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Next-Gen LH2 Transportation: Extending Dormancy Period to 400 Days with Highly Effective MOF Adsorbents

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KEYWORDS: Liquid Hydrogen · Metal-organic frameworks · Hydrogen storage · Physisorption · Cryo-adsorption

Abstract

Liquid hydrogen (LH2) offers high energy density but faces challenges like boil-off losses (3-15% per day) due to its cryogenic temperature, limiting its use in long-term storage and transportation. In this study, we explore the use of metal-organic frameworks (MOFs), specifically MIL-53 and IRMOF-20, to enhance hydrogen (H₂) long-distance transportation by mitigating H₂ boil-off losses. Our results show that these MOFs can achieve an adsorption capacity of up to 97% of the volumetric capacity of a traditional LH2 tank. This significant adsorption capacity extends the dormancy period of LH2 from 83 to 407 days, demonstrating the MOFs' effectiveness in mitigating boil-off losses. The super-dense H₂ adsorption, which remains relatively stable up to 35 K, may closely resemble the conditions of solid H₂, leading to increased H₂-H₂ interactions and enhanced sorption capacity. These findings highlight the potential of MOFs to improve the efficiency and sustainability of cryogenic H₂ storage, advancing H₂'s role as a sustainable energy carrier.

Main

As the global demand for renewable energy sources intensifies, the need for efficient Hydrogen (H_2) storage/transport solutions becomes paramount.^{1,2} Currently, H_2 is stored and transported via compression or liquefaction,³ with liquid Hydrogen (LH2) offering better stability and energy density.^{4,5} However, LH2 storage at around 20 K faces significant challenges due to heat influx from the ambient environment,^{6,7} leading to potential evaporation and boil-off gas. This boil-off requires pressure relief, causing H_2 losses of 3-15% per day, depending on the tank size.⁸⁻¹⁰ Most research on reducing these losses focuses on vessel insulation design, which is economically challenging and limited by vacuum insulation constraints.¹¹⁻¹³

Common liquid cryogenic insulation techniques, such as laminated, high vacuum, vacuum powder, multi-layer, and multi-shielded insulation, use materials with low thermal conductivity to minimize heat transfer and maintain low temperatures.^{7,14} These methods have several disadvantages, such as the need for continuous vacuum pumping to achieve high vacuum insulation.¹⁵⁻¹⁷ Reliquefaction methods like mechanical compression and heat exchange recondense vaporized gas but are complex and very costly.¹⁸⁻²⁰ Moreover, despite all these efforts, completely preventing heat transfer is still impossible. Therefore, alternative approaches are needed to address LH2 boil-off losses.

Adsorbent-adsorbate interactions are typically stronger than adsorbate-adsorbate interactions, making materials with large surface areas, such as metal-organic frameworks (MOFs), highly effective for H_2 storage. These materials use van der Waals interactions to trap H_2 in micropores, which can raise the H_2 boil-off onset temperature and potentially increase H_2 density at liquefaction temperatures. Despite their advantages, such as rapid adsorption/desorption kinetics, however, the skeletal structure of porous materials can reduce storage capacity. Thus, achieving an optimal balance between minimizing boil-off and maximizing storage capacity is crucial, but research on adsorption states remains limited.

Previously, Oh et al.²¹ first investigated the use of a MOF (MIL-101) to manage pressure increases caused by the boiling of H_2 due to heat leakage. H_2 adsorbed in MIL-101 remained stable up to 37 K, above H_2 's critical point ($T_c = 32.98$ K). These results suggest that cryo-adsorption-based storage methods can enhance dormancy and are suitable for cryogenic tanks, providing a larger operational temperature window without boil-off losses. Similarly, Park et al.²² found that the intrinsic void volume of DUT-6 exceeded approximately 10% of the expected storage capacity, suggesting that further studies are needed to explore the possibility of a higher density of adsorbed phases

compared to LH₂. Recently, partial evidence for high-density H₂ adsorption has also been provided by Balderas-Xicohténcatl et al.²³ They demonstrated that H₂ can be adsorbed with a super-dense state on a type of silica known as KIT-6 at densities much higher than those of bulk LH₂. Similar work has also been reported by Oh et al.²⁴ They found that highly dense H₂, which is almost twice as dense as LH₂, can be stabilized within small pores by using a magnesium borohydride framework with a partially negatively charged non-flat interior at ambient pressure.

In this context, our study aims to experimentally investigate the highly dense state of H₂ adsorption in MOFs (MIL-53 and IRMOF-20) at 20 K, a temperature relevant for LH₂ storage. By understanding the mechanisms of this adsorption process, we seek to develop advanced H₂ (long-distance) transport technologies to mitigate H₂ boil-off losses in cryogenic tanks. Reducing H₂ boil-off is crucial for enhancing the efficiency and safety of H₂ transport systems, thereby supporting the broader adoption of H₂ as a sustainable energy carrier. Fig. 1 illustrates the crystal structure and pore configurations of adsorbents, with dimensions of 17 Å for IRMOF-20 and 2.6x13/8.5x8.5 Å for closed/open MIL-53. MIL-53 is known for its flexibility and unique breathing effect, allowing its structure to expand and contract in response to gas adsorption. IRMOF-20 is recognized for its exceptionally high volumetric uptake, making it highly efficient for H₂ storage. By leveraging the breathing effect of MIL-53 and the high uptake capacity of IRMOF-20, we analyzed the super-dense adsorption phase and investigated the potential boil-off reduction effects of these materials.

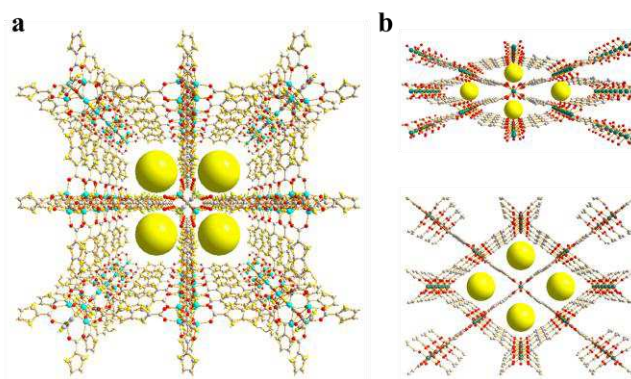


Fig. 1. Crystal structure of MOF

a, IRMOF-20 (CCDC 298053), **b**, MIL-53 system of Closed-pore (top, CCDC 220476), and Open-pore (bottom, CCDC 220477).²⁵

Characterization of MOF and determination of physical upper limit of storage capacity

Two representative MOFs, MIL-53 and IRMOF-20, were synthesized using previously reported methods.^{26,27} The agreement between the experimental XRD patterns and the simulated ones confirms the phase purity of these samples (Fig. S1). Furthermore, the N₂ specific surface areas (SSA) of MIL-53 and IRMOF-20 are determined to be 1,370 m² g⁻¹ and 4,530 m² g⁻¹, respectively. These values are consistent with previously reported data,^{26,28} providing further validation of their quality (Fig. 2a, Fig. S2-S3, and Table S1). The maximum storage capacity (gravimetric and volumetric) for each substance must first be determined from the adsorption isotherm of H₂ at 20.3 K (see Fig. 2b). The isotherms of two samples show fully reversible type-I H₂ adsorption behavior.²⁹ The saturation uptakes right before liquefaction for H₂ adsorption at 20 K and 1 bar are noted to be 66.7 mmol g⁻¹ (34.01 mol cc⁻¹) for IRMOF-20 and 21.3 mmol g⁻¹ (18.58 mol cc⁻¹) for MIL-53, respectively. The H₂ storage capacities achieved at 1 bar and 20.3 K are considered the experimentally determined physical upper limits of storage capacity. Consequently, the loading percentage mentioned defines the experimentally determined physical upper limits of storage capacity as 100%. This allows us to predict the pressure change inside the tank filled with MOF. To compare the boil-off phenomenon of the liquefied H₂ tank, it is necessary to conduct isochoric sorption measurements to confirm the impact of internal pressure changes due to heat leakage into the tank. The loading amount of H₂ is adjusted to reach between 85 % and 100 % of the maximum capacity for each MOF material. Complete adsorption results in the initial pressure being close to zero under these conditions. The pressure inside the container was recorded at a ramping rate of 3 K per minute after exposure. (see more measurement details in Fig. S4) In the case of an empty container, the pressure increased quickly as the temperature rose (mimicking the LH2 boil-off effect) and reached 1 bar rapidly (see Fig. S4 and S5). On the other hand, when 100 % and 80~85 % of H₂ are loaded for the storage capacity of each MOF (Fig. 2c), the pressure within the MOF-filled container develops differently. (Please note that only 80-85% of the commercial tank is filled with liquefied H₂, leaving 15-20% as buffer space.) As shown in Fig. 2c, the utilization of adsorbents has been observed to yield a positive impact through the shift of desorption temperature. The higher onset temperature of MIL-53 suggests that the flexible structures caused by breathing influence the desorption through structural compression. On the other hand, for rigid materials like IRMOF-20, the onset temperature is lower than that of MIL-53 due to the presence of weak accessible adsorption sites. In the case of IRMOF-20, there were temperature changes of 8 K (at 100% loading capacity) and 13 K (at 85% loading

capacity) under nearly 1 bar. In the case of MIL-53, the temperature shift achieved was up to 28 K (100%) and 32 K (80%). Indeed, when the maximum allowance operating pressure (~ 10 bar) in the liquefied H_2 tank is reached, the desorption on-set temperature shifts to a much higher temperature of ca. 20 K (IRMOF-20) and 45 K (MIL-53), respectively. Using MOF in this manner can significantly extend the dormancy period in the tank, even with minor thermal leakage. Moreover, it's important to note that even a small temperature increase of 0.1 K within the tank from 20 K can lead to the rapid vaporization of H_2 . By introducing MOF, it is noteworthy that the operating temperature window allows for a tolerance of at least 8 K to 45 K.

However, the main challenge is maintaining the storage capacity, which is reduced by the volume occupied by the MOF material in the tank. It is essential to examine the impact of the adsorbent filling capacity within the container on its uptake capacity, influenced by the volume difference due to the MOF's structure. We compared the LH2 absorption capacity of a 1 L container fully filled with adsorbent to that of a 1 L container without adsorbent to correct for isotherms measured at different capacities.

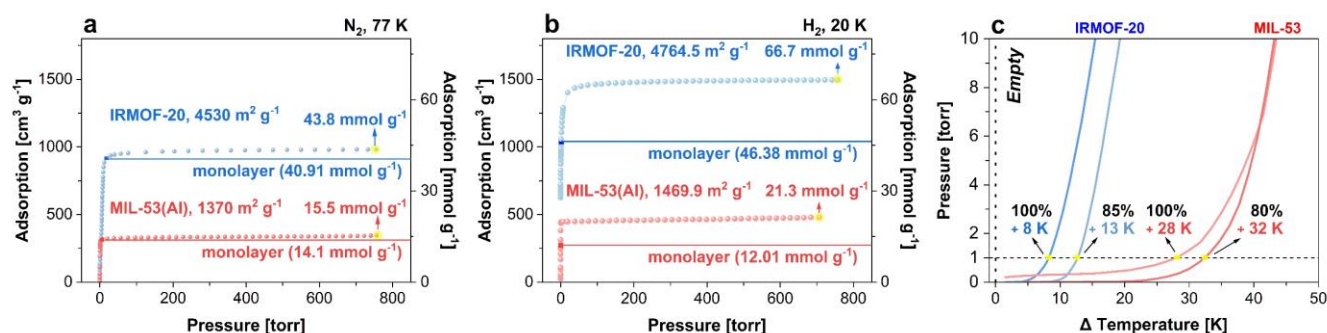


Fig. 2. Determination of physical upper limit of storage capacity and isochoric measurements.

a, H_2 sorption isotherms of IRMOF-20 (blue) and MIL-53 (red) were measured at liquefaction temperature (20.3 K) and 1 bar. The saturation uptake (surface adsorption + pore filling (multilayer adsorption)) at 20 K, 1 bar, implies the physical upper limit of each sample capacity. The BET model determined the monolayer point, which is 46 and 12 $mmol g^{-1}$ for IRMOF-20 and MIL-53, respectively. **b**, Normalized isochoric process after 85 % H_2 loading of the physical upper limit capacity at 20.3 K for IRMOF-20 (blue), MIL-53 (red), and empty sample cell (black). **c**, Normalized isochoric process after 100 % H_2 loading of the physical upper limit capacity at 20.3 K for IRMOF-20 (blue), MIL-53 (red), and empty sample cell (black). Note that the isotropic maximum pressure is fixed at 10 atm, the operating temperature of general LH2.^{30,31}

Isochoric Sorption Measurements for Boil-Off Comparison

The theoretical density of LH2 is 35.2 mol L^{-1} at 20 K, and based on that, the corresponding volumetric uptake capacity of the 1L empty container was evaluated to be 35.2 mol L^{-1} .³² Fig. 3a and Table 1 list the storage capacities of a tank containing MOF (MIL-53 and IRMOF-20 at 20 K), obtained through the physical maximum adsorption capacity indicated in Fig. 2b, which compares with the volumetric capacity of a 1 L LH2 tank. The capacity of a cryo-adsorption tank system is determined by the crystal density, saturation capacity (such as surface area and pore volume), and chemical functionality of MOFs.²² Observed uptake capacities in containers with adsorbents do not directly correlate with crystal density or gravimetric saturation uptake. Therefore, total volumetric storage capacity is crucial in fixed volumes. Using adsorbents with low skeletal density minimizes the dead volume caused by MOFs on LH2 container capacity, reducing the impact on the capacity of LH2 storage tanks. The comparison between a 1 L tank filled with the MOFs and a 1 L LH2 vessel reveals the potential for significant technological advancement. For instance, in the case of a tank filled with MIL-53, the temperature at which desorption begins was found to be twice as high as that of IRMOF-20 (Fig. 2c). However, when comparing the actual storage capacity to the liquefied H₂ tank capacity, only 53% of the H₂ could be stored. This was lower than the theoretical value, which was about 59% when excluding the space occupied by MIL-53 inside the tank. On the other hand, cryogenic IRMOF-20-based storage can achieve a volumetric capacity of up to 96.6% (refer to Fig. 3a and Table 1) when compared to LH2 storage capacity, which is an extremely promising result. Evaluation of the space occupancy of the LH2 tank with IRMOF-20 showed that MOFs filled at least 16% of the volume (dead volume), leaving only 84% effective space. In other words, the maximum storage capacity when filled with LH2 should be close to 84 % of the LH2 system if there are no exceptional interactions. However, based on experimental H₂ adsorption, the IRMOF-20 filled vessel at 20 K achieved almost 97 % of the LH2 system (almost 13 % higher). This difference can only be explained by the higher H₂ density inside the pores of the framework material, a discovery that opens up new possibilities for the field. Assumably, the stronger interaction between the H₂ molecule and the frameworks compared to that of H₂-H₂ in liquid form at 20 K results in the difference, leading to a shorter bond length. Consequently, this contributes to an increase in the H₂ density proximate to the pore wall at 20 K.

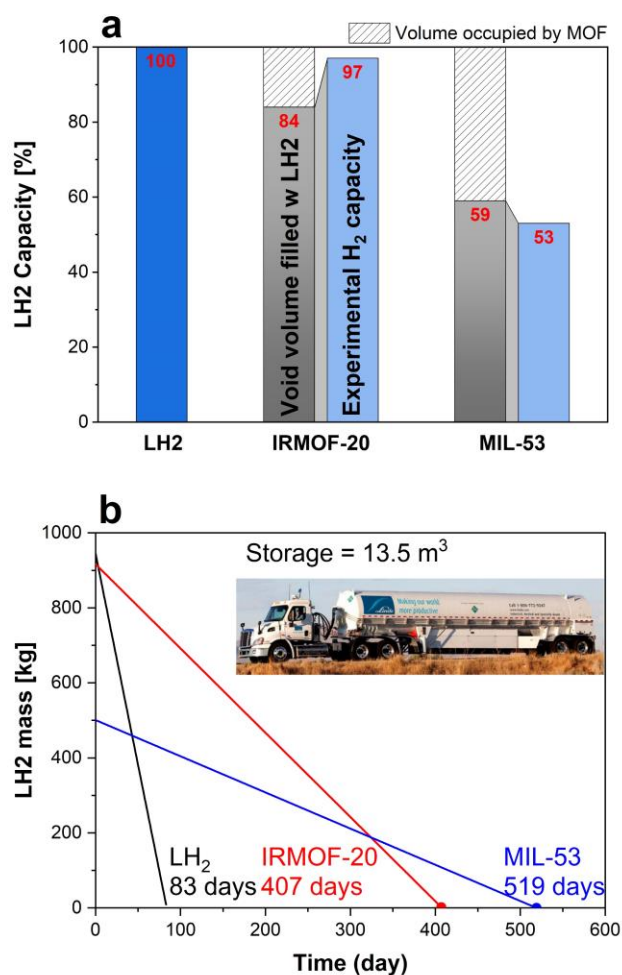


Fig. 3. Comparison of the volumetric capacity and mass loss of BOR LH2 storage vessel with MOF

a, Comparison of the volumetric capacity between 1 L LH2 and MOF sorption capacity at 20 K. **b**, Mass loss of BOR for 13.5 m³ LH2 storage vessel with IRMOF-20 and MIL-53 (calculated by heat of adsorption 4.4 kJ/mol³³ and 5.6 kJ/mol³⁴, respectively) The plot includes three lines: a black line for the empty vessel, a red line for IRMOF-20, and a blue line for MIL-53.

In addition to storage capacity, the thermal management of cryogenic tanks is another critical aspect that affects the overall efficiency of H₂ storage systems. Effective insulation techniques are essential to minimize heat ingress and maintain the low temperatures required for LH2 storage. Advanced materials and multi-layer insulation (MLI) systems, along with the tank design, significantly impact the thermal performance and boil-off rate of LH2. Incorporating MOFs in insulated tanks can greatly enhance thermal stability through adsorbed H₂ at low temperatures,

reducing the overall boil-off rate (BOR). This synergy between thermal management and adsorption capabilities is vital for optimizing cryogenic H₂ storage/transportation systems. Fig. 3b effectively illustrates the significant advantages of employing adsorbents in decreasing the rate at which LH2 evaporates and demonstrates the amount of mass lost due to H₂ evaporation from a 13.5 m³ storage container (approximately 955 kg of LH2), commonly utilized for long-distance transportation within the country. The mass of LH2 in the empty vessel (black line) decreases rapidly, reaching zero in approximately 83 days. With IRMOF-20 (red line), the mass decreases more gradually, with the LH2 lasting around 407 days before complete boil-off. MIL-53 (blue line) shows the slowest BOR, with LH2 lasting about 519 days. This comparison highlights the inefficiency of an empty vessel in preventing H₂ evaporation and the significant extension in retention time when using MOF adsorbents. Despite its lower initial storage capacity, MIL-53 is particularly effective due to the stronger interaction and gas compression by breathing effect, providing the longest retention time. Consequently, adsorbents play a crucial role in extending the dormancy period of LH2, thereby reducing BOR. Extended storage times lead to lower costs and enhanced safety due to reduced refilling frequency and minimized risk of H₂ loss.

Investigation of H₂ sorption states via INS experiments

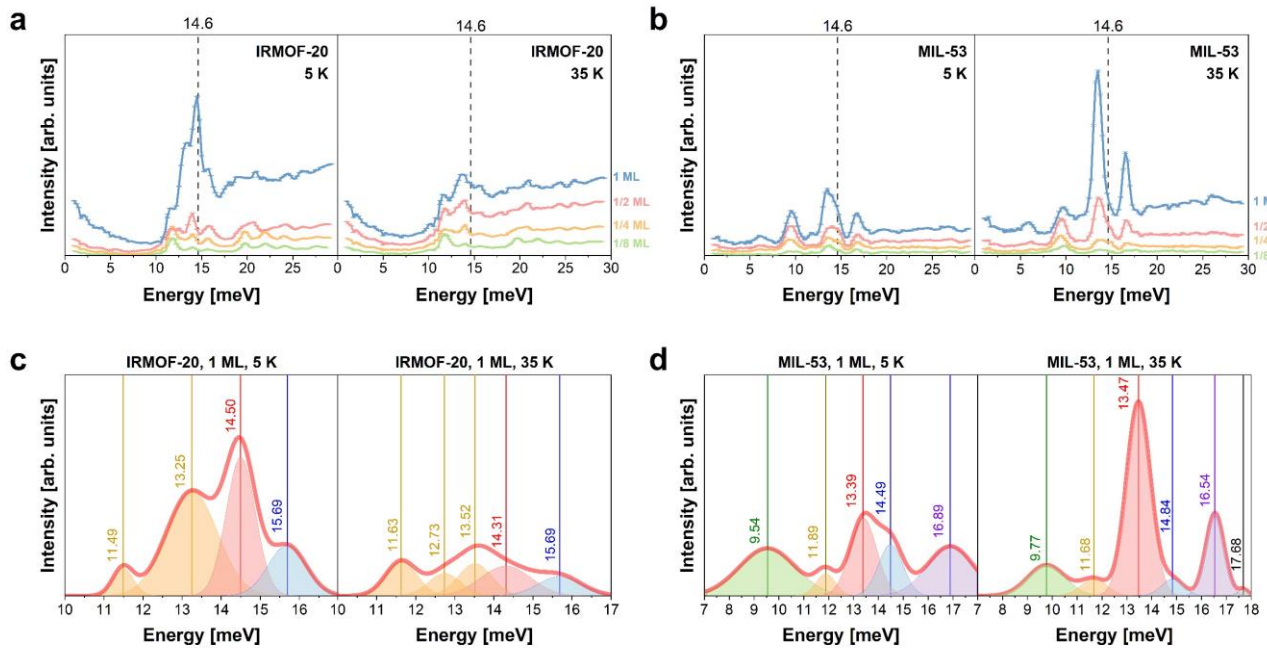


Fig. 4. INS spectra and 1 monolayer (ML) peak analysis

INS spectra of IRMOF-20 **a, c** and MIL-53 **b, d** loaded with different amounts of para-H₂ at 20 K. **a** and **b** show the INS spectra up to 30 meV, while **c** and **d** provide a detailed analysis of the 1 monolayer (ML) INS peak at 5 K and 35 K, respectively.

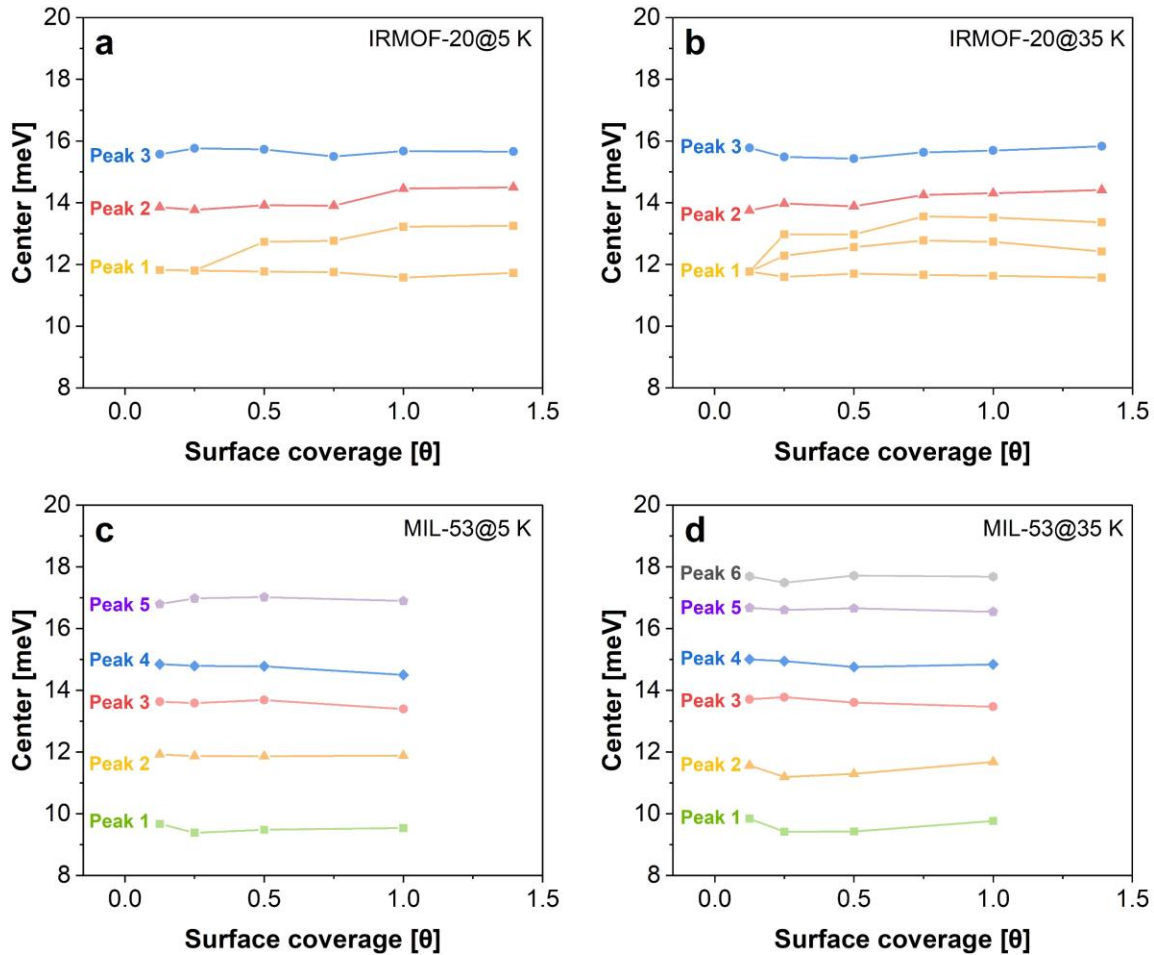


Fig. 5. Central peak analysis of neutron measurements and subsequent analysis

The upper panels show data for IRMOF-20 at 5 K (**a**) and 35 K (**b**), with peaks 1 (yellow), 2 (red), and 3 (blue). The lower panels present MIL-53 data at 5 K (**c**) and 35 K (**d**), with peaks 1 to 5 represented in green, yellow, red, blue, purple, and black, respectively.

To investigate the microscopic view behind the unexpectedly high H₂ adsorption capacity at 20 K, we conducted INS experiments on the IN1-Lagrange instrument (ILL) in Grenoble, France.^{35,36} The final neutron energy was set

to 4.5 meV by the array of PG (002) analyzers. The Si (111) and Si (311) monochromators were employed to reach the incident energy from 4.5 to 39 meV. With such experimental conditions, the energy resolution was 0.8 meV. First, we dosed H₂ into the empty cell and cooled it down to 18K (below the boiling point) to observe the LH2 neutron signal. Subsequently, we further decrease the temperature to 10K (below the melting point) to observe the solid H₂ signal (Fig. S7). The observed 14.6 meV peak at 10 K is associated with the hindered rotational transition ($J = 0 \rightarrow J = 1$) of the H₂ molecules. (Fig. S6) This transition is hallmark of H₂'s interaction within a solid matrix, indicating strong binding and restricted rotational freedom. The mobility of H₂ molecules becomes greater with increasing temperature, and at 18 K, the rotational transition signal disappears, leaving only the recoil signal.³⁷

Fig. 4 and S8-12 illustrate the INS spectra of IRMOF-20 and MIL-53 loaded with various amounts of para-H₂ at 20 K. Fig. 4a and 4b present the INS spectra at 5 K and 35 K, respectively, for different coverages (1 ML, 1/2 ML, 1/4 ML, 1/8 ML, from 5.8 to 46.4 mmol g⁻¹). Fig. 4c and 4d offer detailed analyses of the 1 monolayer (ML) INS peaks up to 30 meV at 5 K and 35 K. The observed vibrational modes in the INS spectra are attributed to the interaction between para-H₂ molecules and the MOF frameworks. This interaction is significant because it affects the rotational level transition ($J = 0 \rightarrow J = 1$) of the H₂ molecules, lifting the degeneracy or shifting the energy level of rotational excitations. Consequently, the interaction between the surface and the H₂ molecules is responsible for the observed changes in vibrational modes. For IRMOF-20, lower temperatures (5 K) typically exhibit sharper peaks due to more restricted vibrational states in solid-like H₂ (as the inside pore is filled with H₂ beyond surface adsorption, and then it could be condensed.), while higher temperatures (35 K) show peak broadening and shifts due to increased molecular motion. This behavior is consistent with the increased energy and mobility of H₂ molecules at higher temperatures. Even if condensation disappears due to high temperature, the peaks at 5 K and 35 K remain similar up to 1/2 ML loading. This suggests that the initial few sorption layers maintain a stable adsorption environment (or maybe density) like 5 K even as the temperature increases to 35 K (Fig. 4a, 4c). In contrast, the overall intensity signal of MIL-53 at 5 K is much weaker compared to 35 K. At 5 K, the MIL-53 framework is in a contracted state, which restricts H₂ adsorption. The limited pore accessibility results in fewer H₂ molecules interacting with the adsorption sites, leading to weaker INS signals. As the temperature increases to 35 K, the breathing effect of the MIL-53 framework occurs, expanding the pores and significantly increasing the adsorption capacity.

More H₂ molecules can now enter and interact with the framework, enhancing the INS signals across all vibrational modes (Fig. 4b, 4d).

Fig. 5 presents the changes in the central peak position (between 10–17 meV) in the INS spectra at different surface coverages of para-H₂ at 5 K and 35 K (Fig. S13 to S20). IRMOF-20 exhibits distinct behavior in response to H₂ loading, particularly in the splitting of the 12 meV peaks (Fig. 5a and 5b). This first peak around 12 meV at 5 K splits and shifts towards higher energies, approaching 14.6 meV, as the temperature increases to 35 K and H₂ loading increases. This splitting suggests the presence of heterogeneous adsorption energy within the IRMOF-20 framework, where H₂ molecules experience varying interaction strengths or intermolecular bond lengths, leading to different energy levels. The increase in temperature and H₂ loading enhances the interaction between H₂ molecules and the adsorption sites, causing the energy levels of the split peaks to shift toward higher values. The 14.6 meV peak is characteristic of solid H₂ and corresponds to the rotational transition ($J = 0 \rightarrow J = 1$) of tightly bound H₂ molecules, reflecting strong intermolecular bonds. The shift of the split peaks in IRMOF-20 towards 14.6 meV may indicate that the interaction between H₂ molecules within the MOF framework and/or the H₂ molecule bond length becomes more like the interactions in solid H₂ when the IRMOF-20 is sufficiently filled with H₂. Especially with the reduced bonding length, one can possibly understand the reason for overreaching the H₂ loading capacity up to 97 %. As H₂ loading increases, the density of adsorbed H₂ molecules within the pores of IRMOF-20 may also increase, leading to enhanced H₂-H₂ interactions similar to those observed in solid H₂. In contrast, MIL-53 exhibits rather stable peak positions regardless of H₂ loading, indicating relatively homogeneous adsorption energy and interactions. The lack of significant peak splitting in MIL-53 suggests that the framework provides a homogeneous environment for H₂ molecules by relaxing its structure of the framework to a large pore (Fig 1(b)), whereas the structure of IRMOF-20 remains unchanged under the H₂ loading. This uniformity results in stable H₂ adsorption densities and interactions, preventing the formation of distinct high-density regions that lead to peak splitting.

Conclusion

Our study demonstrates that using MOFs significantly improves the long-term storage performance of LH₂. This improvement includes raising the temperature at which H₂ begins to boil off while maintaining the H₂ storage capacity compared to the LH₂ system. The desorption onset temperature for IRMOF-20 increased by 13 K, reaching

a storage capacity of 97% with enhanced dormancy time compared to the LH2 system. The INS experiments revealed that the interaction between H₂ molecules and the adsorption sites within IRMOF-20 closely mimics the conditions of solid H₂, resulting in enhanced H₂-H₂ interactions and increased adsorption capacity. This behavior was particularly evident in the significant extension of the boil-off onset temperature, allowing the system to withstand higher temperatures before H₂ evaporation occurs. In contrast, MIL-53, with its flexible structure and breathing effect, demonstrated a significantly lower BOR (519 days) compared to the LH2 tank (83 days), even though it has almost half the storage capacity. This extended dormancy period can also highlight MIL-53's effectiveness in reducing H₂ boil-off due to its strong adsorption interactions and structural flexibility. Our findings emphasize that MOFs play a crucial role in enhancing the efficiency and safety of LH2 storage by reducing H₂ boil-off and improving cryogenic storage performance. This highlights MOF-based storage as a promising solution for broader H₂ adoption as a sustainable energy carrier.

Methods

Materials Synthesis (MIL-53 and IRMOF-20)

MIL-53 was synthesized according to the previously reported method.²⁶ Aluminum nitrate nonahydrate (Al(NO₃)₃·9H₂O, 1.3 g, 3.47 mmol) and terephthalic acid (H₂BDC, 0.29 g, 1.73 mmol) were dispersed in 5 mL of water. The mixture was then transferred to an autoclave and heated at 220 °C for 3 days. After cooling to RT, the resultant solid was washed with water and dimethylformamide (DMF) to remove any unreacted reactant. The DMF suspension was heated at 150 °C for 15 h to remove trapped terephthalic acid in the pores completely. The resultant crystals were sequentially washed with DMF and ethanol and slightly dried in an 80 °C oven for 30 min. The white powder was further heated at 280 °C in an air atmosphere for 12 h using a muffle furnace to remove guest molecules. IRMOF-20 was synthesized according to the previously reported method with slight modification.[ref. 26] Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, 0.15 g, 0.50 mmol) and thieno[3,2-*b*]thiophene-2,5-dicarboxylic acid (H₂TTDC, 0.057 g, 0.25 mmol) were separately dissolved in 5 mL of N,N-diethylformamide (DEF). The two solutions were mixed in a glass jar and heated in a 100 °C oven for 24 h. The resulting crystals were washed three times with DEF. Before the degassing procedure, DEF was completely exchanged to dichloromethane.

H₂ isochoric measurement procedure

In the isochoric procedure, a specific amount of H₂ was filled based on the total H₂ uptake capacity. Prior to gas filling, the sample cell was cooled to the liquefaction temperature of H₂ (20 K), followed by gas injection. The increase in pressure, up to 800 torr, was recorded due to heating at a rate of 3 K min⁻¹. An immediate phase transition from liquid to gas is observed in the case of the empty sample cell (Fig. S4 and S5). The rapid increase in pressure in the empty sample cell resembles the H₂ boil-off phenomenon in the LH2 container or tank. Therefore, the inevitable heat leakage (heat inflow from the outside) in any container system storing LH2 leads to the vaporization of LH2, which increases the internal pressure of the LH2 tank.

Normalization is necessary for comparison due to variations in MOF sorption properties and dead volume occupied by MOF in the Tank.

- 1) The temperature was measured according to the pressure change when injected H₂ was boiled off from the LH2 tank, and it was set as a reference point. Afterward, when the MOF-filled tank was filled with H₂, the desorption temperature change (ΔT) at the same pressure (as the empty LH2 tank) was measured (Fig. S5a).
- 2) When comparing different MOFs, the amount of MOF required to completely fill a 1L tank was assumed and calculated based on the crystal density of each MOF (Fig. S5b).
- 3) Considering parameters such as the specified 1 L volume and the required amount of MOF to fill the 1 L volume of the liquefied H₂ tank, the maximum sorption amount of H₂ for each MOF was experimentally determined, and the anticipated pressure change in the tank up to 10 bars could be predicted and compared (Fig. S5c).

H₂ BOR calculation details

The boil-off rate (BOR) of LH2 storage is crucial for evaluating the efficiency and practicality of cryogenic tanks. The BOR is influenced by various factors, including the total heat flux penetrating the tank, the density of LH2, and the volume of LH2. Additionally, the latent heat of vaporization or the average heat of adsorption of MOFs also plays a significant role in determining the boil-off rate. To quantify the heat flux (Q) penetrating the LH2 tank, we use the equation derived from LNG BOR methods.³⁸

$$Q = U \times A \times \Delta T \quad (1)$$

where U represents the overall heat transfer coefficient, A is the area available for heat transfer, and ΔT is the temperature difference between the inner hull and the LH2.

The overall heat transfer coefficient (U) is calculated using the relationship:

$$U = \left(\sum \frac{t_i}{k_i} \right)^{-1} \quad (2)$$

where t_i denotes the thickness of the tank layers, and k_i represents the thermal conductivity of these layers.

Therefore, to calculate the Boil-Off Rate (BOR) and heat flux for the LH2 storage system, we used the following formulas:

$$BOR = \frac{\sum Q_{leak}}{\rho_{LH2} \times V_{LH2} \times \lambda} \times 3600 \times 24 \times 100\% \quad (3)$$

where $\sum Q_{leak}$ is total heat flux that penetrates from outside to inside LH2 tank, ρ_{LH2} is LH2 density, V_{LH2} is volume of LH2 in cargo tanks, λ is latent heat for vaporization or average heat of adsorption of MOFs.

Gaussian Function in Analysis of Inelastic Neutron Scattering (INS)

For thorough spectroscopic investigation, the Gaussian function used in the analysis of various peak signals is represented as:

$$y = y_0 + \frac{A}{\omega \sqrt{\pi/2}} \cdot e^{-2 \frac{(x-\mu)^2}{\omega^2}} \quad (4)$$

where y is the dependent variable, y_0 is the baseline offset, A is the amplitude of the peak, ω is the full width at half maximum (FWHM) of the peak, x is the independent variable, μ is the center of the peak, and ω is the width parameter. This function describes the Gaussian distribution used to model the data obtained from the INS experiments, allowing for precise quantification of the H₂ adsorption characteristics in the MOF structures at low temperatures.

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CONTRIBUTION

H.R.M., J.T.P., and H.O. conceived the original ideas and supervised the project. J.P., H.K., S.J., T.P., M.J.R., M.R., and J.T.P. conducted the inelastic neutron scattering experiments. J.H., H.K.L and H.R.M. synthesized

materials and characterized them. J.P. and O.H. conducted the volumetric gas adsorption measurements. J.P, H.K, S.J, J.M., T.P, J.T.P, and H.O analyzed and visualized the data. H.O. was responsible for funding acquisition and provided supervision throughout the project. J.P., J.T.P., and H.O. wrote the original draft. All authors reviewed and edited the paper.

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SUPPORTING INFORMATION.

Supplementary Figs. 1–20,

Table 1. Comparison of the volumetric capacity between 1 L LH2 tank and containers filled with IRMOF-20 and MIL-53 at 20 K, respectively, according to each sample's crystal density and maximum uptake.

	Max. Saturation H ₂ uptake (mmol g ⁻¹)	Crystal Density (g cm ⁻³)	Cryo-adsorbed system (density x uptake) (mol L ⁻¹)	MOF/LH ₂ x100 (%)	Void fraction (%)
IRMOF-20	66.68	0.51027	34.01	96.6	84 ³⁹
MIL-53	19.00	0.978 ⁴⁰	18.58	52.8	59 ⁴¹
LH ₂	-	-	35.20	100.0	100

Supplementary Files

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