Recent Advancement in Natural Gas Storage using Metal-Organic Frameworks

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Abstract. The global quest for cleaner energy sources has highlighted the potential of natural gas. Despite its environmental advantages and abundance, challenges such as energy density, cost, and storage methods hinder its broader use. This paper explores these issues, specifically investigating Metal-Organic Frameworks (MOFs) for methane adsorption and storage. MOFs possess high surface area, tunable pore sizes, strong methane affinity, and stability. This paper reviews recent advancement in this field, particularly, the research surrounding adsorbent HKUST-1, a MOF known for its high gravimetric uptake but falling short in volumetric methane adsorption capacity. Through a sol-gel process, a denser, mechanically stable version of HKUST-1 was synthesized, meeting the Department of Energy's standards. Simultaneously, the study developed a production protocol for UiO-66, improving the volumetric methane working capacity by 11%. Additionally, another study demonstrated that composites of HKUST-1 and γ-Al2O3 exhibited superior methane adsorption, thermal stability, and potential for large-scale synthesis. These advancements in MOFs present the possibility of efficient methane storage, pushing towards wider natural gas adoption, reducing reliance on traditional fossil fuels, and promoting a cleaner, sustainable energy future.

Keywords: Metal-Organic Frameworks (MOFs), Natural Gas Storage, Methane Adsorption, HKUST-1.

1. Introduction

With the increasing global demand for cleaner energy sources (the global consumption of energy is forecasted to rise exponentially in the coming 50 years) [1], natural gas has become a favourable alternative due to its abundance in nature and environmental benefits. Natural gas is mostly composed of methane (CH_4), which has the highest hydrogen to carbon ratio [2], meaning that when combusted, natural gas emits significantly less carbon dioxide, carbon monoxide, and nitrogen dioxide compared to other fossil fuels such as petroleum. As a result, it stands as a more environmentally friendly alternative to other fossil fuels, underlining its significance in reducing the overall carbon footprint.

However, there still exist many challenges for the widespread application of natural gas. Particularly, at ambient temperature, the volumetric energy density of natural gas is significantly lower than that of gasoline. This volumetric energy density can be intensified through compression and liquefaction [3], yet both technologies also face several challenges that prevent them from being suitable for light-duty vehicles. For example, natural gas liquefaction requires the use of expensive and complex multi-stage compressors to create a high-pressure environment. On the other hand, compressed natural gas (CNG) has a lower energy density than liquefied natural gas (LNG), which means that more storage space and weight are required for the same amount of energy. CNG also requires more energy for compression than LNG for liquefaction, which reduces the overall efficiency of the process. Another alternative is adsorbed natural gas (ANG). Natural gas adsorption involves the bonding of natural gas molecules to the surface of porous solid materials like activated carbon or metal-organic frameworks (MOFs). The ANG can be stored in low-pressure tanks at normal or near-normal temperatures and transported by trucks or ships. ANG has a higher energy density compared to CNG, which means that less storage space and weight are needed to store the same amount of energy. Additionally, ANG requires less energy for adsorption compared to LNG for the process of liquefaction, resulting in improved overall efficiency. However, ANG faces certain challenges when compared to LNG, including higher capital and operating costs, limited availability and scalability of adsorbent materials, and reduced stability and durability of the adsorption system.

To overcome the identified shortcomings, the U.S. Department of Energy (DOE) has set a goal for natural gas (NG) storage [4]. The objective is to achieve a volumetric adsorption capacity of 263 cm^3cm^{-3} at a pressure of 65 bars, equivalent to the storage of CNG at a pressure of 250 bars and a temperature of 298K. This moderate pressure of 65 bars set by the DOE is highly feasible, as it can be attained using cost-effective compressors and light-storage tanks. This not only improves safety but also enhances large-scale industrial applications. The emerging method of storing ANG at low pressures on porous materials is seen as a secure and budget-friendly way to reach this ambitious goal.

2. Metal-Organic Frameworks (MOFs)

MOFs have emerged as exceptional materials for methane adsorption due to several unique features.

Firstly, MOFs possess an extremely high surface area, which is critical for gas storage. Due to the high surface area to volume ratio, a substantial quantity of methane can be stored within a relatively small volume of a MOF. This high surface area allows MOFs to store large amounts of methane, thereby facilitating their use as effective storage materials. Secondly, MOFs can be engineered to have tunable pore sizes. The control over the structure at the molecular level allows the pore size to be adjusted to maximize the adsorption of methane. This is particularly advantageous because the pore size can be tuned to closely match the kinetic diameter of the methane molecule, causing a significant increase in the storage capacity. Thirdly, MOFs often demonstrate a strong affinity for methane due to the presence of metal centers and potential functional groups. These sites can interact with methane molecules, facilitating their adsorption onto the MOF. As a result, MOFs are capable of storing methane at lower pressures than some other materials, reducing the need for high-pressure storage systems. Lastly, MOFs are often highly stable and robust, maintaining their structure and functionality over a wide range of temperatures and pressures. This makes them well-suited for use in practical applications, such as methane storage in natural gas vehicles.

However, while MOFs hold great promise, challenges remain in their large-scale production, stability, and cost-effectiveness, which are currently being addressed by ongoing research and development.

3. Methane Adsorption Capacity

The most important challenge faced by methane storage using MOFs is the lack of adsorbents with high methane adsorption capacity [5]. In 2014, a group of researchers compared isotherms of several studied MOFs and made them into graphs for better visualization.

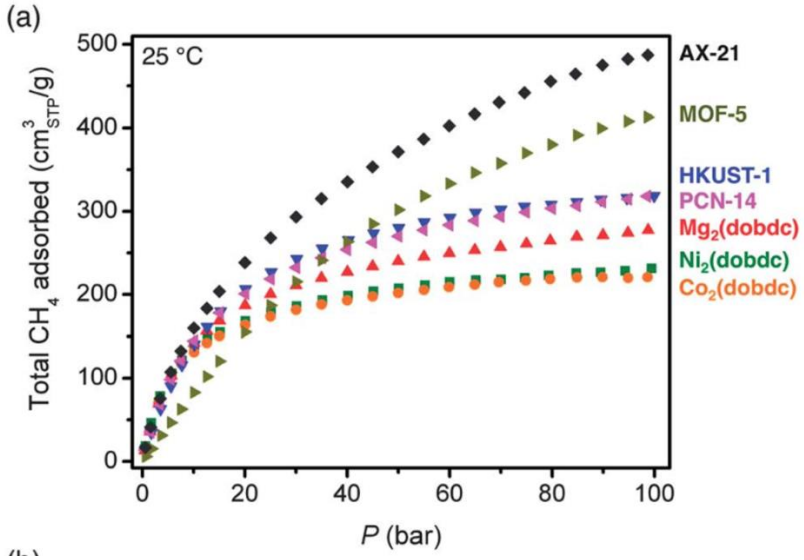


Fig. 1 Gravimetric Methane Adsorption Capacity [3].

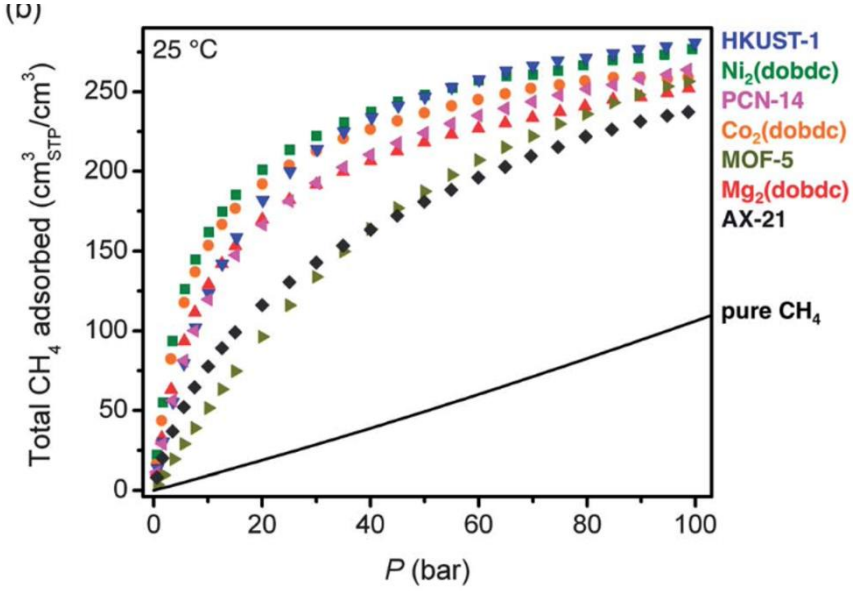


Fig. 2 Volumetric Methane Adsorption Capacity [3].

Figure 1 represents the gravimetric adsorption capacity of those MOFs. AX-21, an activated carbon, possesses the greatest gravimetric absorption across all pressure levels. For MOFs, HKUST-1 has the highest gravimetric uptake at 35 bar, but as the pressure increases to 40 bar, MOF-5 has the highest gravimetric uptake. However, when evaluating MOFs for natural gas storage, having a high volumetric adsorption capacity is more essential than a high gravimetric capacity for increasing a vehicle's driving range. Figure 2 illustrates that AX-21 and MOF-5, at low pressures, exhibit shallower isotherms and only raise to near saturation at much higher pressures compared to other MOFs. This occurrence is linked to the lack of robust adsorption locations in both AX-21 and MOF-5, and it carries considerable consequences for the real quantity of CH4 that can be dispensed by each substance [3].

Besides adsorption capacity, other factors such as cost, and the spaces it takes for industrial purposes should also be considered. On the other hand, HKUST-1, which has a high gravimetric adsorption capacity, also has a relatively high volumetric adsorption capacity.

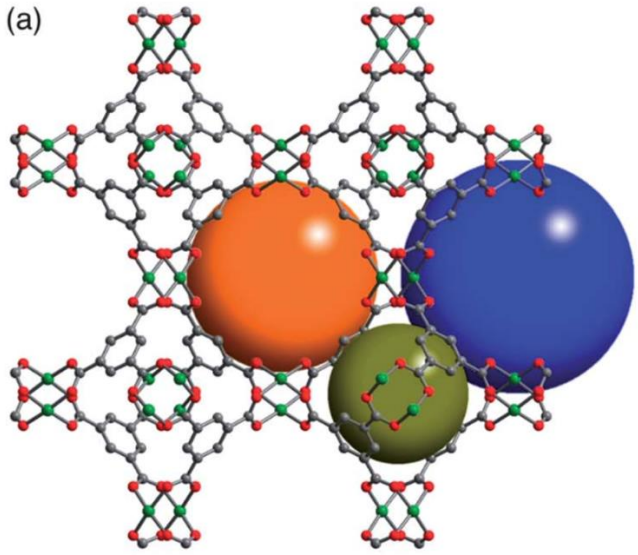


Fig. 3 Crystal Structure of HKUST-1 [3].

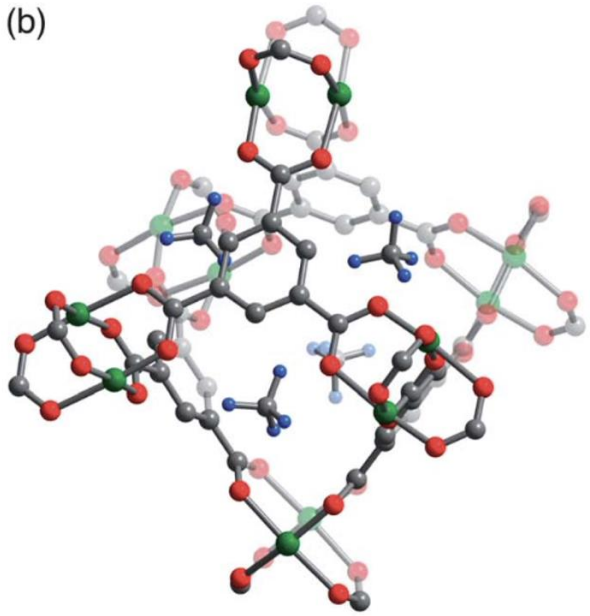


Fig. 4 Adsorbed CH_4 in an Octahedral Cage [3].

Figure 3 shows the crystal structure for HKUST-1, the 3 colored spheres represent 3 different pores. The largest pore, the blue one represents a coordination site for copper ions. The Cu^{2+} cations, when exposed, act as potent binding locations, contributing up to 98 cm^3cm^{-3} to the overall volumetric capacity by binding one CH_4 to each metal ion (Figure 4). In addition to this, HKUST-1 possesses more robust adsorption locations situated in the four windows of each octahedral cage. These are filled simultaneously with the Cu^{2+} sites, indicating that both types of adsorption sites share similar CH_4 binding energies. These window locations add another 65 cm^3cm^{-3} to HKUST-1's total volumetric capacity, culminating in a combined contribution from all strong adsorption sites of 163 cm^3cm^-3 [3]. However, this still does not meet the goal established by the Department of Energy. A volumetric energy density of 263 cm^3cm^{-3} is required to match that of compressed natural gas.

4. Mechanical Stability

The mechanical stability of MOFs refers to the material's capability to preserve its pore size and overall structure when subjected to mechanical stress. When external forces like pressure are applied, the material may deform, altering the size and form of the pores. Such changes can lead to a substantial decline in the material's performance.

Mechanical stability is particularly in the context of MOFs application in methane storage, as one of the main challenges faced by this technology is the insufficient methane adsorption capacity by adsorbents. For instance, one of the most studied MOFs for methane storage is HKUST-1. It has a theoretical maximum adsorption capacity of 267cm^3cm^{-3} at 65 bar, but it only has an experimental capacity of about 180 cm^3 cm^{-3}. This 33% loss in capacity is due to the partial mechanical collapse of the internal pore structure in powder MOFs [6]. As a result, enhancing the mechanical stability of MOFs through chemical modifications has emerged as a significant area of interest.

To prevent this loss in adsorption capacity, in 2017, a group of researchers developed a new synthetic method, a sol-gel process, to synthesize high-density HKUST-1. This new HKUST-1 is named monolithic HKUST-1. The process is depicted in Figure 5. It does not require the use of high pressure or chemical binders, which are the reasons for the loss in capacity, and either conventional powder-like MOFs or condensed, monolithic MOFs can be obtained by changing the last step in the process, the drying condition. Figure 6 shows the image of a monolithic MOF, which has high density, and is condensed into a single block structure rather than powders.

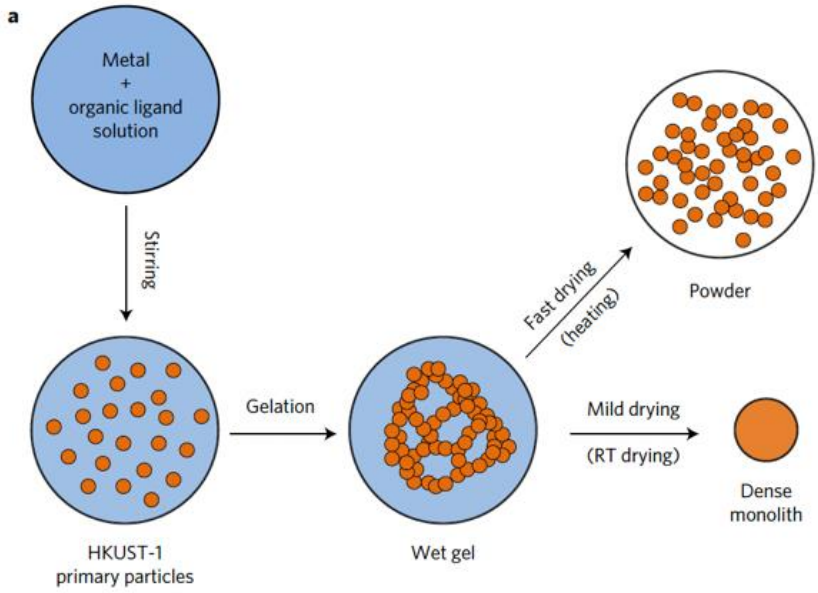


Fig. 5 Sol-gel process [7].

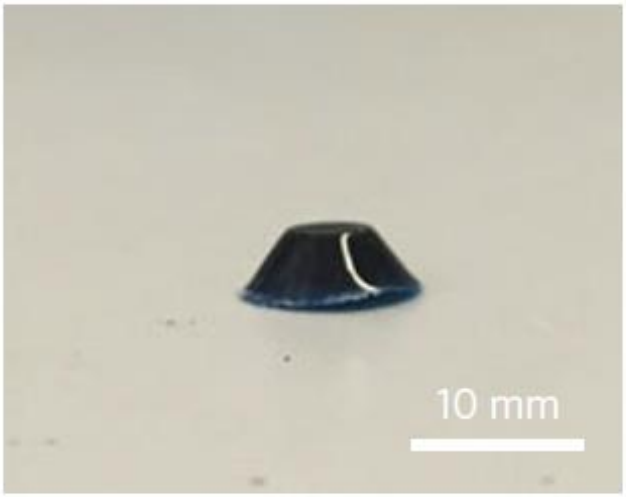


Fig. 6 Optical image of $_{mono}$HKUST-1 [8].

To examine the effectiveness of this newly synthesized HKUST-1, researchers compared it with the conventional powder-like HKUST-1. Figure 7 shows the volumetric methane adsorption of different types of HKUST-1 at 298K. The red-filled circles represent monolithic HKUST-1, and the black squares, blue diamonds, and green triangles represent powder-like HKUST-1. The red dotted line represents the goal set by the Department of Energy. This isotherm shows that monolithic HKUST-1 is significantly better at adsorbing methane, especially as pressure increases. More importantly, monolithic HKUST-1 has 259 cm3/cm3 adsorption capacity at 70 bar, which reaches the goal set by the Department of Energy [8]. This is the first example of an adosrbent to achieve this.

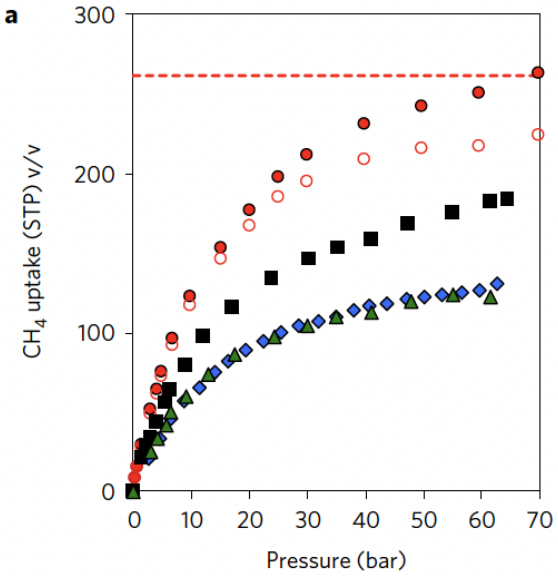


Fig. 7 Volumetric Methane Adsorption Capacity at 298 K [8].

In 2019, the same group of researchers further modified this synthetic method to design one of the most stable MOFs called Uio-66 [7]. This new synthetic protocol has several benefits over traditional powder MOFs design. Conventional methods of shaping MOF powder often involve the use of high-pressure or chemical binders, leading to collapsed porosity or the creation of low-density structures that diminish the volumetric adsorption capacity. In contrast, this novel synthetic approach fabricates MOFs that maintain high stability and density, without the need for high-pressure or chemical binders. As a result, there will not be collapse in porosity or loss in the volumetric adsorption capacity.

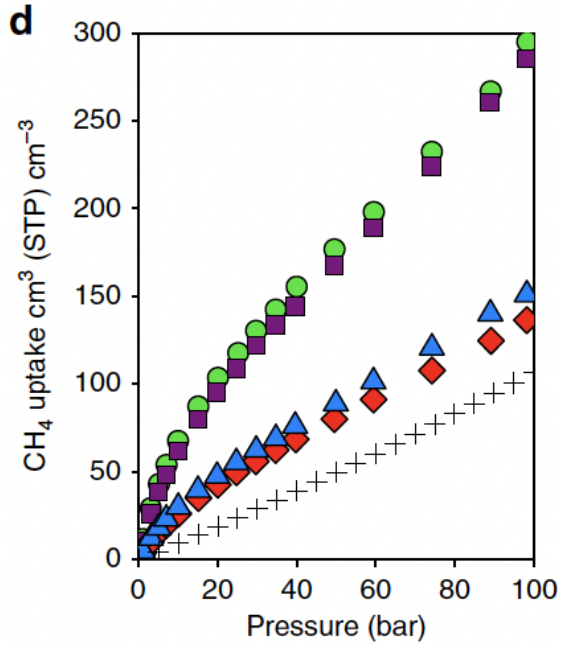


Fig. 8 Volumetric Methane Adsorption Capacity of different UiO-66 structure [8].

Figure 8 shows the isotherm of Uio-66 with different structures. The optimal structure, Uio-66D (green circles) exhibits a volumetric CH4 working capacity of 172 cm^3 $_{(STP)}cm^{-3}$ at 65 bar and 261 cm^3 (STP) cm^{-3} at 100 bar. This is an 11% enhancement compared to the standard set by monoHKUST-1. Despite the requirement of a higher working pressure, it is still industrially viable. More importantly, this outcome signifies an advancement in the development of materials aimed at optimizing the working capacity for CH4 storage [7].

5. Optimization of MOFs for Natural Gas Storage

The HKUST-1 MOF is regarded as one of the most promising adsorbents for the adsorption of methane [9]. Nevertheless, its potential is reduced due to a significant decrease in adsorption capacity in humid conditions. To mediate this issue, in 2023, David Ursueguía conducted a study through synthesizing composites of HKUST-1 and γ-Al_2O_3 particles and examined their methane adsorption [10]. This study addresses two main challenges hindering the large-scale usage of HKUST-1 for methane adsorption. 1) the significant drop in adsorption capacity under humid conditions due to water-induced structural damage and blockage of adsorption sites, and 2) the high-pressure drop during fixed-bed adsorption processes due to its fine-powder form.

To combat these issues, composites of HKUST-1 and γ-Al_2O_3 (alumina) were created. Alumina was chosen because of its hydrophilic properties, which may minimize water damage, and its ability to form larger particles that can reduce the pressure drop in fixed-bed processes.

Two impregnation methods were used - solvothermal and drip impregnation - with various HKUST-1/Al_2O_3 mass ratios. The properties and morphology of the composites were confirmed using various techniques, and the composites' methane adsorption capacities were tested before and after humid treatment.

Results showed that while the adsorption capacity of pure HKUST-1 decreased by about 37% under humid conditions, composites with low MOF loads (<9%) improved methane adsorption capacity by over 38%. These composites also showed better thermal stability. The study proposes a straightforward and economical approach to augment the practical use of HKUST-1 in industrial environments.

A more general approach to enhance the industrial application of MOFs for methane storage was done in 2022, when Chen conducted a study to enhance the methane storage capabilities of the MOF named NOTT-101 [11]. They replaced some of the ligand terphenyl-3,3″,5,5″-tetracarboxylic acid (H4TPTC) in the framework with isophthalic acid (H2IPA). This new version of NOTT-101 was named NOTT-101-IPA.

The structural analysis confirmed that the modification had maintained the framework and pore environment of NOTT-101, while the NOTT-101-IPA version showed larger pore sizes. Nitrogen adsorption isotherms measured at 77 K showed an increased pore volume and BET surface area for NOTT-101-IPA compared to NOTT-101. The results suggest an improved pore geometry for NOTT-101-IPA, which is attributed to the replacement of one diisophthalate linker with two independent isophthalate linkers.

The improvement in pore structure was additionally validated through dye adsorption tests, showing that NOTT-101-IPA has the ability to house larger molecules. The methane storage capability of NOTT-101-IPA surpassed that of NOTT-101. The volumetric working capacity of NOTT-101-IPA, ranging from 5 to 80 bar at 298 K, was found to be on par with those of benchmark MOFs such as HKUST-1, MAF-38, and MOF-177. The findings show that the ligand tailoring strategy has the ability to effectively optimize the methane storage working capacity by tailoring the pore geometry and maintaining the framework structure of the MOF.

6. Conclusion

The global need for cleaner energy sources has propelled the research and development of natural gas storage, particularly methane, using Metal-Organic Frameworks (MOFs). With their remarkable properties such as high surface area, tunable pore sizes, strong affinity for methane, and mechanical stability, MOFs present a promising approach to natural gas storage. However, challenges such as mechanical stability, cost, large-scale production, and adsorption capacity under real-world conditions still require further study and development.

The recent advances in MOFs synthesis and modification, such as the sol-gel process, mechanical reinforcement, and ligand substitution, have demonstrated significant improvements in both gravimetric and volumetric methane adsorption capacities. By reaching and even surpassing the

DOE's target for storage efficiency, these developments have brought MOFs a step closer to practical, large-scale applications.

The synthesis of MOF composites and the optimization of existing MOFs to operate efficiently under humid conditions further enhance their potential in real-world applications. Studies like those conducted by David Ursueguía and Chen have shown innovative ways to overcome some of the practical challenges MOFs face, paving the way for their widespread adoption in various industries.

Despite the promising advancements in utilizing MOFs for natural gas storage, particularly in the enhancement of methane adsorption capacities, there are still distinct limitations that hinder their immediate widespread industrial application. The industrial-scale production of MOFs remains a complex and expensive process, and issues related to stability, especially in humid conditions, are yet to be fully resolved. Even with innovations in mechanical stability and the creation of MOF composites, meeting the specific adsorption targets set by authorities like the U.S. Department of Energy is challenging and often requires conditions that may not be immediately practical for industrial usage. Additionally, the optimization of MOFs to meet various criteria, including adsorption capacity, cost, and mechanical stability, often involves trade-offs that complicate the development of a universally applicable solution. Thus, while significant strides have been made, further research and development are necessary to overcome these limitations and realize the full potential of MOFs in natural gas storage applications.

Collaborative efforts between academia, industry, and government agencies, along with continuous innovation and research, will be vital to achieving the promise of MOFs as a groundbreaking solution for clean energy storage.

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