various MOFs under defined pressure- and temperature-swing conditions, with the dashed line indicating the DOE system-level target. These data were collected from the different literatures [19, 95, 97, 169]. Superscripts next to the MOF names indicate the method used for volumetric calculation: ^acalculated based on packing density, ^bcalculated based on crystallographic density, ^ccalculated based on envelope density obtained from mercury intrusion porosimetry.



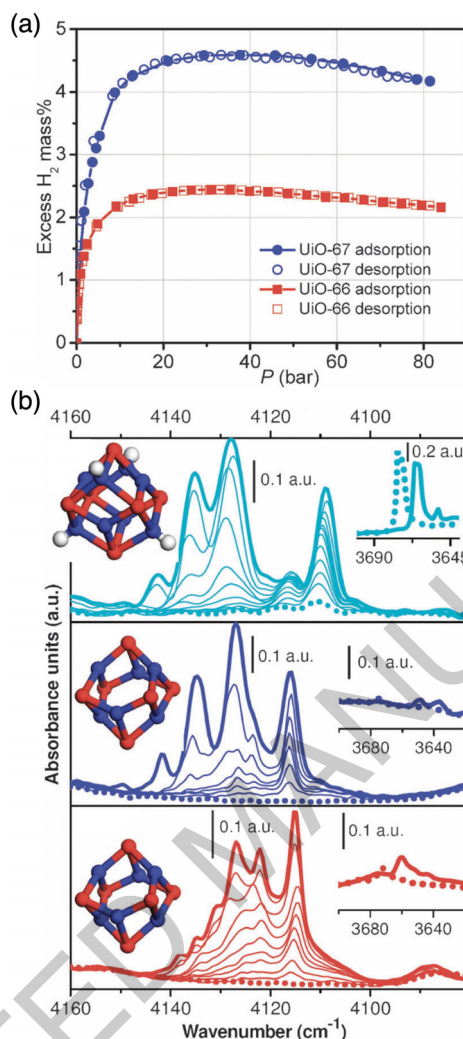


Figure 7. (a) H₂ excess isotherms recorded at 77 K on UiO-66 (red squares) and UiO-67 (blue circles). Filled and open symbols refer to the adsorption and desorption branches, respectively. (b) VT-FTIR spectra of H₂ adsorbed on hydroxylated UiO-67 (top panel), dehydroxylated UiO-67 (middle panel), and dehydroxylated UiO-66 (bottom panel) as a function of temperature (100–115 K). Dotted curves represent the activated material before H₂ dosage (spectra collected at 15 K). Bold curves represent the highest H₂ coverage (spectra collected at 15 K). Intermediate curves, from bold to dotted curves, represent spectra collected at increasing temperatures. Right insets show the ν(OH) stretching region of the IR spectra before (dotted curves) and after (bold curves) H₂ dosage. In the structural models, red, blue, and white spheres represent Zr, O, and H atoms, respectively. Reproduced with permission [176] 2012, Royal Society of Chemistry.

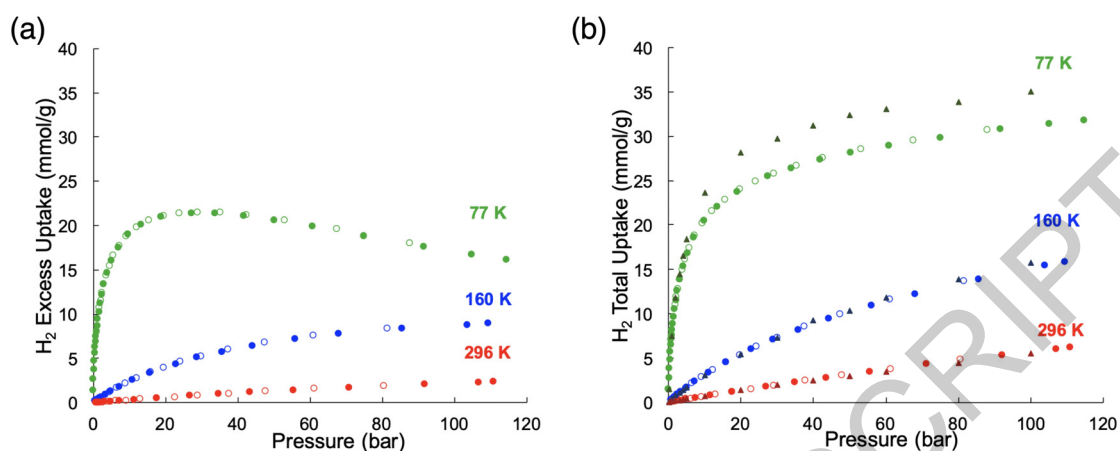


Figure 8. (a, b) Temperature-dependent excess (a) and total (b) hydrogen adsorption (filled points) and desorption (open points) isotherms at 77 (green), 160 (blue), and 296 K (black). Filled triangles represent simulated isotherms for UiO-67 based on grand canonical Monte Carlo calculations. Reproduced with permission [97] 2018, American Chemical Society.

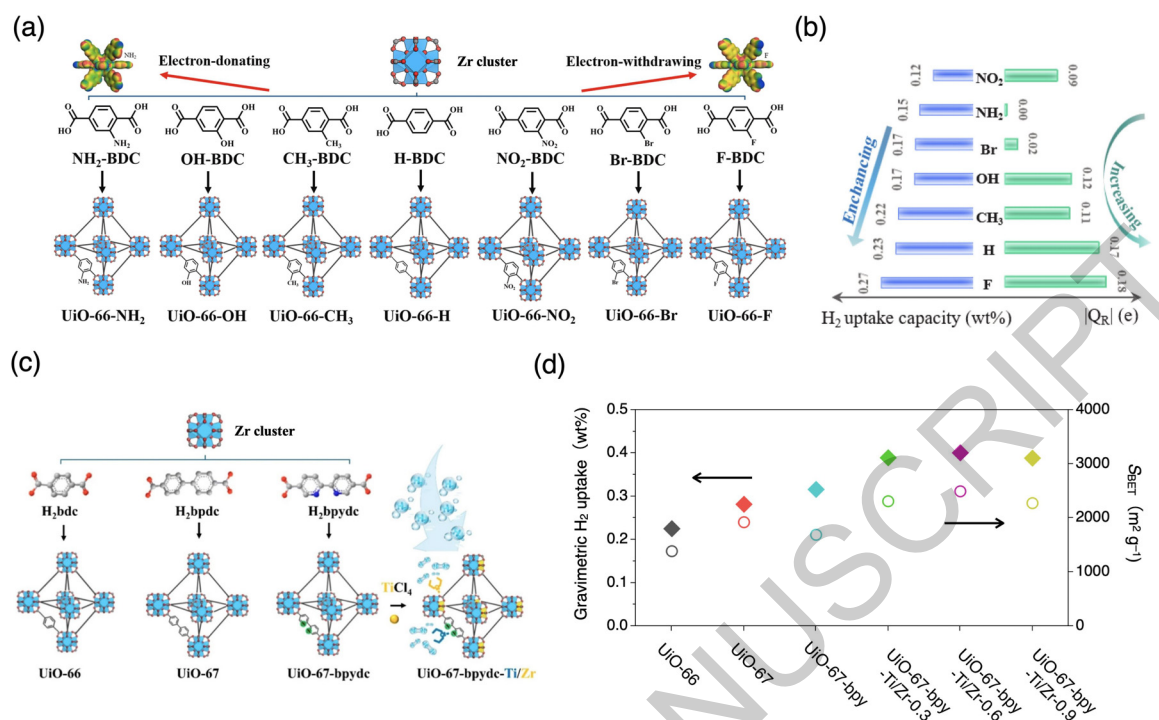


Figure 9. (a, b) Illustration of a series of UiO-66-X (X = H, CH₃, NH₂, OH, F, Br, and NO₂) (a) and the relationship between the excess H₂ capacity of UiO-66-X at 298 K and absolute value of the average electrostatic potential-derived charge ($|Q_R|$) (b). Reproduced with permission [182] 2026, Elsevier. (c) Schematic of the synthesis of UiO-66, UiO-67, UiO-67-bpydc, and UiO-67-bpydc-Ti/Zr. Reproduced with permission [183] 2025, American Chemical Society. (d) Plots of their excess H₂ uptake measured at 298 K and 10 MPa (left axis) and S_{BET} values (right axis) for these UiO materials. Data extracted from ref. 153 and plotted by the authors.

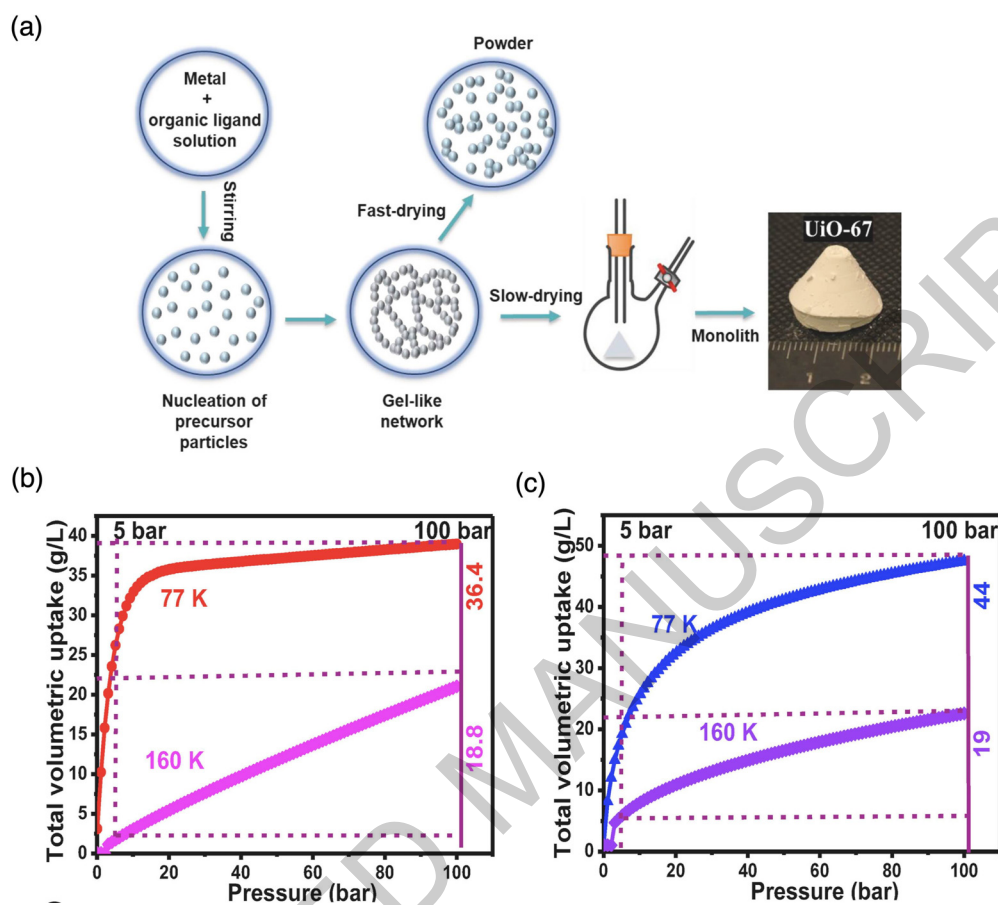


Figure 10. (a) Schematic representation of monolithic and powder MOF synthesis. (b, c) Total volumetric H_2 storage at 77 and 160 K for $_{\text{powd}}\text{UiO-67}$ (b) and $_{\text{mono}}\text{UiO-67}$ (c) obtained using packing density. Reproduced with permission [94] 2025, Elsevier.

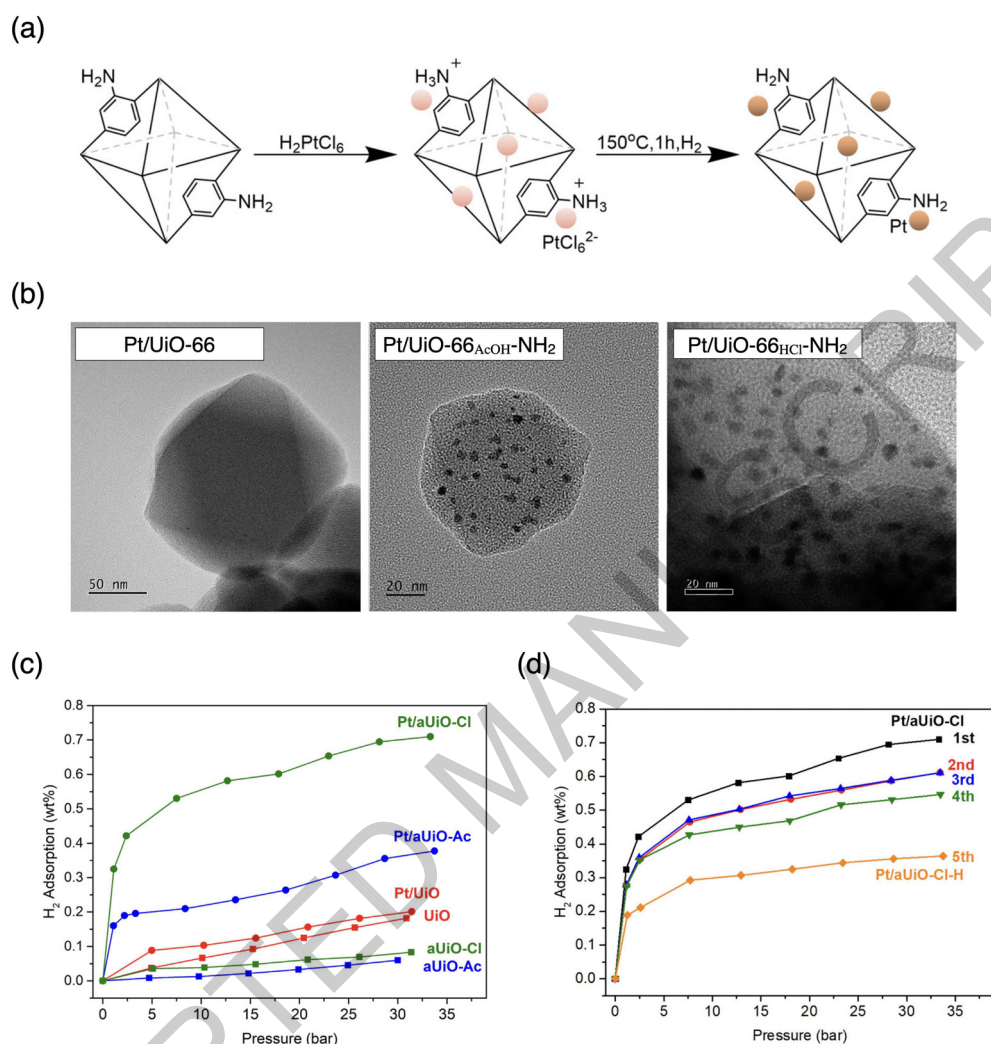


Figure 11. (a) Schematic of the synthesis of Pt/UIO-NH₂ with the assistance of amino decoration to anchor platinum precursors. (b) FE-TEM images of Pt/UIO-66 (left), Pt/UIO-66_{AcOH}-NH₂ (middle), and Pt/UIO-66_{HCl}-NH₂ (right). (c) Hydrogen adsorption isotherms of pure MOFs (UiO-66, UiO-66_{AcOH}-NH₂, and UiO-66_{HCl}-NH₂) and Pt-doped MOFs (Pt/UIO-66_{AcOH}-NH₂ and Pt/UIO-66_{HCl}-NH₂) at 30 °C up to 3.5 MPa H₂. (d) Hydrogen adsorption cycling test of Pt/UIO-66_{HCl}-NH₂ at 30 °C up to 3.5 MPa H₂. Reproduced with permission [203] 2021, American Chemical Society.

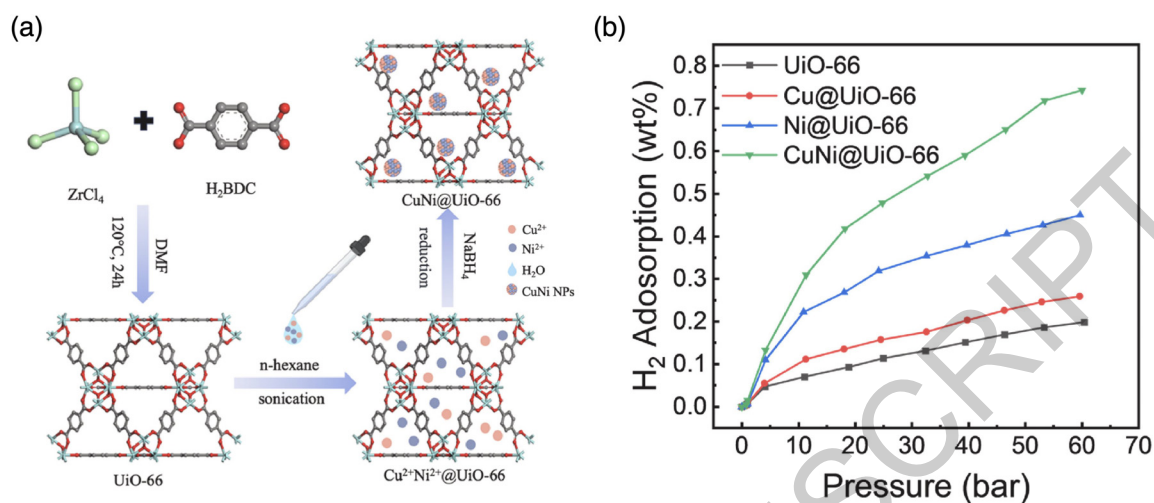


Figure 12. (a) Schematic of the synthesis process for the CuNi@UiO-66 composite. (b) Hydrogen adsorption isotherms of UiO-66, Cu@UiO-66, Ni@UiO-66, and CuNi@UiO-66 at 298 K and 6.0 MPa. Reproduced with permission [208] 2024, Elsevier.

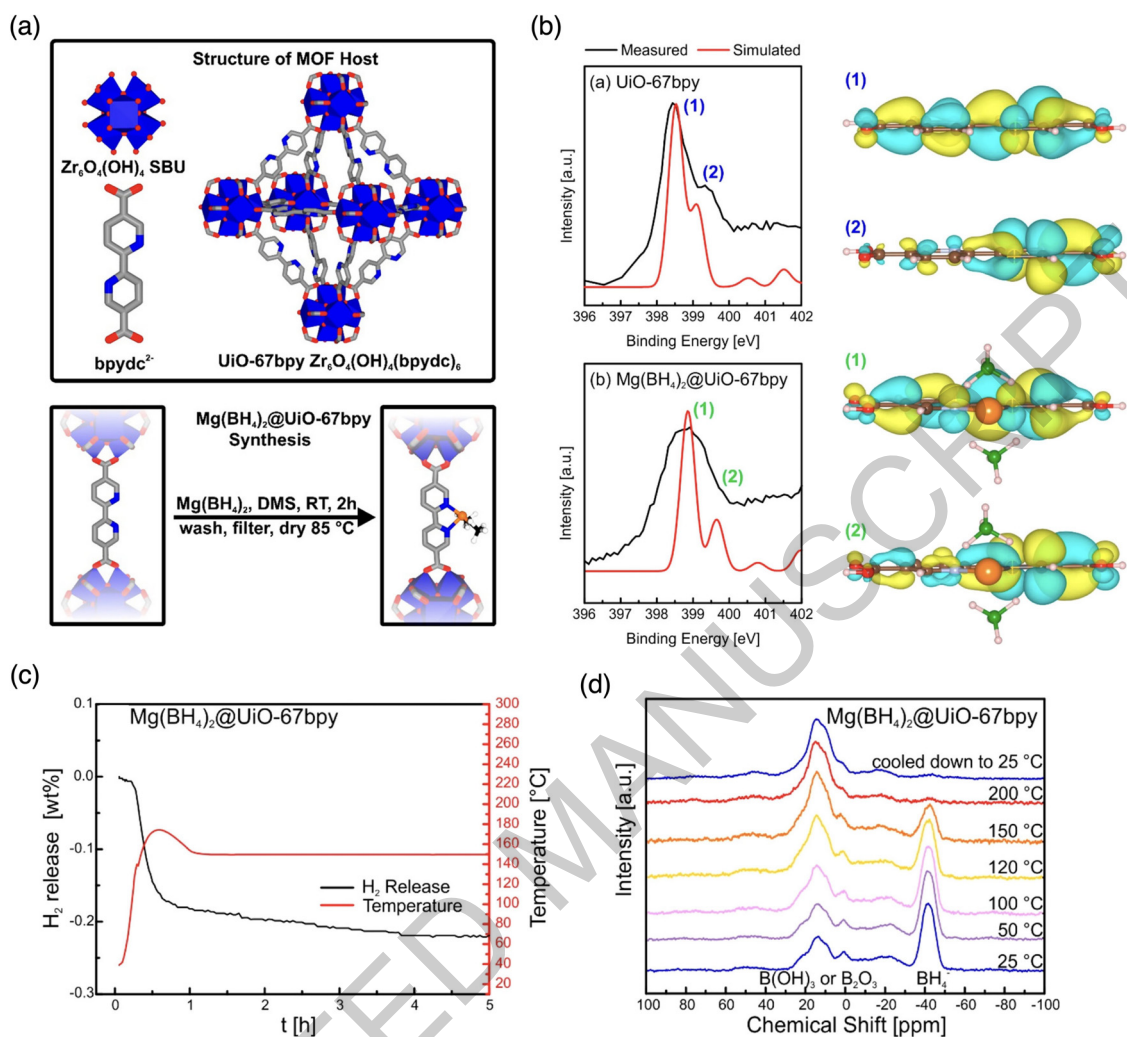


Figure 13. (a) Schematics of the organic and inorganic building blocks of UiO-67bpy and the octahedral pore (top) and the installation of $\text{Mg}(\text{BH}_4)_2$ at the bipyridine sites of UiO-67bpy (bottom). (b) N K-edge X-ray absorption spectra of UiO-67bpy (top) and $\text{Mg}(\text{BH}_4)_2@ \text{UiO}-67\text{bpy}$ (bottom). The black and red solid lines represent the experimental results and simulated spectra, respectively. (1) and (2) denote the 1st and 2nd excited states, and corresponding charge densities are shown in the right panel. (c) Sieverts measurement of $\text{Mg}(\text{BH}_4)_2@ \text{UiO}-67\text{bpy}$ used to quantify the amount of gas released at 150°C . The red curve represents the temperature profile, and the black curve represented the wt% of released hydrogen. (d) Variable-temperature ^{11}B -MAS NMR spectra of $\text{Mg}(\text{BH}_4)_2@ \text{UiO}-67\text{bpy}$. Reproduced with permission [219] 2025, American Chemical Society.

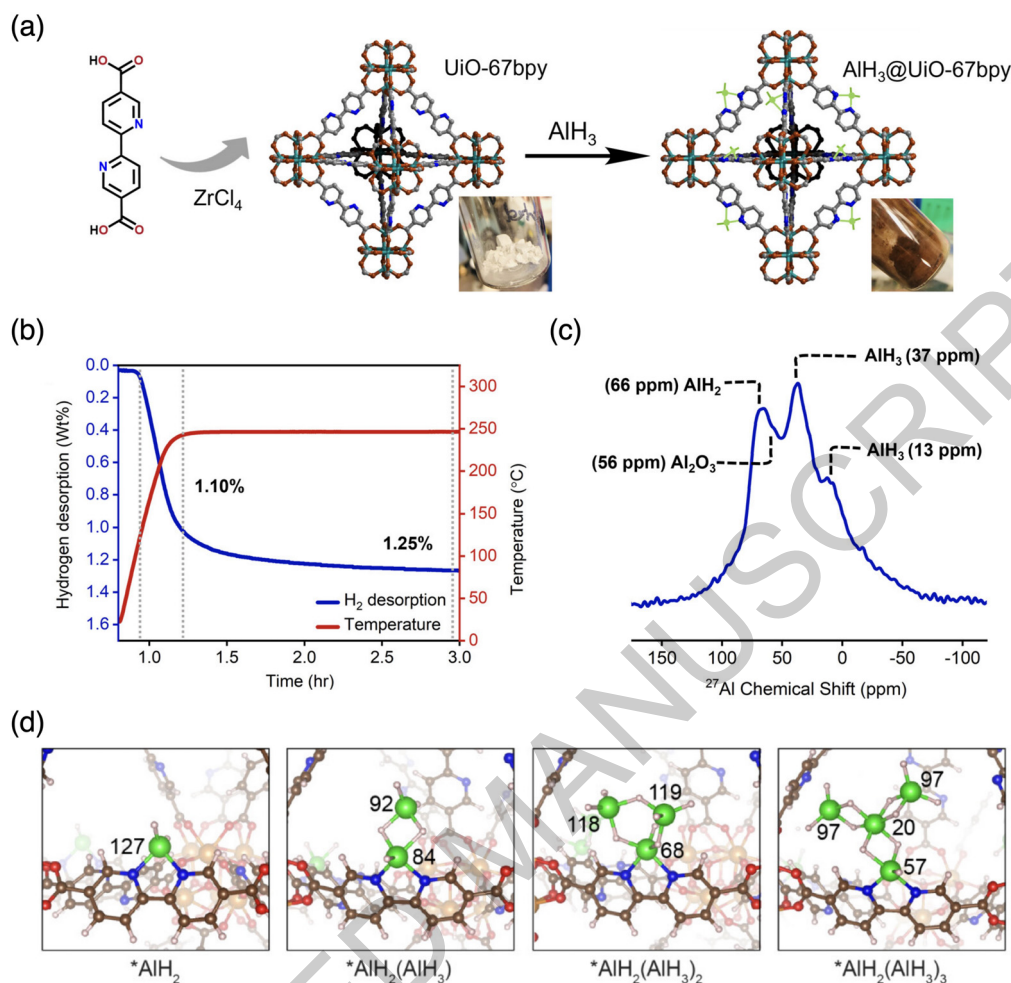


Figure 14. Synthesis and characterization of $\text{AlH}_3@ \text{UiO-67bpy}$. (a) Schematic of UiO-67bpy synthesis. Color changes observed upon infiltration with AlH_3 are shown in the top right. (b) First cycle Sieverts measurements for $\text{AlH}_3@ \text{UiO-67bpy}$. (c) ^{27}Al -MAS NMR profile of $\text{AlH}_3@ \text{UiO-67bpy}$. The three major ^{27}Al signals at 13, 37, and 66 ppm correspond to AlH_3 , AlH_3 , and $^*\text{AlH}_2$, respectively. A small peak was found at 56 ppm for Al_2O_3 . (d) DFT-optimized structures of complexed AlH_2 bound by $(\text{AlH}_3)_x$ ($x = 0-3$). In the structural models, green and pale pink spheres represent Al and H, respectively. The predicted Al chemical shifts of all Al atoms are shown for each structure. Reproduced with permission [224] 2025, American Chemical Society.

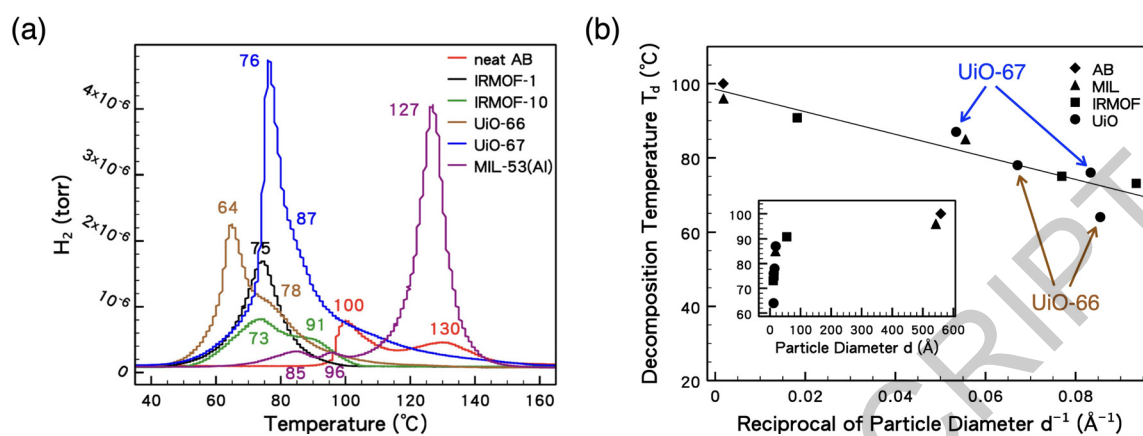


Figure 15. Temperature-programmed desorption with mass spectroscopy (TPD-MS) results for hydrogen desorption from AB (red) and AB in IRMOF-1 (black), IRMOF-10 (green), UiO-66 (red), UiO-67 (blue), and MIL-53(Al) (purple). AB decomposition peaked temperatures (T_d) of neat AB (◆) and AB incorporated in MOFs of MIL MOFs (▲), IRMOFs (■), and UiO MOFs (●) vs. the reciprocal particle size (d) of corresponding hydrides. T_d vs. d is shown in the inset. Reproduced with permission [232] 2017, American Chemical Society.

Table 1. List of representative hydrogen storage materials.

Material class	Representative material	Main storage mechanism	Typical condition	Representative H ₂ capacity/uptake	Strength	Limitation	Ref
UiO-type MOF	UiO-66	Physisorption	77 K/high pressure	5.0 wt% (total), 29–74 g/L (total)	High chemical/thermal stability, tunable framework	Low room-temperature uptake	94
	UiO-67			4.8–5.4 wt% (total), 36–44 g/L (total)		Low room-temperature uptake	95
	UiO-68			–		Limited experimental H ₂ -storage data	–
Benchmark MOFs	NU-1501-Al	Physisorption		14.5 wt% (total), 48 g/L (total)	High gravimetric and volumetric H ₂ uptake	Complex framework design	96
	MOF-177			6.3–7.5 wt% (total), 33–47 g/L (total)	High gravimetric uptake	Lower robustness than Zr-MOFs	95
	HKUST-1	Physisorption and open metal site interaction		5.7 wt% (total), 43 g/L (total)	Open Cu sites enhance H ₂ interaction	Moisture sensitivity and low-coverage saturation of open metal sites	97
	Mg-MOF-74			4.9 wt% (total), 45 g/L (total)	Open Mg sites enhance H ₂ interaction		98
Porous carbons	ZTC	Physisorption		6.0 wt% (total), 30–50 g/L (total)	High surface area, chemically robust carbon framework	Low room-temperature uptake	99
	C-PAF			17.49 wt% (total), 45.3 g/L (total)		Synthesis and processability issues	100
Metal hydride	MgH ₂	Reversible metal-hydride formation	Catalyst/nanostructure-assisted, moderate pressure	theor. 7.6 wt% (practical 4.5–6.7 wt%)	High gravimetric hydrogen capacity	High operating temperature and slow kinetics without modification	101
	LaNi ₅ H ₆		Near room temperature/moderate pressure	ca. 1.3–1.5 wt%	Reversible H ₂ absorption/desorption near room temperature	Low gravimetric capacity due to heavy alloy composition	102
Inorganic hydride	LiBH ₄	Chemical hydrogen release	Thermolysis/hydrolysis/catalytic dehydrogenation	theor. 18.5 wt% ca. 5–10 wt% reported	High theoretical gravimetric capacity	High dehydrogenation temperature and poor reversibility	103
	NH ₃ BH ₃			theor. 19.6 wt%		Byproduct formation	104
	NH ₃ (liquid)	Catalytic decomposition	Catalytic cracking at elevated temperature	theor. 17.6 wt%	Carbon-free carrier; established production/transport infrastructure	Toxicity, corrosiveness, and need for NH ₃ cracking/removal	105
Liquid organic hydrogen	MCH	Catalytic hydrogenation/dehydrogenation	Catalytic dehydrogenation at elevated temperature	theor. 6.1 wt%	Liquid at ambient conditions, compatible with existing fuel	Cost and catalyst durability issues	106
	12H-NEC			theor. 5.8 wt%		Cost and catalyst	107

carrier					infrastructure	durability issues	
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Table 2. List of selected UiO-type MOFs and reported H₂ uptake values discussed in this review.

MOFs	S _{BET} (m ² g ⁻¹)	V _p	Temp. (K)	Pres. (MPa)	Excess (wt%)	Ref.	Category
UiO-66	969	0.52	77	3.1	2.4	176	Physisorption
UiO-67	1877	0.95	77	3.8	4.6		
UiO-66	1434	–	77	6.0	4.2	177	
			298	6.0	0.5		
UiO-66	1358	0.43	77	1.8	3.35	178	
UiO-67	2360	0.91	77	3.0	4.4	97	
			160	11	1.8		
			298	11	0.5		
UiO-68-ANT	2950	1.17	77	3.0	5.3		
			160	11	2.3		
			298	11	0.6		
UiO-66	1386	0.56	298	10	0.23	182	Physisorption (linker functionalization)
			77	5.0	2.10		
UiO-66-CH ₃	949	0.4	298	10	0.22		
			77	5.0	2.10		
UiO-66-NH ₂	946	0.43	298	10	0.16		
			77	5.0	1.56		
UiO-66-OH	1077	0.43	298	10	0.17		
			77	5.0	1.74		
UiO-66-F	1023	0.54	298	10	0.27		
			77	5.0	1.89		
UiO-66-Br	748	0.31	298	10	0.17		
			77	5.0	1.41		
UiO-66-NO ₂	851	0.35	298	10	0.11		
			77	5.0	1.40		
UiO-66	1386	0.56	298	10	0.23	183	
			77	5.0	2.11		
UiO-67	1920	0.75	298	10	0.28		
			77	5.0	3.00		
UiO-67bpy	1688	0.71	298	10	0.32		
			77	5.0	3.50		
UiO-67bpy-Ti/Zr-0.3	2304	0.87	298	10	0.39		
			77	5.0	4.50		
UiO-67bpy-Ti/Zr-0.6	2488	0.96	298	10	0.40		
			77	5.0	4.53		
UiO-67bpy-Ti/Zr-0.9	2268	0.88	298	10	0.38		
			77	5.0	4.46		
UiO-66 powder	1737	0.96	77	10	2.1	94	Physisorption (compaction)
UiO-66 pellet	1707	0.81	77	10	2.7		
UiO-66 powder@80 °C	1413	0.61	77	10	3.1	191	

UiO-66 pellet@80 °C	1300	0.6	77	10	2.5		
UiO-67 powder	2513	0.81	298	10	0.51	95	
UiO-67 monolith	2303	0.73	298	10	0.42		
UiO-66	1390	0.61	303	3.0	0.18		
UiO-66AcOH-NH ₂	1170	0.54	303	3.0	0.06		
UiO-66HCl-NH ₂	1070	0.44	303	3.0	0.08	202	
Pt/UiO-66AcOH-NH ₂	930	0.46	303	3.0	0.38		
Pt/UiO-66HCl-NH ₂	890	0.36	303	3.0	0.71		
Pd/UiO-66-NH ₂	-	-	298	2.0	3.7	207	
UiO-66	1231	0.6	298	6.0	0.2		
Cu@UiO-66	958	0.53	298	6.0	0.26		
Ni@UiO-66	1050	0.58	298	6.0	0.45	208	
CuNi@UiO-66	928	0.51	298	6.0	0.74		
Mg(BH ₄) ₂ @UiO-67bpy	230-250	-	423	-	0.22	219	
AlH ₃ @UiO-67bpy	96	-	523	-	1.25	224	
AB@UiO-66	0.52	-	337, 351	-	1.08		
AB@UiO-67	0.95	-	349, 360	-	0.98	232	

Chemisorption
(Spillover-assist)

Chemical
desorption
(Hydride in UiO)

Short biographical notes



Osamu Oki received Doctor of Engineering degree from the University of Tsukuba in 2022, followed by a postdoctoral fellowship at Eindhoven University of Technology from 2022 to 2024. He is currently an Assistant Professor in the Department of Materials Science, Institute of Pure and Applied Sciences, University of Tsukuba. His research focuses on the design and development of advanced energy-related nanomaterials for applications in catalysis, hydrogen storage, and sustainable energy technologies.



Takahiro Kondo is a Professor in the Department of Materials Science, Institute of Pure and Applied Sciences, University of Tsukuba, and serves as Director of the Hydrogen Boride Research Center. He is also a Principal Visiting Researcher at the National Institute for Materials Science and holds a Specially Appointed Professorship at Tohoku University. He received his Ph.D. in Engineering from the University of Tsukuba in 2003, followed by a postdoctoral fellowship at RIKEN. His research focuses on the development of new materials and concepts to address critical challenges related to energy, the environment, and resource sustainability.

Statement of Novelty

This review highlights UiO-type MOFs as robust and tunable platforms for both physisorption- and chemisorption-related hydrogen storage, linking performance with functionalization, densification, spillover, and hydride nanoconfinement.

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