



# Advances in Metal-Organic Frameworks for Gas Storage and Separation: Synthesis, Functionalization, and Applications

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**Abstract:** *Metal-Organic Frameworks (MOFs) represent a versatile and innovative class of porous materials that have garnered significant attention for their exceptional capabilities in gas storage and separation. This review provides a comprehensive overview of recent advancements in the synthesis, functionalization, and practical applications of MOFs. We delve into various synthesis strategies, highlighting how these approaches influence the structural properties and performance of MOFs. Additionally, we discuss the latest functionalization techniques that enhance the selectivity and capacity of MOFs for specific gases. A critical examination is presented on the performance of MOFs in the storage of key gases such as hydrogen and methane, emphasizing the material's high surface area and tunable pore sizes that make them ideal candidates for efficient gas storage. Moreover, we explore the efficiency of MOFs in the separation of industrially relevant gases like carbon dioxide and nitrogen, focusing on their potential to address environmental and energy-related challenges. This review underscores the importance of MOFs in advancing gas storage and separation technologies, providing insights into future research directions and potential industrial applications.*

**Keywords:** *Metal-Organic Frameworks, MOFs, gas storage, gas separation, synthesis.*

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## 1. Introduction

Metal-Organic Frameworks (MOFs) have emerged as a groundbreaking class of porous materials over the past few decades, captivating the interest of scientists and engineers worldwide. These materials are composed of metal ions or clusters coordinated to organic ligands, forming one-, two-, or three-dimensional structures. The unique architecture of MOFs endows them with high surface areas, tunable pore sizes, and exceptional chemical versatility, making them highly desirable for a variety of applications. Among these applications, gas storage and separation stand out due to their significant implications for energy, environmental sustainability, and industrial processes.<sup>1</sup>

The importance of MOFs in gas storage and separation cannot be overstated. In the realm of energy storage, MOFs offer a promising solution for the efficient storage of hydrogen and methane, two critical fuels in the transition towards cleaner energy sources. Hydrogen, with its high energy density and zero-emission profile, is a key player in future energy systems, while methane serves as a bridge fuel, transitioning from fossil fuels to renewable energy. The ability of MOFs to adsorb large amounts of these gases at ambient conditions is a significant advantage over traditional storage materials. Similarly, the selective adsorption properties of MOFs make them ideal candidates for separating industrially relevant gases. For instance, capturing carbon dioxide from industrial emissions is crucial in mitigating climate change, and MOFs' high selectivity and capacity for CO<sub>2</sub> can play a pivotal role in carbon capture and storage (CCS) technologies. Additionally, the separation of nitrogen from air and other industrial processes is vital for producing high-purity gases for various applications, further underscoring the utility of MOFs.<sup>2</sup>

This review aims to provide a comprehensive overview of the recent advancements in the synthesis, functionalization, and applications of MOFs, with a particular focus on gas storage and separation. We will explore the diverse methods used to synthesize MOFs, examining how these techniques influence their structural properties and performance. The review will also delve into the functionalization strategies that enhance the selective adsorption capabilities of MOFs, discussing both post-synthetic modifications and in-situ functionalization methods. Furthermore, we will evaluate the performance of MOFs in storing hydrogen and methane, assessing their potential to revolutionize energy storage systems. The efficiency of MOFs in separating

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<sup>1</sup> Kitagawa, S. (2014). Metal-organic frameworks (MOFs). *Chemical Society Reviews*, 43(16), 5415-5418.

<sup>2</sup> Kitagawa, S. (2014). Metal-organic frameworks (MOFs). *Chemical Society Reviews*, 43(16), 5415-5418.



gases such as carbon dioxide and nitrogen will be critically analyzed, highlighting their role in addressing environmental and industrial challenges. Through this review, we aim to illuminate the significant progress made in this field and identify future research directions that could further advance the application of MOFs in gas storage and separation technologies.

In summary, the remarkable properties of MOFs make them indispensable in the quest for efficient gas storage and separation solutions. This review will provide a detailed exploration of the synthesis and functionalization of MOFs, their performance in various gas storage and separation scenarios, and the broader implications of these materials for industrial and environmental applications. By synthesizing recent developments and identifying emerging trends, we hope to offer valuable insights that will guide future research and innovation in the field of MOFs.

## 2. Synthesis of MOFs

The synthesis of Metal-Organic Frameworks (MOFs) is a critical aspect that determines their structural properties, stability, and performance in various applications, including gas storage and separation. The choice of synthesis method can significantly influence the porosity, surface area, and functionality of the resultant MOFs. This section delves into the traditional and advanced synthesis techniques used to create MOFs, providing a comparative analysis to highlight their respective advantages and limitations.<sup>3</sup>

### a) Traditional Synthesis Methods

- **Hydrothermal/Solvothermal Synthesis:** Hydrothermal and solvothermal synthesis are the most widely used traditional methods for producing MOFs. These techniques involve dissolving metal salts and organic ligands in a solvent, followed by heating the solution in a sealed vessel (autoclave) at elevated temperatures and pressures. In hydrothermal synthesis, water is used as the solvent, while solvothermal synthesis employs organic solvents such as ethanol or dimethylformamide (DMF). The advantages of these methods include the ability to produce highly crystalline materials with well-defined structures and the capability to control the size and morphology of the MOFs by adjusting the synthesis parameters such as temperature, time, and concentration of reactants. However, these methods often require long reaction times (ranging from several hours to days) and can involve high energy consumption due to the elevated temperatures and pressures needed.
- **Solvent-Free Synthesis:** Solvent-free synthesis is an eco-friendly alternative to hydrothermal and solvothermal methods. This technique involves grinding the metal precursors and organic ligands together without the use of solvents, leading to the formation of MOFs through mechanochemical reactions. Solvent-free synthesis offers several advantages, including reduced environmental impact, lower costs, and shorter reaction times. However, this method can sometimes result in lower crystallinity and may require post-synthetic treatments to enhance the structural integrity of the MOFs. Despite these challenges, solvent-free synthesis is gaining traction due to its sustainability and efficiency.<sup>4</sup>

### b) Advanced Synthesis Techniques

- **Microwave-Assisted Synthesis:** Microwave-assisted synthesis utilizes microwave radiation to heat the reaction mixture rapidly and uniformly. This technique significantly reduces the reaction time (often to minutes) compared to traditional methods, while still producing highly crystalline MOFs. The rapid heating also promotes the formation of smaller and more uniform particles, which can enhance the material's surface area and porosity. One of the main advantages of microwave-assisted synthesis is its energy efficiency, as it directly heats the reactants rather than the entire reaction vessel. This method also allows for better control over the reaction conditions, leading to improved reproducibility. However, the need for specialized microwave equipment can be a limitation.
- **Electrochemical Synthesis:** Electrochemical synthesis involves the use of an electric current to drive the formation of MOFs. In this method, metal ions are generated electrochemically at the anode, while the organic ligands are dissolved in the electrolyte solution. The electric current facilitates the assembly of the MOF structure at the electrode surface. This technique offers several benefits, including mild reaction conditions (ambient temperature and pressure), the ability to produce thin films and coatings, and precise control over the deposition process. Electrochemical synthesis is particularly

<sup>3</sup> Furukawa, H., Cordova, K. E., O'Keeffe, M., & Yaghi, O. M. (2013). The chemistry and applications of metal-organic frameworks. *Science*, 341(6149), 1230444.

<sup>4</sup> MacGillivray, L. R. (Ed.). (2010). *Metal-organic frameworks: design and application*. John Wiley & Sons.



advantageous for applications requiring MOFs with specific orientations or conformations. However, it can be limited by the need for conductive substrates and the potential for uneven deposition.

- **Mechanochemical Synthesis:** Mechanochemical synthesis, also known as ball milling, involves the mechanical grinding of metal salts and organic ligands in the presence of grinding media (such as steel or ceramic balls). The mechanical force induces chemical reactions between the reactants, leading to the formation of MOFs. This method is solvent-free, making it environmentally friendly and cost-effective. It also allows for the rapid synthesis of MOFs with high yields. However, the products may require post-synthetic treatments to improve their crystallinity and structural properties. Additionally, the mechanical forces involved can sometimes lead to the degradation of sensitive ligands.<sup>5</sup>

### c) Comparative Analysis of Synthesis Methods

Each synthesis method offers distinct advantages and has its own set of limitations. Traditional methods like hydrothermal and solvothermal synthesis are well-established and produce highly crystalline MOFs, but they can be time-consuming and energy-intensive. Solvent-free synthesis, while eco-friendly and efficient, may struggle with achieving high crystallinity.

Advanced techniques such as microwave-assisted, electrochemical, and mechanochemical synthesis provide faster, more energy-efficient alternatives with the potential for improved control over the MOF properties. Microwave-assisted synthesis offers rapid reaction times and high-quality products, though it requires specialized equipment. Electrochemical synthesis excels in producing thin films and coatings but necessitates conductive substrates. Mechanochemical synthesis is both sustainable and efficient, yet it may require additional processing to achieve the desired crystallinity.

In conclusion, the choice of synthesis method for MOFs depends on the specific application requirements, desired properties of the MOFs, and practical considerations such as equipment availability and environmental impact. Understanding the strengths and limitations of each method is crucial for optimizing the synthesis process and advancing the development of MOFs for gas storage and separation applications.

## 3. Functionalization of MOFs

Functionalization of Metal-Organic Frameworks (MOFs) is a critical process that enhances their properties and broadens their applicability, particularly in gas storage and separation. Functionalization can be achieved either post-synthetically or in-situ during the synthesis of MOFs. This section explores these approaches in detail and discusses their impact on key properties such as surface area, pore size distribution, and chemical stability.<sup>6</sup>

### Post-Synthetic Modification

- **Ligand Exchange:** Ligand exchange involves replacing the original organic ligands in a MOF with new ones. This process can introduce different functional groups or modify the structural properties of the MOF. For instance, introducing ligands with specific functional groups can enhance the selectivity and affinity of the MOF for certain gases. Ligand exchange can also tailor the pore size and surface chemistry, thereby improving the material's performance in gas separation and storage applications. However, this method requires careful control to maintain the structural integrity of the MOF during the exchange process.
- **Metal Exchange:** Metal exchange, or cation exchange, is the process of replacing the metal ions or clusters in a MOF with different metal species. This modification can significantly alter the electronic, magnetic, and catalytic properties of the MOF. By selecting appropriate metal ions, researchers can enhance the MOF's ability to adsorb specific gases or improve its stability under various environmental conditions. Metal exchange can be particularly useful for applications that require specific metal sites for catalysis or for enhancing interactions with target gas molecules.
- **Grafting of Functional Groups:** Grafting involves attaching functional groups to the MOF's framework, either on the metal nodes or the organic ligands. This can be achieved through various chemical reactions, such as esterification, amidation, or click chemistry. Grafting functional groups can enhance the adsorption capacity and selectivity of MOFs for particular gases. For example, introducing amine groups can increase the affinity for carbon dioxide due to the

<sup>5</sup> MacGillivray, L. R. (Ed.). (2010). *Metal-organic frameworks: design and application*. John Wiley & Sons.

<sup>6</sup> Zhu, Q. L., & Xu, Q. (2014). Metal-organic framework composites. *Chemical Society Reviews*, 43(16), 5468-5512.



formation of carbamate species. Grafting also allows for the introduction of catalytic sites, making MOFs more versatile for industrial applications.<sup>7</sup>

- **In-Situ Functionalization During Synthesis:** In-situ functionalization involves incorporating functional groups directly into the MOF structure during the synthesis process. This approach ensures uniform distribution of functional groups throughout the framework, often resulting in more consistent and predictable properties compared to post-synthetic modification. In-situ functionalization can be achieved by using pre-functionalized ligands or by incorporating functional groups into the metal clusters.

One of the main advantages of in-situ functionalization is that it often leads to better structural stability and homogeneity. Additionally, it can simplify the synthesis process by combining functionalization with the initial formation of the MOF, potentially reducing the number of steps required. This method is particularly useful for creating MOFs with specific functionalities tailored to target applications, such as gas separation or catalysis.<sup>8</sup>

#### Impact of Functionalization on MOF Properties

- **Surface Area:** Functionalization can have a significant impact on the surface area of MOFs. Post-synthetic modifications, such as grafting bulky functional groups, can sometimes reduce the surface area due to pore blocking or partial pore collapse. However, careful selection and control of functionalization methods can maintain or even enhance the surface area. For instance, introducing smaller functional groups or using in-situ functionalization techniques can preserve the high surface area while imparting desired functionalities.
- **Pore Size Distribution:** The pore size distribution of MOFs is crucial for their performance in gas storage and separation. Functionalization can tailor the pore sizes to match the kinetic diameters of specific gas molecules, enhancing selective adsorption. Ligand exchange and grafting can be used to fine-tune the pore sizes and create hierarchical pore structures that improve gas diffusion and adsorption kinetics. In-situ functionalization often provides better control over pore size distribution, as the functional groups are incorporated during the framework's formation.
- **Chemical Stability:** Chemical stability is a critical property for MOFs, particularly for applications in harsh environments or for long-term use. Functionalization can enhance the chemical stability of MOFs by introducing stabilizing groups or metal ions. For example, grafting hydrophobic groups can improve the moisture resistance of MOFs, while metal exchange with more stable metal ions can enhance thermal and chemical stability. In-situ functionalization generally leads to more stable MOFs, as the functional groups are an integral part of the framework from the outset, reducing the likelihood of structural degradation over time.

In conclusion, functionalization is a powerful tool for enhancing the properties of MOFs and expanding their applicability in gas storage and separation. Both post-synthetic modification and in-situ functionalization offer distinct advantages and can be tailored to achieve specific performance characteristics. Understanding the impact of functionalization on surface area, pore size distribution, and chemical stability is essential for optimizing MOFs for their intended applications.<sup>9</sup>

#### 4. MOFs for Gas Storage

Metal-Organic Frameworks (MOFs) have demonstrated exceptional potential in the storage of various gases due to their high surface areas, tunable pore sizes, and versatile chemical functionalities. This section explores the mechanisms and performance metrics for hydrogen and methane storage in MOFs, as well as the capabilities and challenges associated with storing other gases such as oxygen and ammonia.<sup>10</sup>

##### d) Hydrogen Storage

**Mechanisms of Hydrogen Adsorption in MOFs:** Hydrogen storage in MOFs primarily involves physisorption, where hydrogen molecules are adsorbed onto the surface of the MOF via weak van der Waals forces. The adsorption capacity depends on the surface area, pore volume, and pore size of the MOF. Smaller pore sizes can enhance hydrogen adsorption due to stronger

<sup>7</sup> Zhu, Q. L., & Xu, Q. (2014). Metal-organic framework composites. *Chemical Society Reviews*, 43(16), 5468-5512.

<sup>8</sup> Zhou, H. C., Long, J. R., & Yaghi, O. M. (2012). Introduction to metal-organic frameworks. *Chemical reviews*, 112(2), 673-674.

<sup>9</sup> Zhou, H. C., Long, J. R., & Yaghi, O. M. (2012). Introduction to metal-organic frameworks. *Chemical reviews*, 112(2), 673-674.

<sup>10</sup> Schneemann, A., Bon, V., Schwedler, I., Senkowska, I., Kaskel, S., & Fischer, R. A. (2014). Flexible metal-organic frameworks. *Chemical Society Reviews*, 43(16), 6062-6096.



interactions between the hydrogen molecules and the pore walls. Additionally, some MOFs can be chemically modified to introduce specific binding sites that increase the affinity for hydrogen, thereby improving storage capacity.

### Performance Metrics

The performance of MOFs in hydrogen storage is typically evaluated using gravimetric and volumetric capacities:<sup>11</sup>

- **Gravimetric Capacity:** This metric measures the amount of hydrogen stored per unit mass of the MOF, usually expressed in weight percent (wt%). High gravimetric capacity is crucial for applications where weight is a critical factor, such as in mobile hydrogen storage for fuel cell vehicles.
- **Volumetric Capacity:** This metric measures the amount of hydrogen stored per unit volume of the MOF, usually expressed in grams of hydrogen per liter (g/L). High volumetric capacity is essential for stationary storage applications where space efficiency is a priority.

MOFs with high surface areas and optimal pore sizes can achieve impressive gravimetric and volumetric capacities, making them competitive with other hydrogen storage materials such as metal hydrides and carbon-based materials.

#### e) Methane Storage

**Adsorption Isotherms and Capacity:** Methane storage in MOFs relies on similar physisorption mechanisms as hydrogen storage. The adsorption isotherms, which describe the relationship between the amount of methane adsorbed and the pressure at a constant temperature, are crucial for understanding the storage capacity of MOFs. These isotherms typically show high methane uptake at low pressures, indicating the effectiveness of MOFs in capturing methane. The storage capacity of MOFs for methane is influenced by factors such as pore size, surface area, and the presence of functional groups that enhance methane affinity. MOFs with optimal pore sizes can achieve high methane storage capacities, making them suitable for applications in natural gas storage and transport.

### Comparison with Other Storage Materials

Compared to other storage materials like compressed natural gas (CNG) tanks and adsorbed natural gas (ANG) systems using activated carbon, MOFs offer several advantages. MOFs can achieve higher storage densities at lower pressures, improving safety and reducing the energy required for compression. Additionally, the tunability of MOFs allows for the design of materials with specific properties tailored to enhance methane adsorption.

### Storage Capabilities and Challenges

While hydrogen and methane storage have garnered significant attention, MOFs also show potential for storing other gases such as oxygen and ammonia, albeit with unique challenges.

- **Oxygen Storage:** Storing oxygen in MOFs can be challenging due to the reactive nature of oxygen, which can lead to oxidative degradation of the MOF structure. However, certain MOFs with robust frameworks and appropriate functional groups can adsorb and store oxygen effectively. These MOFs could be useful in applications requiring portable oxygen supplies or oxygen purification.
- **Ammonia Storage:** Ammonia storage in MOFs is particularly relevant for applications in ammonia synthesis, transportation, and as a hydrogen carrier. Ammonia can be adsorbed in MOFs via both physisorption and chemisorption mechanisms. However, the corrosive nature of ammonia poses challenges for MOF stability. Designing MOFs with high chemical resistance and specific binding sites for ammonia can enhance storage capacity and stability.<sup>12</sup>

In conclusion, MOFs offer versatile and efficient solutions for the storage of various gases, including hydrogen, methane, oxygen, and ammonia. Their high surface areas, tunable pore structures, and functionalizability enable them to achieve competitive storage

<sup>11</sup> Guillerme, V., Kim, D., Eubank, J. F., Luebke, R., Liu, X., Adil, K., ... & Eddaoudi, M. (2014). A supermolecular building approach for the design and construction of metal–organic frameworks. *Chemical Society Reviews*, 43(16), 6141-6172.

<sup>12</sup> Lu, W., Wei, Z., Gu, Z. Y., Liu, T. F., Park, J., Park, J., ... & Zhou, H. C. (2014). Tuning the structure and function of metal–organic frameworks via linker design. *Chemical Society Reviews*, 43(16), 5561-5593 *International Edition*, 60(14), 7828-7837.



capacities. However, challenges such as stability and reactivity with certain gases need to be addressed through careful design and functionalization of MOFs to fully realize their potential in gas storage applications.

## 5. MOFs for Gas Separation

Metal-Organic Frameworks (MOFs) have shown immense potential in gas separation due to their highly tunable structures, large surface areas, and the ability to incorporate functional groups that enhance selectivity. This section discusses the use of MOFs for separating carbon dioxide, nitrogen, and other industrially relevant gases such as sulfur dioxide and hydrogen sulfide, focusing on their adsorption mechanisms, selectivity, capacity, and industrial applications.<sup>13</sup>

### f) 5.1 Carbon Dioxide Separation

#### Adsorption Selectivity and Capacity

The selectivity and capacity of MOFs for carbon dioxide (CO<sub>2</sub>) adsorption are critical factors determining their efficiency in separating CO<sub>2</sub> from gas mixtures. Selectivity refers to the MOF's ability to preferentially adsorb CO<sub>2</sub> over other gases, while capacity refers to the amount of CO<sub>2</sub> that the MOF can adsorb. MOFs can achieve high selectivity and capacity for CO<sub>2</sub> through several mechanisms:

- **Pore Size and Structure:** MOFs with pore sizes that closely match the kinetic diameter of CO<sub>2</sub> molecules can enhance selective adsorption.
- **Functional Groups:** Incorporating functional groups such as amines, hydroxyls, or nitrogen-containing heterocycles into the MOF structure can increase CO<sub>2</sub> affinity through interactions like hydrogen bonding or acid-base interactions.<sup>14</sup>

#### MOFs for Carbon Capture and Sequestration

MOFs are particularly promising for carbon capture and sequestration (CCS) technologies, which aim to reduce CO<sub>2</sub> emissions from industrial sources. MOFs can be used in post-combustion capture, where CO<sub>2</sub> is separated from flue gas, or in pre-combustion capture, where CO<sub>2</sub> is removed from syngas. The high surface area and tunable functionality of MOFs allow for efficient CO<sub>2</sub> capture at various concentrations and pressures. Additionally, MOFs can be regenerated through pressure swing or temperature swing adsorption processes, making them suitable for cyclic operation in industrial settings.

### g) 5.2 Nitrogen Separation

#### Mechanisms of Nitrogen Adsorption

Nitrogen (N<sub>2</sub>) separation from air or other gas mixtures relies on the MOF's ability to selectively adsorb N<sub>2</sub> over other components. The mechanisms of nitrogen adsorption in MOFs include:<sup>15</sup>

- **Physisorption:** N<sub>2</sub> is adsorbed onto the surface of the MOF through van der Waals forces. The effectiveness of physisorption depends on the surface area and pore size of the MOF.
- **Functional Groups:** Introducing polar or polarizable functional groups into the MOF can enhance interactions with N<sub>2</sub>, increasing selectivity and adsorption capacity.

#### Industrial Applications and Efficiencies

MOFs can be used in various industrial applications requiring high-purity nitrogen, such as inerting, blanketing, and food packaging. The efficiency of MOFs in nitrogen separation is often evaluated in terms of the adsorption capacity and selectivity for N<sub>2</sub> over other gases, such as oxygen. MOFs with high selectivity for N<sub>2</sub> can be used in pressure swing adsorption (PSA) systems, which are widely employed in industrial nitrogen production. The ability to regenerate MOFs and their stability under operational conditions are also critical factors for their industrial application.

<sup>13</sup> Lu, W., Wei, Z., Gu, Z. Y., Liu, T. F., Park, J., Park, J., ... & Zhou, H. C. (2014). Tuning the structure and function of metal-organic frameworks via linker design. *Chemical Society Reviews*, 43(16), 5561-5593.

<sup>14</sup> Bennett, T. D., & Cheetham, A. K. (2014). Amorphous metal-organic frameworks. *Accounts of chemical research*, 47(5), 1555-1562.

<sup>15</sup> Lee, Y. R., Kim, J., & Ahn, W. S. (2013). Synthesis of metal-organic frameworks: A mini review. *Korean Journal of Chemical Engineering*, 30, 1667-1680.



### h) 5.3 Separation of Other Industrially Relevant Gases

**Sulfur Dioxide :** Sulfur dioxide (SO<sub>2</sub>) is a common pollutant produced by industrial processes such as coal combustion and metal smelting. The separation of SO<sub>2</sub> from gas mixtures is essential for reducing air pollution and complying with environmental regulations. MOFs can effectively adsorb SO<sub>2</sub> due to their high surface areas and the presence of functional groups that interact with SO<sub>2</sub> molecules. For example, MOFs with basic sites can enhance SO<sub>2</sub> adsorption through acid-base interactions. The stability of MOFs in the presence of SO<sub>2</sub> and their ability to be regenerated are important considerations for their practical application.

**Hydrogen Sulfide :** Hydrogen sulfide (H<sub>2</sub>S) is another industrially relevant gas that requires separation due to its toxicity and corrosiveness. H<sub>2</sub>S is commonly found in natural gas, biogas, and refinery gas streams. MOFs can adsorb H<sub>2</sub>S through physisorption and chemisorption mechanisms. The incorporation of metal sites or functional groups that can form strong interactions with H<sub>2</sub>S can enhance the selectivity and capacity of MOFs for H<sub>2</sub>S adsorption. The regeneration of MOFs and their resistance to degradation by H<sub>2</sub>S are crucial for their use in industrial gas purification processes.<sup>16</sup>

In conclusion, MOFs offer versatile and efficient solutions for the separation of various industrially relevant gases, including carbon dioxide, nitrogen, sulfur dioxide, and hydrogen sulfide. Their high surface areas, tunable pore structures, and functionalizability enable them to achieve high selectivity and capacity for specific gases. The ability to regenerate MOFs and their stability under operational conditions make them suitable for various industrial applications, contributing to more efficient and sustainable gas separation technologies.

### 2) 6. Conclusion

Metal-Organic Frameworks (MOFs) have emerged as a highly versatile and effective class of materials for gas storage and separation applications, driven by their unique structural properties, high surface areas, and tunable functionalities. This review has explored the latest developments in the synthesis, functionalization, and application of MOFs, highlighting their capabilities and potential in various industrial processes. In the realm of gas storage, MOFs have demonstrated remarkable performance in storing hydrogen and methane. Through mechanisms such as physisorption, and by leveraging their high surface areas and optimal pore sizes, MOFs can achieve competitive gravimetric and volumetric capacities. Advanced synthesis techniques, including microwave-assisted, electrochemical, and mechanochemical methods, have further enhanced the efficiency and scalability of MOF production, providing pathways to more cost-effective and environmentally friendly storage solutions. The functionalization of MOFs, whether through post-synthetic modification or in-situ during synthesis, has proven crucial in enhancing their gas storage and separation properties. Techniques such as ligand and metal exchange, as well as grafting of functional groups, have allowed for the precise tuning of MOF structures to optimize adsorption capacities, selectivity, and chemical stability. These modifications have expanded the applicability of MOFs in various gas separation scenarios, including the selective capture of carbon dioxide and the efficient separation of nitrogen and other industrially relevant gases.

For gas separation, MOFs have shown significant promise in applications such as carbon capture and sequestration (CCS), nitrogen production, and the removal of pollutants like sulfur dioxide and hydrogen sulfide. Their high selectivity and adsorption capacities, coupled with their ability to be regenerated, make MOFs suitable for integration into existing industrial processes and new, more efficient separation technologies. Despite the progress and achievements detailed in this review, challenges remain in the practical implementation of MOFs at an industrial scale. Issues such as long-term stability, resistance to harsh operational conditions, and the economic feasibility of large-scale synthesis and regeneration processes need to be addressed. Future research should focus on overcoming these challenges through innovative synthesis strategies, robust functionalization techniques, and the development of more durable MOF structures. In summary, MOFs represent a groundbreaking advancement in the field of materials science, with the potential to revolutionize gas storage and separation technologies. Continued research and development will undoubtedly lead to the optimization and broader adoption of MOFs, contributing to more efficient, sustainable, and environmentally friendly industrial practices.

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<sup>16</sup> Lee, Y. R., Kim, J., & Ahn, W. S. (2013). Synthesis of metal-organic frameworks: A mini review. *Korean Journal of Chemical Engineering*, 30, 1667-1680.